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Final Report

EFFECTS OF NUCLEAR RADIATION ON POLYETHYLENE  
AND CERTAIN CHEMICAL TRANSFORMATIONS

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## ABSTRACT

The polymerization of gaseous ethylene by gamma irradiation in the presence of sensitizers such as peroxides and azo compounds was investigated at several temperatures (60, 80, and 100°C) and at a pressure of 2000 psi. Results show that the initial rate of polymerization at 60°C in the presence of dilauroyl peroxide was increased 1.4-fold; this difference in rates would correspond to a temperature difference of about 3°C if equal rates were maintained. On the other hand, no increases in the rates of conversion of ethylene to solid polymer at 80 and 100°C were observed with the following initiators: di-t-butyl peroxide, dicumyl peroxide, azobisisobutyronitrile, and diisopropyl azisobutyrate. In fact, in many cases, a decrease in rate resulted from irradiation, apparently because of the formation of nonsolid products under the influence of radiation.

Effects of gamma radiation on polyethylene were also studied; samples of Poly-Eth 1005 (melt index 1.8) and Poly-Eth 1008.5 (melt index 20) were irradiated at temperatures ranging between -70 and +120°C, and physical properties determined. In general, the tensile and yield strengths passed through a maximum as the radiation dose was increased, while the melt index and percent elongation decreased steadily. However, doses required to improve the strength properties resulted in fabrication difficulties, especially with Poly-Eth 1005.

In another attempt to improve the properties of polyethylene, the effect of incorporating modifiers and fillers in polyethylene prior to irradiation was examined. The addition of such substances as carbon black, styrene, or aniline, resulted in a deterioration of properties; on the other hand, the irradiation of glass-filled polyethylene resulted in a product much tougher than filled unirradiated polyethylene.

The use of vinyl monomers to modify the nature of irradiated polyethylene was also attempted. Best results were found with the grafting of gaseous vinyl chloride to 2-mil film and to 20-mil sheets of Poly-Eth 1008.5. Provided that the polyethylene had been freed from occluded oxygen, irradiation of a film or sheet with a dose of from  $0.8 \times 10^6$  to  $1.2 \times 10^6$  rep in the presence of vinyl chloride yielded a product having improved toughness and remarkable resistance to deformation (that is, shrinking and buckling) on heating.

Because of the close relationship between irradiation-induced cross-linking in polyethylene and the molecular weight distribution, the effect of irradiation on the gel fractions of several polyethylene samples was studied. It was found that a careful examination of curves relating gel fraction to radiation dose could give useful information about the breadth of the molecular weight distribution, and, in some cases, the molecular weight.



Preliminary experiments with the use of gamma radiation in the synthesis of cyclohexanone oxime and the fixation of nitrogen were conducted; results were not promising, as yields were low and difficult to reproduce.

In the one nonradiation study made, it was found that samples of polyethylene having the same melt index could be differentiated by measurements of Mooney viscosity.

#### OBJECTIVE

The primary objective of this investigation was to study the application of nuclear radiation (especially, gamma radiation) to the synthesis and modification of polyethylene.

The secondary objective was to study the use of nuclear radiation to promote certain chemical transformations such as the synthesis of cyclohexanone oxime and the fixation of nitrogen.

## GENERAL INTRODUCTION

The interaction between various types of radiation ( $\alpha$ ,  $\beta$ ,  $\gamma$ , light, etc.) and matter has been of at least academic interest for many years. When radiation is absorbed by a material, energy is transferred to the electrons of the molecules. A complex set of processes then occurs culminating in the formation of excited molecules, ions, and free radicals; the free radicals formed this way then either combine with each other or react with other molecular species in the medium. Thus radiation ( $\alpha$ ,  $\beta$ ,  $\gamma$ , light, etc.) may be used to initiate many free radical reactions.

For many years the most common type of radiation used for the initiation of reactions were ultraviolet light and x-rays; sources of  $\alpha$ ,  $\beta$ , and  $\gamma$  radiation were generally less common. However, during the last few years, sources of nuclear radiation such as Co-60 or spent fuel elements from nuclear reactors have become fairly readily available; at the same time, the cost of these radiation sources has decreased steadily. Indeed it seems likely that nuclear radiation will soon become a competitively priced source of energy; considerable attention has been given, both in industrial and academic laboratories, to the possibility of using this radiation for the initiation of chemical reactions on a commercial scale. This possibility has been especially interesting to the Spencer Chemical Company because of its concern both with commercial power and with the production of a wide range of chemicals and polymers.

One of the most obvious applications of nuclear radiation is the initiation of chemical reactions known to be initiated by ultraviolet light. In spite of some basic differences between the effects of light and nuclear radiation, it is known, for example, that some reactions, such as the chlorination of hydrocarbons, which may be initiated photochemically, are also initiated by nuclear radiation.<sup>1</sup>

Perhaps the most extensive work with the applications of nuclear radiation to chemical reactions has been in the field of polymer chemistry. For example, a good deal of interest has developed in the use of nuclear radiation to initiate polymerization; the polymerization of vinyl monomers such as styrene and ethylene has been studied in some detail.<sup>2,3</sup> Another type of reaction, especially interesting because a small amount of chemical reaction leads to large effects on physical properties, is the modification of polymers already formed. This type of reaction has led to much experimental work, and, indeed, to commercial application. Thus several laboratories both in this country and in Europe have studied the effects of radiation on polyethylene;<sup>4,5</sup> already some irradiated polyethylene products are available commercially.<sup>6,7</sup>

For these reasons, it was decided to undertake a study of the use of

nuclear radiation to promote chemical reactions of commercial importance. More specifically, it was decided to study the synthesis and modification of polyethylene by gamma radiation, and also the synthesis of some compounds of interest to the sponsor—namely, cyclohexanone oxime and nitric oxide or ammonia.

## I. THE POLYMERIZATION OF ETHYLENE BY GAMMA RADIATION

### INTRODUCTION

The initiation of polymerization in ethylene by gamma radiation has been studied by several research groups. Bretton and others<sup>8</sup> obtained solid polymers by the polymerization of ethylene at one atmosphere pressure and at temperatures between room temperature and 167°C. Lewis, Martin, and Anderson<sup>3</sup> reported preparation of solid polyethylene having high crystallinity. According to another study, by Hayward,<sup>9</sup> the use of pressures up to 21 atmospheres is advantageous in this polymerization to avoid the formation of liquid polymers.

On the other hand, little attention has been paid to the incorporation in the ethylene of radiation-sensitive compounds (that is, compounds that form free radicals on dissociation by radiation) to enhance the effect of radiation. A British patent<sup>10</sup> claims that chlorohydrocarbons, aliphatic alcohols, and other oxygen-containing compounds are suitable sensitizers, but it gives no examples. The most obvious sensitizers would be, of course, ordinary initiators such as peroxides. Except for some work on the photochemical decomposition of peroxides,<sup>11-14</sup> however, no studies of the effects of radiation on peroxides appear to have been published.

It was decided, therefore, to examine the effects of gamma radiation on the polymerization of ethylene in the presence of some typical chemical initiators such as peroxides and azo compounds. It was hoped that it might be possible to conduct a conventional polymerization at a given rate in the presence of radiation at a temperature lower than that required for the same rate of polymerization in the absence of radiation.

Originally the study was intended to deal with the continuous polymerization of ethylene at high pressures (20,000 psi). When this was found to be impractical, the batch polymerization of ethylene at lower pressures (2000 psi) was investigated; it was hoped that the results obtained could be extrapolated to continuous operation at higher pressures. To obtain preliminary information about the effect of radiation in initiators, the polymerization of styrene by irradiation in the presence of several initiators was examined. Results are presented and discussed below.

A preliminary investigation was also made to test the feasibility of

irradiating an initiator prior to polymerization. Results of this study, which consisted of the irradiation of a frozen suspension of dilauroyl peroxide, are also given in this section.

#### EXPERIMENTAL

Styrene (99%) was obtained from the Dow Chemical Company; solvents were of technical grade. Two cylinders of ethylene were used—one supplied by the Matheson Chemical Company, and one by the Spencer Chemical Company; data used for the comparison of a radiation experiment with its blank were always obtained using ethylene from one cylinder. Except for the diisopropyl azoisobutyrate (Spencer Chemical Company) and the dicumyl peroxide (Hercules Powder Company), liquid and solid initiators were supplied by the Lucidol Division of Wallace and Tiernan, Incorporated. Dispersions of initiators in mineral oil were supplied by the Spencer Chemical Company. The diphenylpicrylhydrazyl used in some experiments was prepared by the oxidation of diphenylpicrylhydrazine hydrochloride with lead dioxide;<sup>15</sup> the concentration of hydrazyl in solutions was determined spectrophotometrically.

Polymerizations of styrene were conducted in sealed glass tubes. The tubes were filled with 15 ml of toluene, 5 ml of freshly distilled styrene, and, unless specified otherwise, 0.20 g of initiator; before polymerization the contents were degassed. After polymerization the product was precipitated by pouring the contents of the tubes into methanol.

For the ethylene polymerizations, a 250-ml Magne-Dash autoclave was used. The procedure was as follows. After addition of a solution of the initiator (e.g., 1.0-g initiator/50-ml benzene), the autoclave was sealed and then flushed—first, three times with nitrogen (charged to 2000 psi), and finally with ethylene (charged to 900 psi). Next, the autoclave was charged with ethylene and stirred until a constant pressure of between 900 and 950 psi was observed. After charging, the autoclave was placed in an oil bath regulated to  $\pm 1^\circ\text{C}$  at the temperature desired; equilibrium was usually reached within one hour. Ethylene was bled off as required to maintain an initial operating pressure of 2000 ( $\pm 50$ ) psi. For example, at 2000 psi and  $60^\circ\text{C}$ , the autoclave was found to contain approximately 80 g of ethylene. After the warm-up period, the autoclave (in the oil bath) was exposed to gamma radiation at nominal dose rates in air\* ranging from 27,000 to 33,000 rep/hr. It should be noted that the time of irradiation was necessarily less than the time in the bath (Tables III, IV, and V) because of interruptions of the irradiation to remove other samples. When desired, the autoclave was removed from the bath and quenched with cold water; unreacted ethylene was released and the polymer precipitated by the addition of methanol. Blank runs were made in a similar way in the absence of radiation. The extent of polymerization of ethylene by the direct action of

\*Because of absorption of radiation by the bath and autoclave, the actual dose rates would be lower (possibly  $1/3$  lower), but would, of course, still be relative.

radiation was found to be negligible.

The yields of polymers did not always correspond to the decrease in pressure during reaction. The probable explanation is that low molecular weight products, the formation of which would be reflected in a pressure decrease, were not recovered by the precipitation technique used (see also results and discussion).

## RESULTS AND DISCUSSION

### 1. Polymerization of Styrene

To obtain general information about the effects of radiation on different initiators, the polymerization of styrene in the presence of the following initiators was studied in the presence and absence of gamma radiation: di-t-butyl peroxide, dilauroyl peroxide, benzoyl peroxide, dicumyl peroxide, azobisisobutyronitrile, diisopropyl azoisobutyrate, cyclohexanone peroxide, isopropylbenzene hydroperoxide, and cumene hydroperoxide. The degree of conversion was plotted against time for both radiation and blank experiments, and initial rates of conversion determined. As may be seen from Table I, the rate of polymerization was invariably increased by the rate of radiation; the magnitude of the effect varied over a wide range (for di-t-butyl peroxide, the initial rate with radiation was about 3 times the initial blank rate, while for cumene hydroperoxide, the ratio of the two rates was only 1.1).

The effects of reaction variables, such as dose rate, initiator concentration, and temperature, were also examined. Results are given in Table II.

If the rate of initiation is increased by the absorption of radiation, the rate of polymerization should be proportional to the square root of the dose rate. This expectation is confirmed by the results (Table II-a). This proportionality means in turn that the higher the dose rate the lower the efficiency of polymerization per rep.

It may also be seen (Table II-b) that the percent conversion increases regularly with the peroxide concentration; it may be shown, too, that the rate of polymerization varies approximately with the square root of the peroxide concentration.

Table II-c shows that the lower the temperature, the more pronounced is the effect of radiation. This result is consistent with the assumption that the effect of radiation should be independent of temperature. As the temperature is increased, this constant effect is masked more and more by the increasing contribution of thermal polymerization.

Thus the effects of gamma radiation in these experiments are quite straightforward.

TABLE I

EFFECT OF GAMMA RADIATION ON THE POLYMERIZATION OF STYRENE IN SOLUTION

Initiator	Temp, °C	Ratio of Initial Slopes <sup>a</sup>	Initial Rate of Conversion, %/hr
Di-t-butyl peroxide	77	2.87 <sup>b</sup>	3
		2.50 <sup>c</sup>	
Dicumyl peroxide	77	2.00	2
Dilauroyl peroxide	77	1.97 <sup>b</sup>	23
		1.84 <sup>c</sup>	
	113	1.40	
Diisopropylbenzene hydroperoxide	77	1.55	3
Diisopropyl azoisobutyrate	77	1.35	20
Benzoyl peroxide	77	1.29	9
Azobisisobutyronitrile	77	1.28	20
Cyclohexanone peroxide	77	1.10	8
Cumene hydroperoxide	77	1.08	4

<sup>a</sup>That is, the ratio of the initial slope of the conversion curve to the initial slope for a blank run. Unless specified otherwise, dose rate was  $7.0 \times 10^4$  rep/hr.

<sup>b</sup>Dose rate:  $3.8 \times 10^4$  rep/hr.

<sup>c</sup>Dose rate:  $2.4 \times 10^4$  rep/hr.

TABLE II

EFFECT OF REACTION VARIABLES ON THE SENSITIZED POLYMERIZATION OF STYRENE USING GAMMA RADIATION<sup>a</sup>

(a) Effect of Dose Rate at 25°C

Dose Rate, rep/hr	(Dose Rate) <sup>1/2</sup> , (rep/hr) <sup>1/2</sup>	Conversion of Styrene, %	Rate of Conversion, %/hr
---	---	1.03	0.25
7.0 x 10 <sup>3</sup>	84	1.82	0.46
3.0 x 10 <sup>4</sup>	172	2.39	0.60
4.2 x 10 <sup>4</sup>	205	2.38	0.60
1.2 x 10 <sup>5</sup>	347	3.48	0.87

(b) Effect of Initiator Concentration at 77°C

Concentration Initiator, g/25-ml soln	Dose Rate, rep/hr	Conversion of Styrene, %
0.050	4.2 x 10 <sup>4</sup>	23.9
0.050	---	20.3
0.100	4.2 x 10 <sup>4</sup>	30.1
0.100	---	27.0
0.200	4.2 x 10 <sup>4</sup>	42.5
0.200	---	36.6
0.400	4.2 x 10 <sup>4</sup>	52.6
0.400	---	45.5

(c) Effect of Temperature

Temp, °C	Dose Rate, rep/hr	Conversion of Styrene, %	Ratio of Initial Slopes
25	4.2 x 10	2.38	2.31
	---	1.03	
60	4.2 x 10	20.5	1.64
	---	12.5	
77	4.2 x 10	42.5	1.16
	---	36.6	
113	4.2 x 10	54.0	1.20
	---	44.8	

<sup>a</sup>Initiator: Dilauroyl peroxide; time: 4 hr.

## 2. Polymerization of Ethylene

It was originally intended to study the effect of gamma radiation on the continuous polymerization of ethylene at high pressures (say, 20,000 psi) using peroxides or azo compounds as initiators or sensitizers. However, both the cost and the time required for installation and trial operation would have been unduly great in view of the limited time available. Since on the other hand, an autoclave was already available, and since experimental problems are fewer and less difficult at lower pressures, it was decided that more basic information could be obtained in a short time with the autoclave than with the high-pressure unit. Accordingly, plans were changed to comprise batch experiments at relatively low pressures (say, 2000 psi).

Studies of the following initiators, both in the presence and absence of radiation, were completed: dilauroyl peroxide (at 60°C); dicumyl peroxide, di-t-butyl peroxide, and diisopropyl azoisobutyrate (each at 80 and 100°C). In addition, blank experiments were made with dilauryl peroxide at 80 and 100°C and for dicumyl peroxide, di-t-butyl peroxide, and diisopropyl azoisobutyrate at 60°C.

Generally the products obtained from the solution in the autoclave were whitish waxy granules. (However, with dilauroylperoxide at 100°C, a solid mass was obtained rather than a liquid benzene solution.) It is believed that these products are usually similar; molecular weights calculated (Ref. 16, p. 310) from the melting points (118-127°C) would be of the order of  $10^3$  (if the product is essentially an n-paraffin) or  $10^4$ - $10^5$  (if it is a high molecular weight polyethylene).

a. Dilauroyl Peroxide.—The data summarized in Table III show that, in general, the yields of solid polymer obtained at 60°C in the presence of radiation were greater than the yields for the unirradiated blanks. Melting points of the products were similar. The data also show that the precision of the results is fairly good for experiments of this nature (see Fig. 1); the deviation of a point from the "best" line is usually within  $\pm 20$  percent. If an induction period of 30 minutes is assumed (that is, half the time required to raise the temperature of the autoclave from 20 to 60°C), a ratio for slopes of initial yield curves (irradiated/unirradiated) of 1.45 may be calculated. Since the dose rates in these experiments were similar, effects of dose rate were disregarded in this calculation.

From the data for blanks at 60, 80, and 100°C, an approximate activation energy of 18,000 kcal/mole was calculated. From these data it was found that an initial slope ratio of 1.45 corresponds to a temperature difference, if rates of polymerization are equal, of about 3°C. In other words, the initial rate of polymerization in the presence of radiation at 60°C corresponds to the initial rate of polymerization in the absence of radiation at about 63°C. If the contribution of the blank is excluded, the G value would be 2.3 moles of ethylene reacted/1000 rep/1000 g of ethylene charged.



TABLE III

THE EFFECT OF GAMMA RADIATION ON THE POLYMERIZATION OF ETHYLENE  
IN THE PRESENCE OF DILAUROYL PEROXIDE

Initial pressure: 2000 psi  
 Solvent: 50 ml benzene  
 Reactor volume: 275 ml  
 Initiator concentration: 0.10 M

Run No.	Temp, °C	Time in Bath, hr	Dose Rate, rep/hr x 10 <sup>-3</sup>	Dose, rep x 10 <sup>-3</sup>	Yield, %	Melting Point, °C	Final Pressure, psi
36	60	1.0	--	0	0.18	-	2060
38	60	2.0	--	0	0.47	-	2060
45	60	2.5	--	0	0.56	-	1980
39	60	2.5	--	0	0.44	-	2020
35	60	3.5	--	0	0.67	-	2050
40	60	4.5	--	0	1.24	125-127	1620
46	60	5.8	--	0	1.35	-	1850
44	60	7.0	--	0	1.68	-	1820
33	60	3.0	32	54	1.04	-	2250
43	60	4.2	27	81	1.44	-	1850
68	60	6.0	33	106	1.76	125-126	1840
56	81	1.0	--	0	0.05	-	1990
58	81	1.5	--	0	0.08	-	2005
57	81	2.0	--	0	1.35	-	1960
55	81	3.0	--	0	2.90	-	1940
59	81	4.5	--	0	5.25	122-124	1850
67	102	0.75	--	0	3.0	118-120	1990
66	102	1.5	--	0	5.38	-	1970

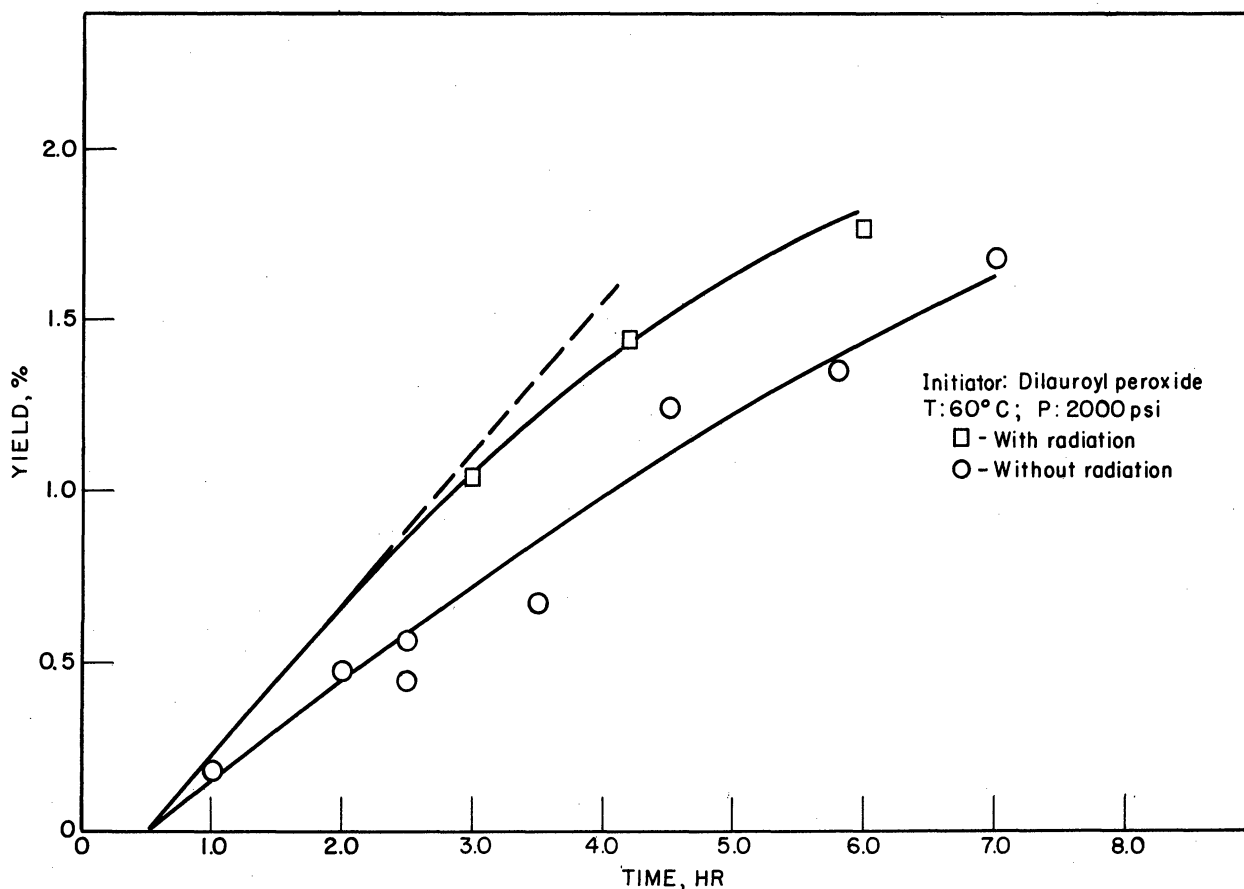


Fig. 1. Effect of gamma radiation on the polymerization of ethylene in the presence of dilauroyl peroxide.

This effect does not seem large, especially in view of the assumption that radiation effects would be most noticeable at low temperatures. This assumption was based in turn on the assumption that the effects of radiation are independent of temperature. However, the possibility that radiation effects are not always independent of temperature has been suggested recently.<sup>16,17</sup> Thus the possibility that a better (higher) temperature could be found should not be excluded without further study.

b. Azo Initiators.—Data for the azo initiators are given in Table IV. Products were white granular solids having similar melting points.

It is clear that the rate of conversion of ethylene to solids at 80°C in the presence of azobisisobutyronitrile is not increased by exposure to radiation. In fact, the rates are invariably lower in the presence of radiation; and the higher the dose rate, the lower they are. Now the rate of decrease of pressure was essentially the same whether or not radiation was used. Thus this curious behavior must reflect an effect of radiation resulting in a lower degree of polymerization, and hence in a greater solubility; this lowering effect should be greater the higher the dose rate.

At 100°C, an enhancement of the rate of conversion may exist,

TABLE IV  
 THE EFFECT OF GAMMA RADIATION ON THE POLYMERIZATION OF ETHYLENE  
 IN THE PRESENCE OF AZO COMPOUNDS

Initial pressure: 2000 psi  
 Solvent: 50 ml benzene  
 Reactor volume: 275 ml  
 Initiator concentrations: azobisisobutyronitrile (ABIN), 1.0 g/50 ml;  
 diisopropyl azoisobutyrate (DIPAIB), 1.6 g/50 ml

Run No.	Initiator	Temp, °C	Time in Bath, hr	Dose Rate, rep/hr x 10 <sup>-3</sup>	Dose, rep x 10 <sup>-3</sup>	Yield, %	Rate of Conversion, %/hr	Melting Point, °C	Final Pressure, psi
83	ABIN	80	3.1	32	32	6.8	2.19	-	1760
79	ABIN	80	5.0	23	81	11.3	2.26	-	1620
82	ABIN	80	5.5	8.7	32	12.9	2.34	-	1580
76	ABIN	80	6.0	20	86	13.5	2.25	122-124	1520
86	ABIN	80	4.2	--	--	10.6	2.52	-	1660
84	ABIN	80	5.5	--	--	14.4	2.62	122-124	1580
74	ABIN	100	5.0	6.8	27	15.6	3.12	122-124	1820
69	ABIN	100	5.3	10	10	16.7	3.18	-	1780
70	ABIN	100	5.5	--	--	14.7	2.68	122-124	1790
80	DIPAIB	80	6.0	21	92	1.85	3.09	124-125	1770
85	DIPAIB	80	6.0	--	--	2.14	3.58	124-126	1870
72	DIPAIB	100	5.5	7.5	34	3.3	4.38	118-120	2040

although a definite conclusion is impossible owing to the scarcity of data.\* If we accept the few data at face value, the ratio of conversion rates (irradiated/nonirradiated) would be only 1.2. On the other hand, the rate of decrease in pressure was not consistently greater for the radiation experiments. In this case, the effect of dose rate noted at 80°C does not exist.

Results of the few experiments made with diisopropyl azoisobutyrate, as with the azobisisobutyronitrile at 80°C, indicate that the use of radiation at 80°C results in a lower rate of conversion of ethylene to solid polymers than is observed for a blank run. An explanation similar to that suggested for the azobisisobutyronitrile experiments may also be applicable in this case.

c. Other Peroxide Initiators.—Data for these initiators are presented in Table V. Again, products were white granular solids having similar melting points.

With di-*t*-butyl peroxide solid products were not obtained at 80°C, although the pressure decreased measurably during the reaction. Small yields were, however, obtained at 100°C. Just as was observed in the previous section, the rate of conversion to solid polymer was lowered by irradiation; on the other hand, irradiation may have resulted in an increase in the rate of decrease of pressure.

A similar situation exists with dicumyl peroxide. At 80°C, a decrease in pressure was observed but no solid polymer was obtained. At 100°C, solid polymers were obtained, but with a lower rate of conversion in the radiation run.

d. General Comments on the Sensitized Polymerizations of Ethylene.—So far, the only clear-cut case in which irradiation improves the rate of conversion of ethylene to solid polymers under the experimental conditions used here is that of dilauroyl peroxide. In the other cases, irradiation apparently usually results in the formation of lower molecular weight, and hence more soluble, polymers. Further and more accurate pressure measurements would be required to determine unequivocally whether or not irradiation in these latter cases results in an increased rate of consumption of ethylene.

The fact that some of the products are soluble in methanol suggests that the products are probably high molecular weight waxes rather than regular polyethylenes.

It had been hoped that results of these low-pressure studies could be extrapolated to the conventional high-pressure polymerization of ethylene. The conclusion that the higher the dose rate, the lower the degree of polymerization should certainly be applicable to a conventional polymerization. However, a final answer regarding the effect of radiation on a conventional polymeriza-

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\*As with dilauroyl peroxide at 100°C, the polymerization resulted in a solid mass rather than a solution.

TABLE V  
 THE EFFECT OF GAMMA RADIATION ON THE POLYMERIZATION OF ETHYLENE  
 IN THE PRESENCE OF PEROXIDES

Initial pressure: 2000 psi  
 Solvent: 50 ml benzene  
 Reactor volume: 275 ml  
 Initiator concentration: dicumyl peroxide (DCP), 1.0 g/50 ml;  
 di-t-butyl peroxide (DTBP), 1.0 g/50 ml

Run No.	Initiator	Temp, °C	Time in Bath, hr	Dose Rate, rep/hr x 10 <sup>-3</sup>	Dose, rep x 10 <sup>-3</sup>	Yield, %	Rate of Conversion, %/hr	Final Pressure, psi
78	DTBP	80	6.25	21	9.5	0	0	1950
77	DTBP	80	6.25	--	--	0	0	1840
61 <sup>a</sup>	DTBP	80	24.0	--	--	0	0	1500
71	DTBP	100	6.15	6.5	20	0.98	0.16	1930
87	DTBP	100	6.0	--	--	1.46	0.24	2020
81	DCP	80	6.5	23	106	--	--	1830
63	DCP	80	4.0	--	--	--	--	1990
73	DCP	100	6.0	7.5	3.0	1.10	0.18	1960
88	DCP	100	6.0	--	--	1.52	0.25	1980

<sup>a</sup>Initiator concentration, 0.5 g/50 ml.

tion system may properly require more experiments at higher pressures which would result in a polymer more typical of polyethylene.

e. Pre-irradiation of Initiators.—Some experiments with the irradiation of frozen solutions of dilauroyl peroxide indicated the presence of free radical activity (as measured by the consumption of the stable free radical, diphenyl picrylhydrazyl) after thawing. To see if it would be possible to irradiate an initiator for polyethylene rather than the reactor itself, 3 gallons of a suspension of dilauroyl peroxide were irradiated (dose,  $1.6 \times 10^6$  rep) while frozen, and 3 gallons of a similar suspension were frozen as a blank. These samples of initiator were sent to the pilot plant of the Spencer Chemical Company for evaluation. However, the efficiency of the irradiated initiator when thawed proved to be no higher than the efficiency of the unirradiated initiator suspension. The basic problem seems to lie in getting the frozen free radicals in contact with the monomer before recombination with one another can occur. So far, then, it seems unlikely that the irradiation of initiators prior to polymerization is practical.

#### CONCLUSIONS

1. The rate of polymerization of styrene (in solution) in the presence of peroxide or azo compounds is increased by gamma radiation. Ratios of initial conversion slopes (irradiated/unirradiated) range from 2.9 with di-t-butyl peroxide to 1.1 with cumene hydroperoxide (both at 77°C). Effects of initiator concentration, dose rate, and temperature were as expected, at least with dilauroyl peroxide.
2. The rate of polymerization of ethylene (to form solid products) at 2000 psi and 60°C in the presence of dilauroyl peroxide may be increased 1.4-fold by gamma irradiation. Products obtained, white waxy solids, are similar to products obtained in the absence of radiation.
3. The rate of conversion of ethylene to solid products at 2000 psi and 80°C in the presence of azobisisobutyronitrile is decreased by gamma irradiation, probably because of a decrease in the molecular weight, and hence an increase in solubility of the product in the precipitant used, caused by irradiation. At 100°C there may be a slight increase in the rate of conversion due to irradiation.
4. The rate of conversion of ethylene to solid products at 2000 psi in the presence of diisopropyl azoisobutyrate or dicumyl peroxide at 80°C, or di-t-butyl peroxide at 100°C, is decreased by gamma irradiation, presumably because of a decrease in the molecular weight of the product.
5. The irradiation of an initiator solution prior to polymerization appears to be impractical, unless some way can be found to prevent recombination of any free radicals formed.

## II. EFFECTS OF GAMMA RADIATION ON POLYETHYLENE

## A. Crosslinking of Polyethylene

## INTRODUCTION

It is well established that the irradiation of polyethylene results in several reactions, even though the mechanisms of these reactions are not yet clear (Ref. 16, Chapter 4.7; and Refs. 17-20). Considerable evidence shows that the irradiation of polymers, for example, polyethylene, results in crosslinking, chain scission, and the development of unsaturation;<sup>5,6,21-28</sup> with a crystalline polymer like polyethylene, a loss of crystallinity also occurs.

The effects of these reactions on physical properties have been examined in some detail in several laboratories. As the radiation dose is increased, the density decreases at first owing to a decrease in crystallinity; at higher doses, when much of the crystallinity has been destroyed, the density increases due to tighter packing (Ref. 16, p. 151). A similar decrease followed by an increase has been noted for Young's modulus (Ref. 16, p. 151). Lawton, Bueche, and Balwit<sup>26</sup> found a maximum in the curve relating the tensile strength of irradiated polyethylene to dose; they also reported a maximum in the curve relating the ultimate elongation to dose. On the other hand, Dole, Keeling, and Rose<sup>25</sup> found little change in tensile strength on irradiation as long as oxygen was absent; Ballantine and others<sup>28</sup> also reported almost negligible initial increases in tensile strength on irradiation (and also a steady, consistent decrease in ultimate elongation as the dose was increased). Other properties are also affected: for example, it is claimed that several commercial products prepared by irradiating polyethylene have improved resistance to heat, chemicals, and stress-cracking;<sup>7,8</sup> Charlesby also claims a similar improvement in resistance to heat and solvents.<sup>29</sup> Although fabrication of these irradiated products is difficult, an improvement in this respect has recently been announced.<sup>30</sup>

It seemed logical, therefore, to investigate the effects of irradiation on samples of typical kinds of polyethylene produced by the Spencer Chemical Company, to see if the physical properties could be improved by irradiation without a corresponding decrease in ease of processing. Results of this study are presented below.

## EXPERIMENTAL

The following samples of polyethylene were supplied by the Spencer Chemical Company: Poly-Eth 1005 (PE 1005), Nat B, lot 42, melt index 1.8; Poly-Eth 1008.5 (PE 1008.5), Nat B, melt index 20.

Irradiations were conducted using the 1-kilocurie Co-60 source at the Fission Products Laboratory. Polymer samples were irradiated, under an atmosphere of nitrogen, in sealed glass tubes.

Samples for tensile measurements were prepared by compression molding at 300°F and 2500 psi. Tensile measurements were made using an Instron tester. Cross-head speeds of either 5 or 10 in./min were used; tests revealed no measurable difference between tensile properties determined at either speed.

## RESULTS AND DISCUSSION

In the first experiment, a sample of Poly-Eth 1005 (melt index 1.8) was exposed at room temperature to doses ranging between  $1 \times 10^5$  and  $2 \times 10^7$  rep. It was found<sup>30</sup> that a plot of the tensile strength as a function of dose passed through a maximum at a dose of  $1.5 \times 10^6$  rep; however, any dose as high or higher than this value resulted in values for melt index sufficiently low to preclude satisfactory extrusion. The softening point was improved by irradiation, but during unmolding tests the molded irradiated samples tended to revert to the original pellets. Extrusion of the material was difficult.

To see if a better balance between crosslinking and processability could be achieved, the effect of temperature of irradiation was investigated. Samples of Poly-Eth 1005 were irradiated at  $-70^\circ\text{C}$  (that is, below the glass temperature) and at  $120^\circ\text{C}$  (that is, above the crystalline melting point). Experiments were also conducted with Poly-Eth 1008.5 (melt index 20) with the hope that this polymer might show a lesser tendency to become crosslinked to a degree that could reduce the ease of fabrication.

Physical properties, including resistance to heat distortion but excluding tests of stress-cracking, were determined. Similar tests were also made with a sample of Poly-Eth 1005 that had been heated at  $120^\circ\text{C}$  but not irradiated. Samples of the following materials were sent to the Plastics Research Laboratory for evaluation:<sup>31</sup> Poly-Eth 1005 ( $1.0 \times 10^5 < \text{dose in rep} < 1.5 \times 10^6$ ) and Poly-Eth 1008.5 ( $1.0 \times 10^5 < \text{dose in rep} < 5.0 \times 10^6$ ). Results are summarized below.

### (a) Poly-Eth 1005 (Irradiated at $-70^\circ\text{C}$ )

Dose: 0 -  $2 \times 10^7$  rep

Tensile strength: Increased from 1860 psi at zero dose to a maximum of 2430 psi at a dose of  $1.5 \times 10^6$  rep (see Fig. 2).

Yield strength: Increased from 1180 psi at zero dose to a maximum of 1330 psi at a dose of  $1.5 \times 10^6$  rep (see Fig. 2).

Percent elongation: Decreased from 570% at zero dose to 540% at a dose of  $1.5 \times 10^6$  rep, and rapidly thereafter (see Fig. 2).



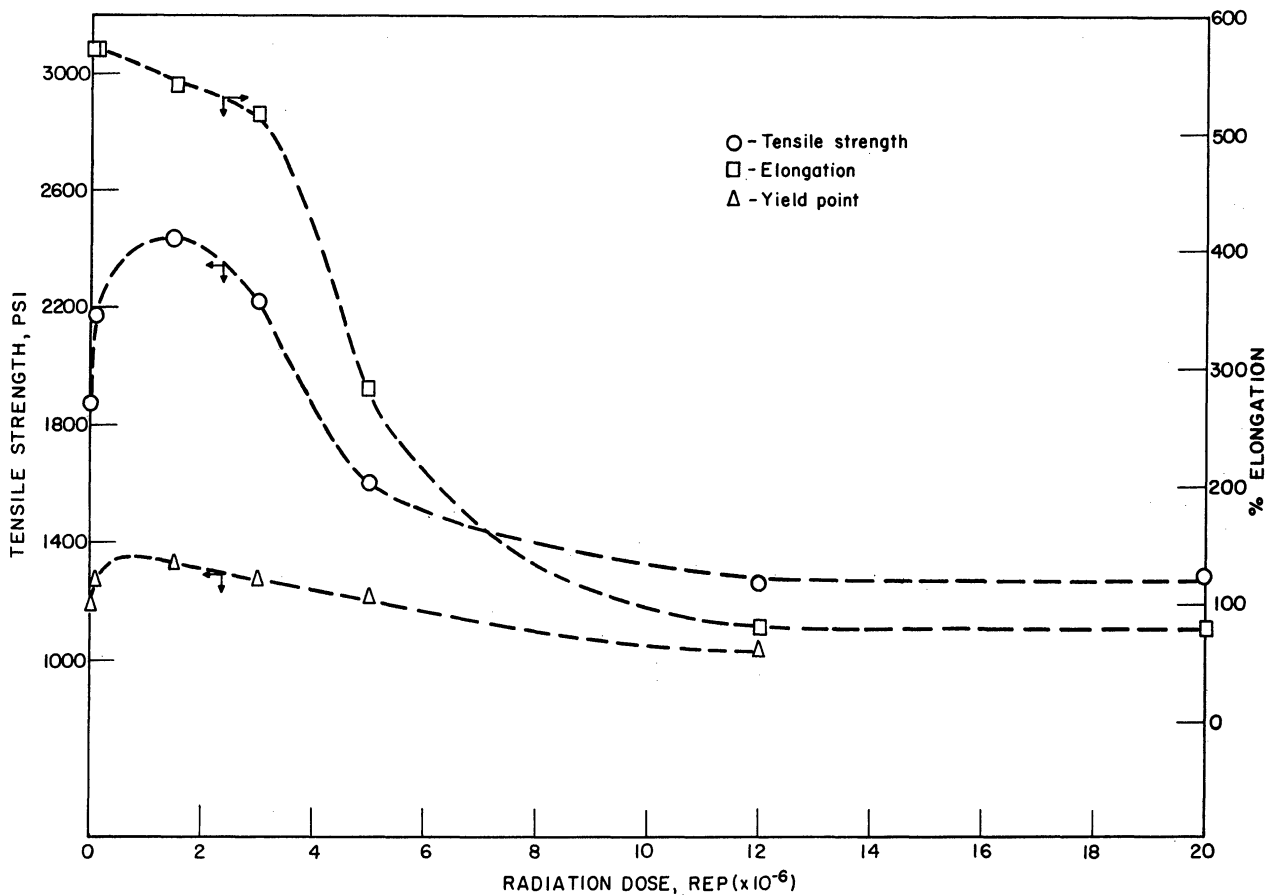


Fig. 2. Effect of gamma radiation on the tensile strength of Poly-Eth 1005 (irradiated at  $-70^{\circ}\text{C}$ ).

Melt index: Decreased; 1.4 at a dose of  $1.0 \times 10^5$  rep, and 0 at a dose of  $1.5 \times 10^6$  rep.

Heat distortion\*: Samples that had been given doses greater than  $1.5 \times 10^5$  rep tended to curl and break apart.

Remarks: Irradiated samples more transparent than control sheet, but not uniformly so.

(b) Poly-Eth 1005 (Irradiated at  $120^{\circ}\text{C}$ )

Dose: 0 -  $8.0 \times 10^6$  rep

Tensile strength: Increased to 1900 psi at a dose of  $1.5 \times 10^6$ , and decreased thereafter.

Yield strength: Increased slightly to a maximum of 1200 psi at a dose of  $3.0 \times 10^6$  rep, and decreased thereafter.

\*In tests reported in this section, samples were held at  $220^{\circ}\text{F}$  for 30 minutes.

Percent elongation: Decreased steadily; 400% at a dose of  $1.5 \times 10^6$  rep.

Melt index: Decreased to 0.8 at a dose of  $1.0 \times 10^5$  rep, and to 0 at a dose of  $1.5 \times 10^6$ .

Heat distortion: Samples which had been given doses greater than  $1 \times 10^6$  rep tended to curl and break apart.

Remarks: Irradiated samples adhered to walls of glass vessel more than did the unirradiated one.

Thus exposure of Poly-Eth 1005 to a low dose resulted in an initial increase in tensile strength and yield strength, especially when the irradiation is conducted at a low temperature. The overall resistance to heat distortion was somewhat improved in comparison with unirradiated samples. However, the amount of radiation required to reach the maximum in tensile strength is large enough to lower the melt index to a level that makes the material difficult to fabricate.

(c) Poly-Eth 1008.5 (irradiated at  $10^\circ\text{C}$ )

Dose: 0 -  $5.0 \times 10^6$  rep

Tensile strength: Increased from 1430 psi at zero dose to 1550 psi at a dose of  $3.0 \times 10^6$  rep.

Yield strength: Increased from 920 psi at zero dose to 1040 psi at  $3.0 \times 10^6$  rep.

Percent elongation: Decreased from 450% at zero dose to 320% at a dose of  $5.0 \times 10^6$  rep.

Melt index: Decreased; 0.14 at a dose of  $1.5 \times 10^6$  rep, and 0 at a dose of  $5.0 \times 10^6$  rep.

Heat distortion: Samples that had been given doses greater than  $1.5 \times 10^6$  rep tended to curl.

Also, a large sample of Poly-Eth 1008.5 was irradiated at  $-10^\circ\text{C}$  (dose is  $7.5 \times 10^5$  rep) and tested for processability at the Plastics Research Laboratory.<sup>32</sup> The melt index after irradiation was 2.3. Although extrusion on film was unsatisfactory, injection molding behavior was satisfactory. It was also observed that the irradiated polymer was more transparent than the control used. Other physical properties were similar, though slightly inferior, to the sample of Poly-Eth 1005 used as control.

(d) Poly-Eth 1008.5 (irradiated at  $-70^\circ\text{C}$ )

Dose: 0 -  $1.5 \times 10^6$  rep.

Tensile strength: Essentially unchanged.

Yield strength: Decreased slightly from 1090 psi at zero dose to 1050 psi at a dose of  $1.5 \times 10^6$  rep.

Percent elongation: Essentially unchanged.

Melt index: Decreased from 20 at zero dose to 16.7 at a dose of  $3.0 \times 10^5$  rep to 0 at a dose of  $1.5 \times 10^6$  rep.

Heat distortion: Samples that had been given doses greater than  $1.0 \times 10^6$  rep tended to curl.

The results show that the melt index of Poly-Eth 1008.5 may be reduced at will by irradiation. However, as with Poly-Eth 1005, fabrication of the final product is difficult.

General Remarks.—So far, at least with Poly-Eth 1005 and Poly-Eth 1008.5, it has not been possible to introduce enough crosslinking to improve strength properties without affecting at least some fabrication properties adversely. Nevertheless, tensile properties of the large sample prepared by the irradiation of Poly-Eth 1008.5 were almost as good as those of the control sample of PE 1005. While the mere duplication of Poly-Eth 1005 is not in itself of interest, it is possible that some properties not determined, such as stress-cracking or resistance to reagents might be better than the corresponding properties for Poly-Eth 1005. It is also possible that other samples of polyethylene might behave differently; for example, control of the molecular weight distribution is probably important. It seems likely from tests reported in a later section that Poly-Eth 1005 contains a small amount of a very high molecular weight tail, which, of course, forms gel at a very low dose; Poly-Eth 1008.5 may also have a broad distribution. Small amounts of gel formed from a high molecular weight tail could very easily cause difficulties in fabrication. The degree of branching may also be an important variable.

Although it is claimed that one product may be extruded satisfactorily,<sup>7</sup> the commercial irradiated polymers mentioned above must, in general, be irradiated after fabrication. Hence the problem of achieving a suitable balance between crosslinking and ease of fabrication has still not been solved.

## CONCLUSIONS

1. The tensile and yield strengths of Poly-Eth 1005 may be improved by gamma irradiation (in the absence of air) with a dose of about  $1.5 \times 10^6$  rep, especially at low temperatures; the resistance to heat distortion may also be improved in this way. However, the dose required to attain the maximum strength lowers the melt index to a level that results in fabrication difficulties.

2. The tensile and yield strengths of Poly-Eth 1008.5 may also be improved by gamma irradiation (in the absence of air) at 10°C, but to a lesser extent than is the case with Poly-Eth 1005; the resistance to heat distortion is also slightly improved. The melt index may be reduced at will by varying the dose received. Again, however, fabrication becomes difficult; for example, the physical properties of a sample of irradiated Poly-Eth 1008.5 with a melt index of 2.3 were only slightly inferior to the properties of Poly-Eth 1005, but extrusion as a film was not satisfactory.

3. It is difficult to obtain a satisfactory balance of properties by irradiation of the two samples studied. Possibly better results might be achieved if a polymer having a narrow molecular weight distribution could be used; irradiation of such a polymer should result in less difficulty in fabrication caused by small amounts of gal.

#### B. Modification of Crosslinking in Polyethylene

#### INTRODUCTION

When the difficulty of achieving a suitable balance between a desirable degree of crosslinking in polyethylene and ease of fabrication became apparent, attention was turned to the possibility of modifying or controlling the crosslinking due to irradiation. If, for example, the use of an additive in polyethylene altered the ratio of crosslinking to degradation, the properties of irradiated polyethylene might be different.

Some information is already available about the effects of additives to polymers on the behavior under irradiation. Charlesby, Alexander, and others<sup>33-35</sup> have done considerable work on the protection of polymers against radiation damage by adding free radical acceptors such as aniline to the polymer before irradiation. Meikle and Graham<sup>36</sup> claim that the use of unspecified additives to polyethylene improves the characteristics (especially at high temperatures) of the irradiated product; the process concerned is now being licensed for commercial use ("Hyrad" process). The addition of carbon black to polyethylene before irradiation has been claimed to be advantageous;<sup>37,38</sup> a commercial application of the use of carbon has also been made.<sup>39</sup> Although the mechanism of the action is not firmly established, it seems possible that the carbon particles act as "traps" for polymeric free radicals and bind together several polymer molecules; the new bonds formed may thus increase mechanical strength.<sup>38,40</sup> Another effect of additives may be to combine with residual oxygen and thus inhibit degradative processes otherwise catalyzed by oxygen.<sup>34</sup>

Because of this interest in the modification of reactions induced in high polymers by irradiation, a preliminary investigation was begun. Several experiments were therefore made in which varying amounts of aniline or carbon

black were milled into Poly-Eth 1008.5 before irradiation. Since styrene, like aniline and carbon, should be a good free radical acceptor, the irradiation of polystyrene-containing polyethylene [in the form of a polyethylene-styrene graft copolymer, (Section C, below)] was also completed. In addition, since it had been observed previously (Section A) that the adhesion of polyethylene to glass was increased by irradiation, several experiments were made with the incorporation of finely divided glass, or "flake" glass, in Poly-Eth 1008.5 before irradiation. Results of these experiments are presented and discussed in this section.

Now the incorporation of all these additives or fillers requires milling, which, of course, decreases the strength properties of polyethylene (see Tables VI-VIII). The incorporation of a modifier in such a manner as to retain the inherent structure of the polyethylene seemed especially desirable. One way of accomplishing this purpose would be to saturate (to some degree) the polyethylene with a gaseous modifier before irradiation. Experiments were accordingly conducted with the irradiation of Poly-Eth 1008.5 that had been previously more or less saturated with vinyl chloride, which, as well as its polymer, should act as an efficient chain transfer agent for reactions of polymeric radicals. At the same time, the formation of polyvinyl chloride should be limited, for polyvinyl chloride is degraded by radiation. Because some information was already available about the reactions of monomers with polyethylene film (see Section C),\* the first experiments were made with films or sheets; a few experiments were made with pellets. The results of this work are reported below.

Similar experiments were made using vapors of the following two groups of monomers: vinyl acetate, and isobutylene—the polymers of which are degraded by irradiation; butadiene and propylene—the polymers of which are, or might be expected to be, crosslinked by irradiation.

#### EXPERIMENTAL

Pellets, 2-mil film, and 20-mil sheets of Poly-Eth 1008.5 were supplied by the Spencer Chemical Company. Styrene (99%) was obtained from the Dow Chemical Company, aniline (reagent grade) from Merck and Company, and vinyl chloride (99.8%) from the Matheson Company. The carbon black used—HCR, SRF, and Thermax—was obtained from the Binney and Smith Company. Flake glass was supplied by the Owens-Corning Fiberglas Corporation. The styrene-containing polymer was sample 7, Table XVIII.

\*Although the reaction of the vinyl chloride and other monomers with polyethylene does, in one sense, constitute grafting, the purpose of these experiments was not to make a graft polymer per se (polymer A on polymer B) but merely to modify the structure of polyethylene by use of a chain transfer agent. For this reason, these experiments are discussed here, rather than in Section C, which deals with graft copolymers.

Additives were incorporated in the polyethylene by milling at 240°F for 5 minutes; a sample of polyethylene was milled in a similar manner as a blank. The milled samples were sealed into evacuated tubes for irradiation at room temperature by the 3-kilocurie Co-60 source at the Phoenix Laboratory (dose rate: about  $3 \times 10^5$  rep/hr). Tensile properties were then determined as in Section B. Adhesive ratings were found by determining the force in grams required to strip a length of Scotch tape from a sheet of polyethylene (the tape having been subjected to a constant weight for a constant time).

In the experiments using monomers, the polyethylene samples were first placed in glass tubes and then degassed using a high-vacuum line for varying periods of time before charging with monomer vapor (see tables). Gaseous monomers were charged to approximately atmospheric pressure directly from cylinders after evacuation of the connecting lines; the other monomers were charged from degassed ampoules of the liquid monomers to the maximum pressure possible. Blank experiments were conducted in a similar way except for the omission of monomers. After irradiations (at room temperature, unless specified otherwise) were complete, the tubes were opened to the atmosphere at once, and physical properties determined [both parallel to (+), and transverse to (-), the machine direction, in the case of films or sheets]. Tests showed that the tensile properties of samples cut from different places on the sheet roll did not vary significantly. It was also found that the tensile properties of monomer-treated film were unchanged by degassing residual monomer. Settings of the Instron are given in relevant sections below. Tensile measurements were usually made with 8 or 10 samples, and the values averaged.

Tests of heat distortion were made by exposing samples cut from the sheets or films and placed on asbestos board to the desired temperature in a circulating oven; tests showed the heating of the asbestos board to be uniform. Infrared measurements were made using a Baird recording spectrophotometer, model B.

## RESULTS AND DISCUSSION

### 1. Solid and Liquid Additives

In Table VI, results are presented for the experiments with the incorporation of styrene, aniline, and carbon black in polyethylene before irradiation; more detailed results for several types of carbon black are given in Table VII.

The results show that the presence of aniline hindered the initial increase in tensile strength expected on irradiation; in fact, the irradiation led to a slight decrease in tensile strength, especially at the higher concentration of aniline. Since all properties listed are considerably decreased from the original properties, no advantage is given by the addition of aniline, at least under conditions used in this study. Similarly, the incorporation of

TABLE VI  
 THE EFFECT OF ADDITIVES<sup>a</sup>  
 ON THE PHYSICAL PROPERTIES OF IRRADIATED POLY-ETH 1008.5

Sample	Additive	Dose, rep x 10 <sup>-6</sup>	Tensile Strength, psi	Adhesive Rating, g	Elongation, %
Styrene graft <sup>b</sup>	None	--	1610	255	540
Styrene graft	None	0.22	1180	146	265
PE-1008.5	2% aniline	0.51	1230	190	240
PE-1008.5	5% aniline	0.51	1200	182	240
PE-1008.5	2% aniline	--	1230	195	230
PE-1008.5	5% aniline	--	1230	182	220
PE-1008.5	2% C black	0.51	1210	261	-
PE-1008.5	2% C black	--	1180	264	-
PE-1008.5	5% C black	0.51	1190	286	-
PE-1008.5	5% C black	--	1290	254	-
PE-1008.5 (Milled)	None	0.5	1400	230	535

<sup>a</sup>Additives milled in with polyethylene, unless specified otherwise.

<sup>b</sup>These samples were not milled.

TABLE VII

THE EFFECT OF TYPE OF CARBON BLACK<sup>a</sup>  
ON THE PHYSICAL PROPERTIES OF CARBON-FILLED IRRADIATED POLY-ETH 1008.5

Type of Carbon	Dose, rep x 10 <sup>-6</sup>	Tensile Strength, psi	Adhesive Rating, g	Elongation, %
Blank <sup>b</sup>	--	1230	222	535
Blank	1.0	1500	240	535
Blank	1.75	1575	209	(375)
Blank	3.75	1540	213	535
HCR-8	--	1190	268	65
HCR-8	1.0	1230	268	65
HCR-8	1.75	1350	277	65
HCR-8	3.75	1180	227	65
SRF	--	1110	225	65
SRF	1.0	--	250	--
SRF	1.75	1250	227	65
SRF	3.75	1200	222	65
Thermax	--	1060	262	65
Thermax	1.0	1120	182	65
Thermax	1.75	1360	240	65
Thermax	3.75	1220	226	65

<sup>a</sup>All samples contained 10% carbon black.

<sup>b</sup>All blank samples were milled before testing.



styrene in the form of a polyethylene-styrene graft copolymer resulted in a marked lowering of all properties measured after irradiation.

Although the use of small amounts of carbon black resulted in a decrease in tensile strength in both the blank and irradiated samples, the adhesive rating of the sample containing 5% carbon was increased by irradiation (Table VI). As might be expected, the effect of carbon black depends on the type used (Table VII). Although the addition of 10% carbon black lowered the overall tensile strength and percent elongation, tensile strengths at a dose of  $1.75 \times 10^6$  rep were all higher than the tensile strength of unfilled, unirradiated polyethylene; the relative increase of tensile strength was greatest for the samples containing Thermax carbon black. Adhesive ratings were in most cases higher than for the unfilled unirradiated polyethylene. Thus the irradiation of carbon-filled polyethylene may to some extent offset the loss in tensile strength incurred by the addition of the filler.

Possibly the reason for the failure to observe dramatic effects with the use of additives lies in the fact that irradiations were conducted in the absence of oxygen; also, tests showed no evidence for post-irradiation degradation that could result from the presence of residual oxygen. This explanation is consistent with the observations of Alexander and Toms reported above.<sup>34</sup>

Results for the glass-filled polyethylene are given in Table VIII. The presence of the glass resulted in a considerable lowering of the percent elongation, but little change in the tensile strength. Irradiation with a fairly low dose ( $4.8 \times 10^5$  rep) resulted in substantial increases in percent elongation. Indeed, the percent elongation for a sample containing 5% glass was increased 15-fold to the level characteristic of unfilled polyethylene. In other words, irradiation of a glass-filled polyethylene results in a substantial increase in toughness.

## 2. Vinyl Monomers as Modifiers

a. Polyethylene Sheets.—Results from preliminary experiments with the irradiation of 20-mil polyethylene sheets are given in Table IX. A striking increase in both tensile strength and percent elongation may be noted for the treated irradiated sheets as compared with the sheets that had been merely irradiated under vacuum. In other words, treatment with vinyl chloride results in increased toughness. Both tensile strength and percent elongation reached a maximum at a dose of  $8.3 \times 10^5$  rep; at this dose, the gain in weight of the film was only 2.1 percent. The incorporation of this small amount of vinyl chloride also affected the permeability slightly. After immersion in benzene for 48 hours, a typical sheet (No. 5) gained 10.6% in weight, as compared to 11.3% for irradiated sheet (having the same dose), and 9.1% for a plain sheet.

Infrared measurements revealed no major differences between the treated and untreated film.

TABLE VIII

THE EFFECT OF FLAKE GLASS ON PHYSICAL PROPERTIES  
OF IRRADIATED POLY-ETH 1008.5

Flake Glass, %	Dose, rep x 10 <sup>-5</sup>	Tensile Strength, psi	Elongation, %
1.0	4.8	1145	280
5.0	-	1220	20
5.0	4.8	1100	330
10.0	-	1230	70
10.0	4.8	1130	165
15.0	-	1200	65
15.0	4.8	1100	185
0.0	5.5	1190	330

TABLE IX

THE EFFECT OF ABSORBED VINYL CHLORIDE ON PHYSICAL PROPERTIES  
OF IRRADIATED POLYETHYLENE SHEETS (POLY-ETH 1008.5, 20-MIL)<sup>a</sup>

Sample	Dose, rep x 10 <sup>-5</sup>	Tensile Strength, psi <sup>b</sup>	Elongation, %	Adhesive Rating, g	Change in Weight, %
-	--	1670	713	-	-
2'	3.0	1715	735	-	-
7'	4.8	1570	653	-	-
5'	8.3	1850	798	175	-
3'	13.0	1820	720	180	-
4'	18.5	1960	760	180	-
2	3.0	1760	710	115	-
7	4.8	2150	823	145	-
5	8.3	2370	800	165	2.1
3	12.4	2250	820	165	-
4	18.5	1870	735	202	0.5

<sup>a</sup>Before irradiation the sheet was kept in contact with vinyl chloride for 3 days.

<sup>b</sup>Cross-head speed 10 in./min; all samples transverse to the machine direction.

On the other hand, as may be seen from Table X, treatment with the other monomers\* had either little effect (as with vinyl acetate) or resulted in deterioration of the properties measured. Again, changes in weight were very small—of the order of parts per thousand. Thus vinyl chloride appears to be unique. Further experiments with this technique were therefore restricted to the use of vinyl chloride.

Before proceeding with further experiments, tests of heat distortion were made on rectangular samples cut from all sheets studied up to that time. Results are given in Table XI; the appearance of the samples after testing (originally the same size and shape) is shown in Fig. 3. Again, the effect of vinyl chloride is unique; although use of the other monomers resulted in sheets having a poorer resistance to heat (especially with respect to shrinkage) than did plain irradiated sheets, the use of vinyl chloride and a dose of  $(0.8 - 1.2) \times 10^6$  rep resulted in a sheet having remarkable stability with respect to both buckling and shrinkage. This optimum dose corresponds to the dose yielding maximum tensile strength and percent elongation, and hence maximum toughness.

It was then decided, first, to try to determine the experimental conditions leading to heat-resistant sheets,\*\* and second, to study the relationships between the unusual stability and tensile properties in both the transverse and machine directions. The experiments with sheets were accordingly repeated; effects of time in contact with the vinyl chloride, time of degassing, and dose were examined in some detail at room temperature. Since particular attention to elastic modulus was desired, the cross-head speed of the Instron tester was set at a very slow speed, 2 in./min. As before, tests of heat resistance were made; since the conditions of test varied somewhat from case to case, some variations in results may be noted below.

Effect of total dose: Results of heat tests made on some typical irradiated treated polyethylene sheets are given in Table XII; see also Figs. 4 and 5. As was the case with the preliminary experiments, the irradiation of a vinyl chloride-treated sheet with a dose of about  $8 \times 10^5$  rep (sample 47) resulted in very good resistance both to shrinkage along the machine direction and to buckling. In contrast, irradiation of untreated film with the same dose (sample 47<sup>†</sup>) resulted in rather poor resistance to heat; the sheet flowed and shrank considerably—to about the same extent as an unirradiated sheet. The

\*In several of these experiments the sheets were irradiated immediately after charging, instead of after a soaking period of 3 days, as with samples described in Table IX. A check was therefore made with a vinyl chloride experiment in which the sheet was irradiated immediately after charging (sample 27). Although the tensile strength was, indeed, lower than the value predicted on the basis of Table IX, the strength was still high.

\*\*The grafting of vinylidene chloride to polyethylene film has been described,<sup>41</sup> but no physical properties were reported; the use of vinyl chloride was not, however, mentioned.

TABLE X

THE EFFECT OF ABSORBED MONOMERS ON PHYSICAL PROPERTIES  
OF IRRADIATED POLYETHYLENE SHEETS (POLY-ETH 1008.5, 20-MIL)

Sample	Monomer	Dose, rep x 10 <sup>-6</sup>	Tensile Strength, psi	Elongation, %	Change in Weight, %
13	Butadiene <sup>a,b</sup>	0.27	1425	540	-0.2
13'	Butadiene <sup>a,b</sup>	0.44	1650	580	+0.2
14	Butadiene <sup>a,b</sup>	0.72	1600	525	+0.2
14'	Butadiene <sup>a,b</sup>	1.16	1510	490	+0.3
15	Butadiene <sup>a,b</sup>	1.61	1420	505	+0.2
Blank	None	None	1735	510	--
16	Isobutylene <sup>c</sup>	0.67	1610	440	+0.1
17	Isobutylene <sup>c</sup>	0.99	1610	435	+0.1
18	Isobutylene <sup>c</sup>	1.49	1710	500	+0.1
19	Vinyl acetate <sup>c</sup>	0.67	1710	510	0.0
20	Vinyl acetate <sup>c</sup>	0.99	1730	550	+0.1
21	Vinyl acetate <sup>c</sup>	1.49	1800	500	0.0
25	Vinyl acetate <sup>a</sup>	0.96	1490	475	+3.0
29	Propylene <sup>a</sup>	0.96	1580	510	+0.1
27	Vinyl chloride <sup>a</sup>	0.96	2100	600	--

<sup>a</sup>Sheet degassed for 24 hours.

<sup>b</sup>Contact time of sheet with monomers before irradiation: 2-1/2 days.

<sup>c</sup>Sheet degassed for 4 hours.

TABLE XI

THE EFFECT OF ABSORPTION OF MONOMERS ON THE  
HEAT RESISTANCE OF IRRADIATED POLYETHYLENE SHEETS (POLY-ETH 1008.5, 20-MIL)

Test: 15 min at 130°C

Sample	Monomer	Dose, rep x 10 <sup>-6</sup>	General Appearance	Approximate Shrinkage, <sup>a</sup> %	Grade <sup>b</sup>
7	None	0.5	No buckling	25	A-
5'	None	0.8	Buckling	25	A-
3'	None	1.3	Buckling	25	A-
4'	None	1.8	Buckling	25	A-
2	Vinyl chloride	0.3	A little distortion	10	A
5	Vinyl chloride	0.8 <sup>c</sup>	No apparent change	0	A+
3	Vinyl chloride	1.2	Very little change	5-10	A
4	Vinyl chloride	1.8	Buckling	30	B+
13	Butadiene	0.3	Soft and distorted	60 <sup>d</sup>	B
13'	Butadiene	0.4	Soft and buckled	60 <sup>d</sup>	B
14'	Butadiene	1.2	More buckled	60 <sup>d</sup>	B-
15	Butadiene	1.6	Some buckling	40 <sup>d</sup>	B+
16	Isobutylene	0.4	Buckling	60	A-
17	Isobutylene	1.0	Buckling	60	B+
18	Isobutylene	1.5	Buckling	60	A-
19	Vinyl acetate	0.4	Buckling	60	A-
20	Vinyl acetate	1.0	Buckling	60	B+
21	Vinyl acetate	1.5	Buckling	60	A-

<sup>a</sup>In machine direction of sheet.

<sup>b</sup>See Ref. 31.

<sup>c</sup>Corresponds to maximum ultimate tensile strength.

<sup>d</sup>Also, shrinkage transverse to machine direction.

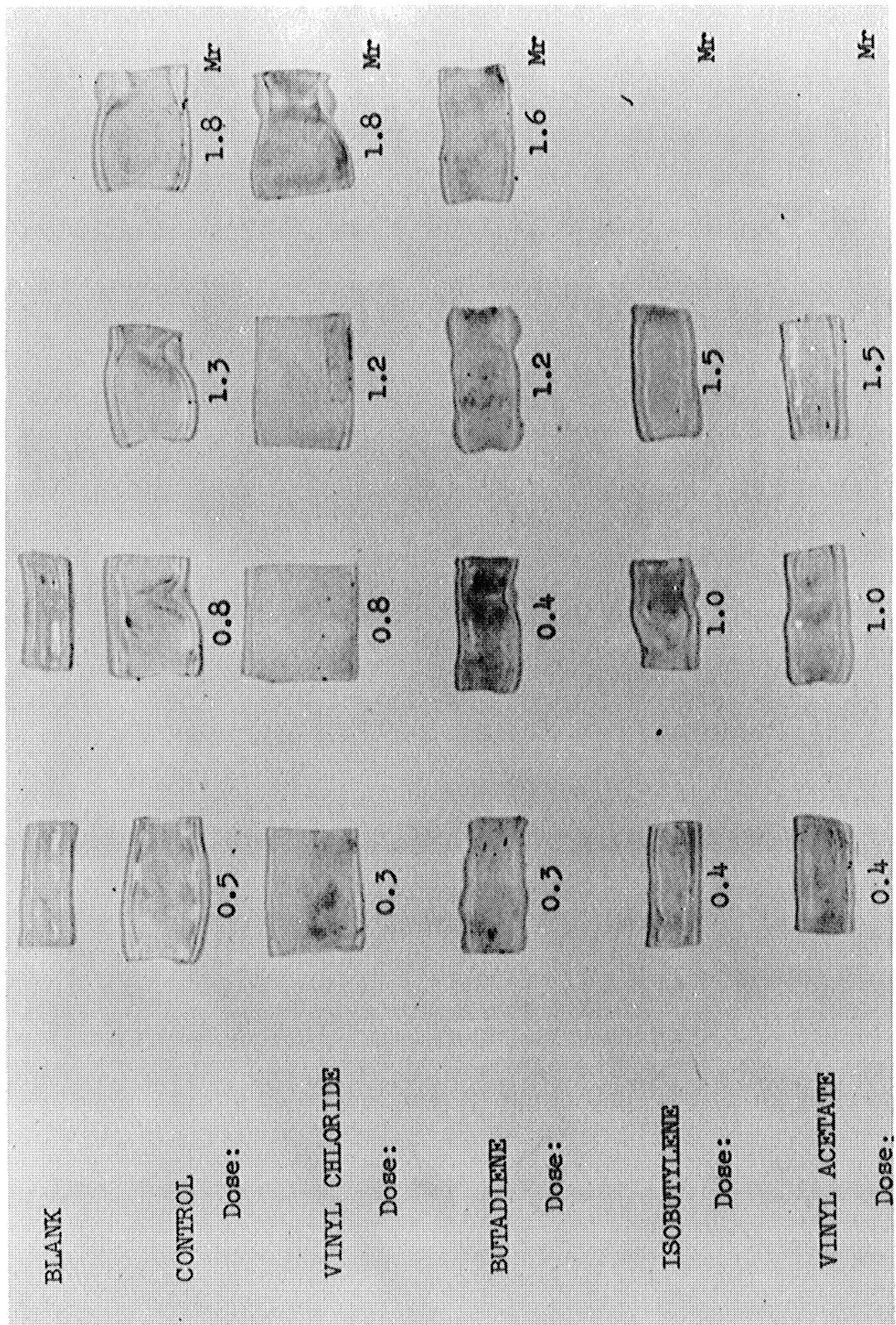


Fig. 3. Effect of absorption of monomers on the heat resistance of irradiated polyethylene sheets (Poly-Eth 1006.5, 20-mil). Test I.

TABLE XII  
THE EFFECT OF TOTAL DOSE ON HEAT RESISTANCE  
OF IRRADIATED TREATED POLYETHYLENE SHEETS (POLY-ETH 1008.5, 20-MIL)

Sample	Fig.	Dose, $\times 10^{-5}$ rep	Degassing		Contact Time, hr	Heat Test		Comments <sup>a</sup>
			Time, hr	Temp, °C		Time, min	Temp, °C	
40	4	2.0	24	24	24	118	11	Shrank 70%; flowed
41		4.0	24	24	24	118	11	Shrank 70%; flowed
42		6.0	24	24	24	118	11	Shrank 70%; flowed
43		8.5	24	24	24	118	11	Little change
44	4	1.0	24	24	3	118	11	Shrank 70%; flowed
44'		1.0	24	24	--	118	11	Shrank 70%; flowed
45		5.0	24	24	3	118	11	Shrank 70%; flowed
45'		5.0	24	24	--	118	11	Shrank 70%; flowed
46		7.0	24	24	3	118	11	Shrank 60%; flowed
46'		7.0	24	24	--	118	11	Shrank 70%; flowed
47		8.0	24	24	3	118	11	Shrank 30%; did not flow
47'		8.0	24	24	--	118	11	Shrank 70%; flowed
Plain Film		---	24	24	--	118	11	Shrank 70%; flowed
43	5	8.5	24	24	24	130	15	Shrank 10%; did not flow
47		8.0	24	24	3	130	15	Shrank 15%; slight buckling
48		8.5	12	3	3	130	15	Shrank 40%; buckled
49		1.0	24	3	3	130	15	Shrank 30%; buckled
50		1.5	24	7	3	130	15	Shrank 15%
51		1.2	24	3	3	130	15	Shrank 25%
52		1.2	24	24	24	130	15	Shrank 25%; buckled
Plain Film		---	24	24	--	130	15	Shrank 40-50%; flowed

<sup>a</sup>All shrinkage was in machine direction (+).

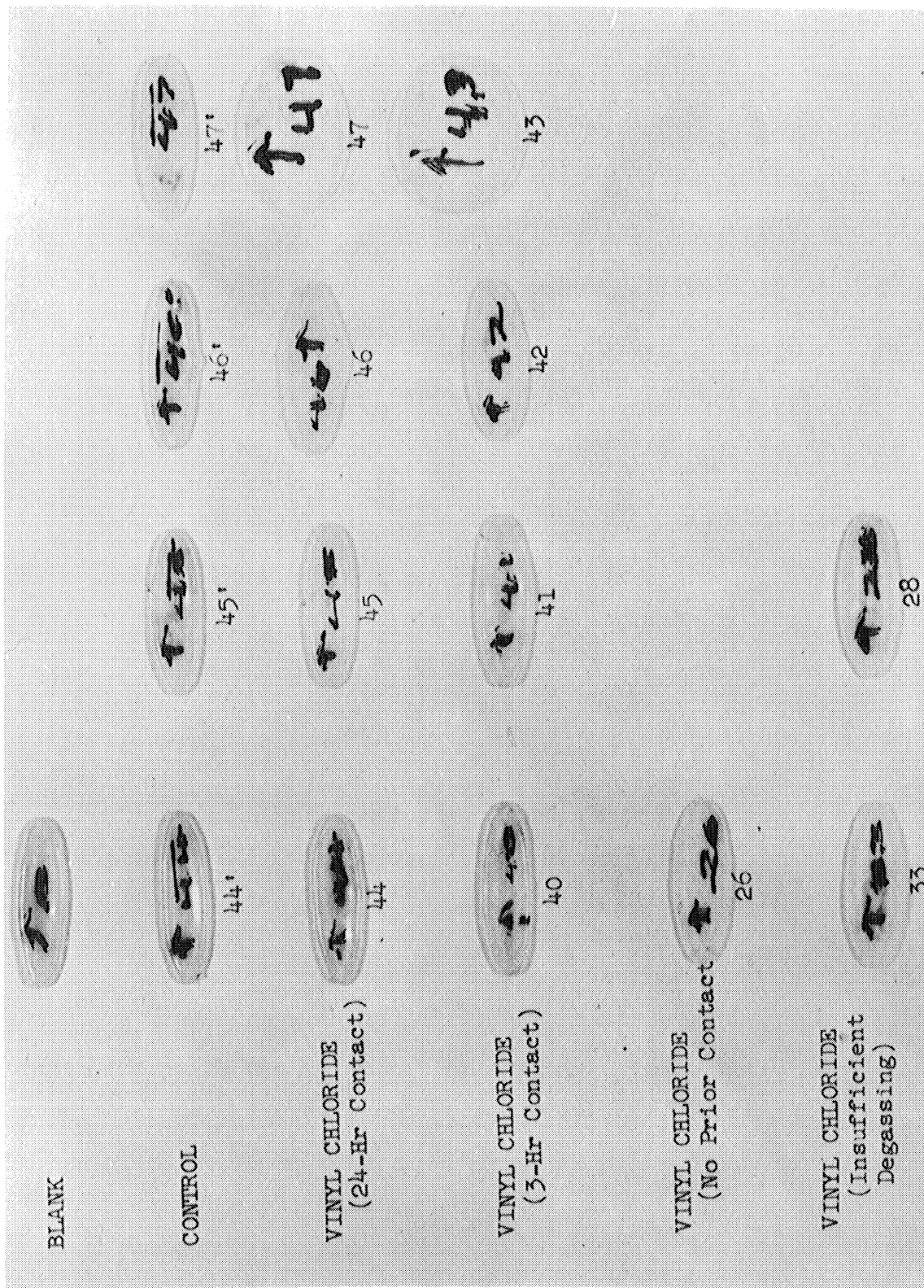


Fig. 4. Effect of vinyl chloride on the heat resistance of irradiated polyethylene sheets (Poly-Eth 1008.5, 20-mil). Test VII.



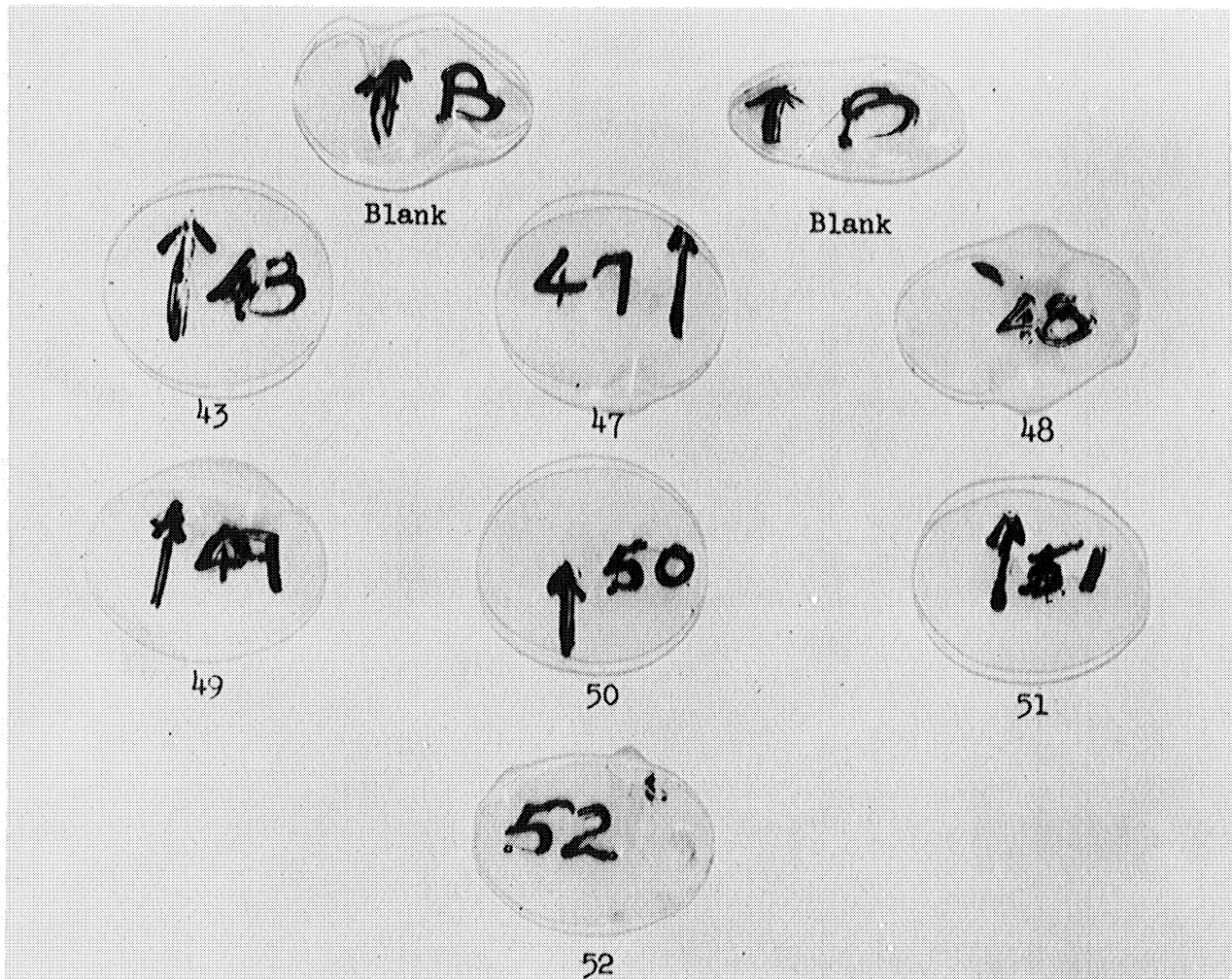


Fig. 5. Effect of vinyl chloride on the heat resistance of irradiated polyethylene sheets (Poly-Eth 1008.5, 20-mil). Test IX.

effect of higher doses is not, however, clear. Results for sheets 49 and 52 support the earlier observation (Fig. 3) that doses higher than  $8 \times 10^5$  rep result in deterioration of heat resistance. Nevertheless, samples 50 and 51 behaved well when exposed to heat.

Regardless of the effects of high doses, it seems reasonable to conclude that exposure of a polyethylene sheet that has been treated with vinyl chloride to a radiation dose of about  $8 \times 10^5$  rep results in a material having remarkable resistance to heat. This resistance is much greater than that conferred by exposure of untreated polyethylene sheet to the same dose.

Effect of time of contact with vinyl chloride: In the preliminary experiments described earlier, results suggested that the tensile strength of the final product was higher the greater the length of time the sheet was in contact with the vinyl chloride. The importance of a long contact time is demonstrated again in Table XIII. Although the heat resistance of

TABLE XIII  
 THE EFFECT OF TIME OF CONTACT WITH VINYL CHLORIDE  
 PRIOR TO IRRADIATION ON PHYSICAL PROPERTIES OF POLYETHYLENE SHEETS<sup>a</sup> (POLY-ETH 1008.5, 20-MIL.)

Sample	Contact Time, hr	Dose, rep x 10 <sup>-5</sup>	Tensile Strength, psi	Yield Strength, psi	Elastic Modulus, psi	Elongation, %	Heat Test at 120°C for 10 min
26	0	8.5	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>	Shrank 70%; buckled
47	3	8.0	+2010 -2040	+1204 -1160	+7500 -7540	+500 -555	Shrank 25%; very little buckling
43	24	8.5	+2170 -2120	+1210 -1170	+7290 -6760	+520 -540	Shrank 20%; no buckling
Plain Film	—	—	+1640 -1590	+1200 -1150	+7260 -7240	+420 -410	Shrank 70%; buckled

<sup>a</sup> Sheets degassed for 24 hr prior to charging with vinyl chloride.

<sup>b</sup> Insufficient sample for determination.

a sheet (sample 26) irradiated immediately after charging with monomer was poor, the heat resistance was markedly improved by an increase in the time of contact with vinyl chloride to 3 hours, or better, to 24 hours.

Apparently, then, the diffusion of monomer into the structure of polyethylene sheet must be an important factor in the development of heat resistance in the sheet.

Effect of time of degassing: Because of the notorious behavior of oxygen in free radical reactions, one might expect that the extent to which oxygen is removed from the polyethylene sheets before irradiation affects physical properties considerably. This expectation is confirmed by the data in Table XIV, which gives properties as a function of the length of time the sheets were degassed before irradiation. As the time of degassing was increased, the heat resistance increased also.

Thus the removal of residual oxygen from the polyethylene film before irradiation appears to be desirable if good heat resistance is to be obtained.

b. Polyethylene Film.—Because of the considerable interest in thin films, some experiments with the irradiation of thin (2-mil) films saturated with vinyl chloride were begun.

Results given in Table XV show that, as with the 20-mil polyethylene, exposure of the film to a dose of  $8 \times 10^5$  rep resulted in superior heat resistance. However, the heat tests with this film were less extensive than with 20-mil sheets, and also less reproducible, possibly because of a high sensitivity to the cutting procedure.

c. Polyethylene Pellets.—A tube filled with pellets of Poly-Eth 1008.5 (degassed for 22 hours) was charged with vinyl chloride and irradiated with a dose of  $9.6 \times 10^5$  rep. After irradiation, the pellets were compression-molded, and the tensile properties determined. It was difficult to obtain homogeneous sheets; values of tensile strength ranged between 1370 and 1890 psi—the average, 1650 psi, being considerably higher than the value of 1450 psi interpolated from previous data (Section A). Possibly the dose was high enough to induce enough crosslinking to cause molding difficulties.

d. Relationship Between Heat Resistance and Other Properties.—So far the best correlation between the unusual stability with respect to heat and physical properties is with ultimate tensile strength and elongation, that is, with toughness (see Tables IX, XII, and XVI). Although it is difficult to visualize the precise meaning of toughness, it seems reasonable that the greater the toughness (and hence the greater the total energy required to deform a sample to the breaking point), the greater should be the resistance to deformation due to heating.

Certainly one would expect the stability to be related to the elastic

TABLE XIV  
 THE EFFECT OF TIME OF DEGASSING ON PHYSICAL PROPERTIES  
 OF IRRADIATED TREATED POLYETHYLENE SHEETS<sup>a</sup> (POLY-ETH 1008.5, 20-MIL)

Sample	Degassing Time, hr	Dose, rep x 10 <sup>5</sup>	Tensile Strength, psi	Yield Strength, psi	Elastic Modulus, psi	Elongation, %	Heat Test, 120°C for 10 min
33	0	8.5	b	b	b	b	Shrank 60%; buckled
28	4	8.5	b	b	b	b	Shrank 60%; buckled
48	12	8.5	+2080	+1165	+7430	+545	Shrank 40%; buckled
45	24	5.0	-1810	-1105	-8040	-650	Shrank 60%; buckled
45'	24	5.0	+1700	+1190	+7330	+450	Shrank 60%; buckled
46	24	7.0	-1430	-1170	-7730	-390	Shrank 60%; buckled
46'	24	7.0	+1540	+1190		+380	Shrank 60%; buckled
47	24	8.0	-1630	-1130		-440	Shrank 60%; buckled
47'	24	8.0	+1580	+1205	+7190	+370	Shrank 60%; buckled
32	24	8.7	-1680	-1160	-6990	-460	Shrank 60%; buckled
Plain Film	—	—	+1710	+1200	+7430	+435	Shrank 60%; buckled
			-1800	-1145	-7380	-510	Shrank 25%; only slight buckling
			+2010	+1204	+7500	+500	Shrank 60%; buckled
			-2040	-1160	-7540	-555	Shrank 15%; no buckling
			+1750	+1200	+6830	+460	Shrank 75%; melted
			-1750	-1150	-6610	-500	
			-2210	-1120	-6650	-590	
			+1640	+1200	+7260	+420	
			-1590	-1150	-7240	-410	

<sup>a</sup>Time of contact with monomer prior to irradiation: 3 hr.

<sup>b</sup>Insufficient sample for determination.

TABLE XV

PHYSICAL PROPERTIES OF IRRADIATED TREATED POLYETHYLENE FILM  
(POLY-ETH 1008.5, 2-MIL)

Sample	Degassing Time, hr	Contact Time, hr	Dose, rep x 10 <sup>-5</sup>	Tensile Strength, psi	Yield Strength, psi	Elastic Modulus, psi	Elongation, %	Heat Test, 132°C for 11 min
Blank	—	—	—	+2860 -1700	+2380 -1360	+ 2,520 - 2,470	+140 -325	Shrank 70% in (+) direction; also curled up
T-4	24	3.0	1.0	+2590 -1720	+2230 -1420	+11,400 -11,800	+130 -330	Buckled and curled up
T-5	24	3.0	3.0	+2540 -1720	+2200 -1430	+11,200 -10,400	+130 -360	Shrank 10% in (-) direction; curled slightly
T-6	24	3.0	5.0	+2710 -1980	+2400 -1430	+11,200 -10,400	+130 -345	Shrank 10% in (-) direction; curled slightly
T-1	24	3.0	8.0	+2900 -1925	+2430 -1440	+16,500 - 9,000	+110 -355	Shrank 5% in (+) direction; no other change
T-3	24	3.0	15.0	+2410 -2380	+2200 -1340	+12,700 -13,700	+165 -470	Poor sample
T-2	0	3.0	8.0	+2650 -2090	+2260 -1390	+10,400 -10,700	+160 -390	Shrank 20% in (-) direction; also curled

TABLE XVI  
 PHYSICAL PROPERTIES OF SOME IRRADIATED TREATED POLYETHYLENE SHEETS  
 (POLY-ETH 1008.5, 20-MIL)

Sample	Degassing Time, hr	Contact Time, hr	Dose, $\times 10^{-5}$ rep	Tensile Strength, psi	Yield Strength, psi	Elastic Modulus, psi	Elongation, %
40	24	24	2.0	+1720	+1160	+7100	+440
41	24	24	4.0	-1720	-1140	-7360	-500
42	24	24	6.0	+1600	+1140	+6030	+430
43	24	24	8.0	-1650	-1100	-6360	-490
44	24	24	1.0	+1760	+1160	+6400	+500
44'	24	3	1.0	-1750	-1110	-6770	-500
45	24	24	8.0	+2170	+1210	+7290	+520
45'	24	24	1.0	-2120	-1170	-6760	-540
46	24	24	5.0	+1420	+1175	+6950	+315
46'	24	24	5.0	-1650	-1120	-7340	-460
47	24	24	1.0	+1630	+1190	+7500	+310
47'	24	24	1.0	-1701	-1140	-7200	-495
48	24	24	5.0	+1700	+1190	+7330	+450
48'	24	24	5.0	-1430	-1170	-7730	-390
49	24	24	7.0	+1540	+1190	+7640	+380
49'	24	24	7.0	-1630	-1130	-7560	-440
50	24	24	3	+1580	+1200	+7190	+370
50'	24	24	3	-1680	-1160	-6990	-460
51	24	24	7.0	+1710	+1200	+7430	+430
51'	24	24	7.0	-1800	-1145	-7380	-500
52	24	24	8.0	+2010	+1200	+7500	+500
52'	24	24	8.0	-2040	-1160	-7540	-555
53	24	24	8.0	+1750	+1200	+7200	+450
53'	24	24	8.0	-1750	-1155	-7500	-500
Plain Film	--	--	--	+1640	+1200	+7260	+420
	--	--	--	-1590	-1150	-7240	-410

modulus. The data, however, are not conclusive (Table XVI).

In any case, one might conclude that the toughness and strength due to crosslinking result in a considerable resistance to buckling. Although it is not clear how vinyl chloride acts so specifically, several possibilities exist. For example, the vinyl chloride may disrupt the crystallinity of the polyethylene slightly, especially at the surfaces. Possibly the resulting situation in which a crystalline material is faced with a more or less amorphous layer is analogous to the situation existing in a polished metal, in which the surface consists of a disorganized layer of metal. It is believed that the strength of a polished metal is associated with the "skin" just mentioned. Alternatively, the vinyl chloride may have a "healing" effect on surface imperfections; it may relieve stresses in the polymer sheet and thus increase the resistance to buckling.

It is more difficult to consider the diminished shrinkage in the machine direction. Apparently in some way treatment with vinyl chloride must more or less equalize "something." One might postulate that the use of vinyl chloride induces crosslinking between regions oriented by fabrication rather than between molecules in the same oriented region; this might be reasonable, as the vapor could diffuse more readily into the amorphous areas between the oriented regions than into the oriented regions themselves. Indeed, it has already been observed that the diffusion of vinyl chloride is important for the development of heat resistance (Table XIII). However, one would expect to find this equalization reflected in physical properties as a function of sheet direction. But strangely enough, neither the tensile and yield strengths nor percent elongation for transverse (-) and parallel (+) samples show a consistent trend that could be correlated with either the stability with respect to heat or toughness. Similarly, no consistent trends may be noted in the elastic modulus.

e. Vinyl Chloride and Crosslinking.—Although the value of treating films and sheets with vinyl chloride before irradiation seems clear, the question of fabricating treated polymers arises. For this reason the milling of some irradiated treated sheet (47), plain sheet, and irradiated sheet (47') was tried at 220°F. While the plain sheet flowed smoothly, it was necessary to increase the temperature to handle the other sheets. Eventually, the irradiated sheet formed a crinkly sheet; the treated sheet seemed to flow a little at first, and then formed a sheet that was much more crinkly than the irradiated sheet. When square samples of each of the three milled sheets were exposed to a temperature of 125°C for 20 minutes, the plain sheet melted, the irradiated sheet flowed into an elongated rectangle, but the treated irradiated sheet retained both its square form and its original appearance, though with a little (10-20%) shrinkage in each direction. In other words, the treated irradiated polymer behaved as though it were highly crosslinked. These results suggest two alternatives: that the use of vinyl chloride results in a greatly enhanced degree of cross linking at the time of irradiation, or that a crosslinking reaction occurs during heating as well as during irradiation. If

the former alternative is true, then fabrication of treated polymers (as in the initial work with pellets) may be no more easy than the fabrication of polymers that have been merely irradiated. If, on the other hand, the latter alternative is true, the use of an inhibitor should help prevent the second-stage crosslinking during molding or milling.\* Further experiments would be required to settle this matter: for example, (a) a study of the effect of inhibitors on fabrication; (b) a study of the effect of very high doses on heat stability of films and sheets; and (c) determination of gel content for plain, irradiated, and irradiated treated sheets and films.

#### CONCLUSIONS

1. By the irradiation of thin polyethylene sheets or films (20-mil or 2-mil) that have been, to some degree, saturated with vinyl chloride, the resistance to shrinking and buckling on exposure to heat may be increased markedly.

2. The optimum dose appears to be about  $(8-9) \times 10^5$  rep. Best results are obtained by allowing the monomer to remain in contact with degassed polyethylene for a long period of time, say, 24 hours; degassing of the polyethylene beforehand is essential.

3. The resistance to heat may be correlated with toughness. Yield strengths and elastic moduli do not, on the other hand, bear much relationship to the thermal behavior.

4. Even if the vinyl chloride acts as a chain transfer agent, the mechanism leading to the observed effects is not clear. So far, several possibilities, not necessarily mutually exclusive, exist: a "healing" effect on surface imperfections, a "skin" effect resulting in greater toughness, the crosslinking of regions of high crystallinity formed by orienting, and the promotion of crosslinking in general. More evidence will be required to understand the mechanism or mechanisms more thoroughly.

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\*Some support of this alternative is given by the observation that the shrinkage observed in heating the irradiated treated sheet was more or less equal in both dimensions. This fact would be consistent with the occurrence of crosslinking at a high temperature, for little distortion of the resulting structure should occur in further heating; on the other hand, a sample already crosslinked at a low temperature before fabrication should tend to shrink on heating.



C. Graft Polymerization of Monomers to Polyethylene

INTRODUCTION

In the search for new high polymers or desirable modifications of old ones, the technique of graft polymerization has received much attention.<sup>42</sup> By this technique, branches composed of one polymer may be added to a backbone chain of another polymer. Functional groups of interest may be added to a backbone chain having desirable characteristics of its own, for example, strength; the properties of the resultant product are generally determined by the sum of the properties of the individual polymers rather than some function less than the sum.

It has been reported that the grafting of monomers to a backbone chain of, say, polyethylene proceeds very favorably under the influence of gamma radiation.<sup>43,44</sup> Ballantine and others<sup>43</sup> have described the grafting of monomers such as styrene and acrylonitrile to polyethylene film by means of irradiation. Similar experiments have been described by Chen and others,<sup>44</sup> who reported the following: by the grafting of styrene to Teflon, a substantial increase in adhesive power; by the grafting of acrylonitrile to polydimethyl siloxane, an increase in solvent resistance; and by the grafting of vinyl carbazole to polyethylene, an improvement in temperature performance as a low-loss dielectric.

Because of these claims of versatility for grafting, it was decided to investigate the grafting of several monomers to polyethylene to see if any useful products would be formed. Results of this study are described below.

EXPERIMENTAL

Pellets of Poly-Eth 1008.5 were obtained from the Spencer Chemical Company. When desired, crumbs were prepared by milling pellets for 5 minutes at 220°F. Polyethylene film was a common commercial wrapping type. The monomers were commercial grade, and were distilled shortly before use.

Graft polymerizations were conducted in tubes sealed under vacuum; the contents of the tubes were degassed before sealing. A few experiments were also made in which samples of Poly-Eth 1008.5 in sheet form that had been irradiated previously with a dose of  $9.6 \times 10^5$  rep were immersed in acrylonitrile.

After reaction, polyethylene film was removed, washed with an appropriate solvent, and dried at 75°C. Polyethylene solutions were precipitated in methanol, filtered off, washed, and dried in the same manner as the film.

Tensile measurements and tests of adhesive rating were made as described in Sections B and C.

## RESULTS AND DISCUSSION

Best results were obtained with grafting to films and grafting in solution. This section is, therefore, concerned with these two topics.

Polyethylene Film, 4.5-mil: Results are given in Table XVII for experiments with acrylonitrile, styrene, and vinyl acetate. It may be seen that the use of acrylonitrile resulted in a marked increase in tensile strength, little change in percent elongation, and, surprisingly, a marked decrease in the adhesive rating. The irradiation of a film in contact with the monomer gave a slightly higher tensile strength than the irradiation in vacuum of a film swollen with monomer. The amounts of acrylonitrile concerned in the grafting reaction must have been small, for no change in the weight of the film could be detected after grafting.

In general, somewhat higher tensile strengths were observed for the styrene copolymers. The adhesive rating was also higher, at least for samples 7, 8, and 8'—and, indeed, higher than for the blanks. On the other hand, the percent elongation was lower for samples 7, 8, and 8'. In this case, the irradiation of a film swollen with monomer, rather than the irradiation of an immersed film, gave the higher tensile strength. Increases in the weight of the films were also observed—14.8% and 15.2% for samples 8 and 8', respectively.

In contrast to the other monomers, the use of vinyl acetate resulted in no consistent difference in properties—certainly in no improvement.

Thus, the grafting of acrylonitrile and styrene to polyethylene is promoted by relatively small doses of gamma radiation.

Polyethylene in Solution: These experiments were made in the hope that grafting in solution would yield a more homogeneous product. Typical results of grafting experiments using acrylonitrile and styrene as monomers are given in Table XVIII.

With acrylonitrile, an improvement in tensile strength over plain film was observed;\* the tensile strength was independent of the concentration of acrylonitrile in the solution. The most interesting observation, however, was that transparency of the polyethylene was considerably improved by grafting, especially with the sample for which the smallest proportion of acryloni-

\*The blanks were not milled. However, milling reduces the tensile strength, and hence any differences observed between values for graft polymers and values for blanks are probably less than the true differences.

TABLE XVII  
PHYSICAL PROPERTIES OF POLYETHYLENE FILMS IRRADIATED IN THE PRESENCE OF MONOMERS

Sample	Monomer	Dose, rep x 10 <sup>-4</sup>	Tensile Strength, psi	Adhesive Rating, g	Elongation, %	Comments
Blank	--	--	2400	200	635	
Blank	--	22	2440	(86)	750	
2	Acrylonitrile	3.2	2630	107	760	
3	Acrylonitrile <sup>a</sup>	0.9	2540	160	620	No increase in weight
4	Acrylonitrile <sup>a</sup>	0.9	2820	160	630	No increase in weight
4'	Acrylonitrile <sup>b</sup>	0.9	2380	150	650	
6	Styrene <sup>a</sup>	3.2	2590	120	680	
7	Styrene <sup>a</sup>	0.9	2740	300	460	14.8% increase in weight
8	Styrene <sup>a</sup>	0.9	2970	250	570	15.2% increase in weight
8'	Styrene <sup>b</sup>	0.9	2720	295	470	
9	Vinyl acetate	4.1	2330	---	650	
9'	Vinyl acetate <sup>b</sup>	0.9	2550	160	630	

<sup>a</sup>In these cases, the film was swollen with monomer and the swollen film irradiated under vacuum.

<sup>b</sup>In these cases, the film was allowed to swell in monomer for 115 hr prior to irradiation in monomer

TABLE XVIII  
 PHYSICAL PROPERTIES OF POLYETHYLENE<sup>a</sup> IRRADIATED IN THE PRESENCE OF MONOMERS IN SOLUTION<sup>b</sup>

Sample	Monomer	Dose, $10^{-5}$ rep	Temp, °C	Tensile Strength, psi	Adhesive Rating, g	Elongation, %	Comments
2	5% acrylonitrile	1.2	114	1500	260	490	Very transparent
1	10% acrylonitrile	1.2	114	1510	230	430	Slightly transparent
5	14% acrylonitrile	1.2	114	1500	240	480	Slightly transparent
8	19% acrylonitrile	1.2	114	1500	240	440	Slightly transparent
4	7% styrene	1.2	114	1760	240	540	Mottled
6	11% styrene	1.2	114	1610	240	420	Mottled
7	16% styrene	1.2	114	1590	260	470	Mottled
3	20% styrene	1.2	114	1520	220	450	Mottled
Blank <sup>c</sup>	---	---	---	1400 <sup>c</sup>	230	535	
Blank <sup>c</sup>	---	0.9	---	1550 <sup>c</sup>	263	---	

<sup>a</sup>Poly-Eth 1008.5.

<sup>b</sup>Solvent: xylene.

<sup>c</sup>Not milled; values for milled samples would, of course, be lower.

trile had been used. Thus the branching reaction apparently disrupted the crystallinity enough to increase the transparency; at the same time, the tensile strength was not adversely affected.

Higher tensile strengths were observed when styrene, especially a small amount of styrene, was used. However, the samples had a mottled appearance.

All these results show that it may be possible to select particular monomers, such as acrylonitrile, to modify the polyethylene structure and at the same time contribute some virtues of their own. If special combinations of properties are required, the technique of grafting may be useful.

#### CONCLUSIONS

1. The tensile strengths of polyethylene film may be increased by irradiation in the presence of acrylonitrile or styrene.
2. The adhesive rating of polyethylene film may be increased by irradiation in the presence of styrene.
3. The structure of polyethylene may be modified without a corresponding reduction in tensile strength by irradiation in a solution containing small amounts (say, 5%) of acrylonitrile.
4. The tensile strength of polyethylene may be increased considerably by irradiation in a solution containing small amounts (say, 7%) of styrene.
5. Since only relatively small doses are required, the technique of grafting provides a convenient method for adding desired groups into polyethylene either for their own sake or to modify the polyethylene structure.

#### D. Determination of Molecular Weight Distribution in Polyethylene by an Irradiation Technique

#### INTRODUCTION

Although the molecular weight distribution in polyethylene is a very important property, experimental determination of the breadth of distribution, as indicated by the ratio  $\bar{M}_w/\bar{M}_n$ , is difficult. Recently a new method for determining this ratio was suggested by Baskett.<sup>45</sup> This method is based upon a mathematical analysis of curves relating the soluble fraction, (1-x), of a polymer crosslinked by irradiation to the fraction of carbon atoms crosslinked,  $\alpha$  ( $\alpha$  assumed to be proportional to the dose received). The method is essentially an extension of work done by Charlesby.<sup>46,47</sup>

Baskett suggests fitting experimental values of  $(1-x)$  to a linear combination of a series of functions of  $p$  [ $p$  being equal to  $-\log(1-x)$ ]— whose inverse Laplace transforms are known. If, for example,

$$1 - x = \frac{b_0 a_0^2}{(p+a_0)^2} + \frac{b_1 a_1^2}{(p+a_1)^2} \dots = W(p),$$

the transform of the series becomes

$$b_0 a_0^2 m e^{-a_0 m} + b_1 a_1^2 m e^{-a_1 m} \dots = W(m),$$

where  $W(m)$  is the distribution function, that is, the weight fraction of molecules containing  $m$  carbon atoms in the original unirradiated material, and where  $a_0$ ,  $a_1$ ,  $b_0$ , and  $b_1$  are arbitrary constants. From the exponential series given,  $\bar{M}_w$  and  $\bar{M}_n$  can be readily found:

$$\bar{DP}_w = 2 \left( \frac{b_0}{a_0} + \frac{b_1}{a_1} \dots \right) \text{ and } \bar{DP}_n = 1/(a_0 b_0 + a_1 b_1 \dots).$$

Two complications must, however, be considered: chain scission, which reduces the gel fraction corresponding to a given degree of crosslinking, and the fact that the extent of scission depends on the degree of branching. Baskett has derived a correction for these effects by assuming that a real sample of polyethylene may be treated as a polymer of simple exponential distribution that has been subjected to a certain degree ( $\alpha_0$ ) of preliminary crosslinking.

Since this method avoids the problems associated with light-scattering and osmotic pressure measurements at elevated temperatures, it was decided that a study of this method would be very useful. In this section results obtained for the following polymers will be presented and discussed: A5L, A10, A22, A34, DYNH, TD385, Blend 7, and Poly-Eth samples 1005, 1405, 1503, and 2205. Irradiations were completed for TD304, TD386, and Poly-Eth 1205, but time did not permit solubility determinations.

#### EXPERIMENTAL

Samples (0.2-0.5 g) in pellet form were degassed by evacuation for from 2 to 4 hours using a high-vacuum line (mercury diffusion pump backed by an oil pump), sealed in glass tubes, and irradiated using the 1-kilocurie or 3-kilocurie Co-60 source. Doses ranged from  $5.0 \times 10^4$  to  $3.0 \times 10^7$  rep, and corresponded approximately to those used by Baskett. All samples were supplied by the Spencer Chemical Company.

When the irradiation was complete for a given sample, the product was extracted by means of a hot Soxhlet extraction for approximately 48 hours. It was found that the use of pellets gave results identical with results obtained

for the thin discs recommended by Baskett. Although the first extractions were conducted using reagent-grade benzene at 80°C, in later work it was necessary to use reagent grade toluene at 100°C. After drying for 24 hours at 80°C under vacuum, the weight of the insoluble fraction, and hence of the soluble fraction, was determined.

Some difficulty was experienced in obtaining reproducible weights for some of the extraction thimbles. Best results for the weights of the dried residues were obtained in the following way. First the thimble containing the dried residue was allowed to come to equilibrium, without desiccation, in the balance room, which was kept at constant temperature (25°C) and humidity (50%, relative); usually a period of 6 hours was sufficient. Next the thimble plus contents was weighed, ignited at 1000°C for 12 hours, and then reweighed. Finally, after being allowed to reach equilibrium again in the balance room, the ignited thimble was weighed, and the weight of residue burned off was determined by difference.

Values of the soluble fraction were then plotted against the total dose received, and corrected for chain scission and the presence of branching by the procedure suggested by Baskett. The resulting corrected curve corresponds approximately to a hypothetical linear polymer of simple exponential distribution,\* which has been slightly crosslinked to form the actual polymer subjected to irradiation.

The data were then treated in two ways. In the early experiments, the plotting of the data as a linear combination of Laplace transforms was attempted. Later, the general procedure described below was used; details of the calculations may be found in the appendix.

First, values of  $\bar{M}_w$  were calculated from the intercept of the upper portion of the uncorrected soluble curve at infinite solubility,  $\bar{M}_w$  being equal to the reciprocal of the intercept and being independent of distribution. The values of  $\bar{M}_w$  for the hypothetical parent polymer (see above) were calculated in a similar way from the intercept of the corrected soluble fraction curve. Since this hypothetical parent polymer has a distribution approximating a normal one, the value of  $\bar{M}_n$  was taken to be one-half of the value found for  $\bar{M}_w$ . Next this value of  $\bar{M}_n$  was corrected to allow for the presence of branching; this new value would correspond approximately to the value for the real polymer. In other words, the effect of a certain number of crosslinks on  $\bar{M}_n$  was determined; the number of crosslinks was taken to be the same number assumed in Baskett's method of correcting the observed soluble fraction curves for branching.

\*That is,  $W(m) = a^2 m e^{-am}$ .

## RESULTS AND DISCUSSION

Most consistent results were obtained using the method described in the appendix. Even with assistance from the Statistical Research Center, attempts to plot the experimental data as a linear combination of Laplace transforms were unsuccessful. Results presented in this section were, therefore, obtained as described in the appendix.

Typical curves of the soluble fraction,  $(1 - x)$ , as a function of radiation dose are given in Figs. 6 and 7. Two general features of the curves are worth noting:

1. The general shape of the curve is related to the breadth of the molecular weight distribution. The broader the distribution, the lower the slope and the greater the curvature of the major portion of the curve. Thus, the curve for A-22 ( $\bar{M}_w/\bar{M}_n \sim 6$ ) is relatively steep and linear, while the curve for A-10 ( $\bar{M}_w/\bar{M}_n \sim 20$ ) slopes off more gradually.

2. At low doses, the curves tend to become asymptotic. It is true that measurements of the soluble fraction are difficult as infinite solubility is approached. Nevertheless, repeated determinations have confirmed that this behavior is, indeed, characteristic of most samples of polyethylene, whether or not the unirradiated sample is completely soluble under the extraction conditions. Apparently, then, most samples of polyethylene must contain very small amounts of very high molecular weight material that either is insoluble to start with or becomes insoluble after exposure to an extremely small amount of radiation; this conclusion is consistent with general experience.

Clearly a precise extrapolation to determine  $\alpha_c$  and hence  $\bar{M}_w$  is difficult, if not impossible, if such a "tail" effect exists. Until it is possible to account quantitatively\* for the effect of this small amount of material, one must ignore its presence and try to extrapolate the major portion of the curve. Of course, any comparison of  $\bar{M}_w$  with  $\bar{M}_w$  from light-scattering, it should be realized that some or all of this high molecular weight component is centrifuged out before light-scattering measurements are made.

Results obtained so far are given in Table XIX; incomplete solubility data are given in Table XX.

Samples I, II, III, IV: Use of data for these samples taken from Baskett's paper, yielded ratios of  $\bar{M}_w/\bar{M}_n$  that agree well with ratios cal-

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\*Mr. Graessley is studying the effects of small proportions of high molecular weight material on the solubility curve. So far, it appears that only 2-3 percent of material with  $\bar{M}_w$  500 times the  $\bar{M}_w$  for the major portion of the polymer could result in the tail effect observed.



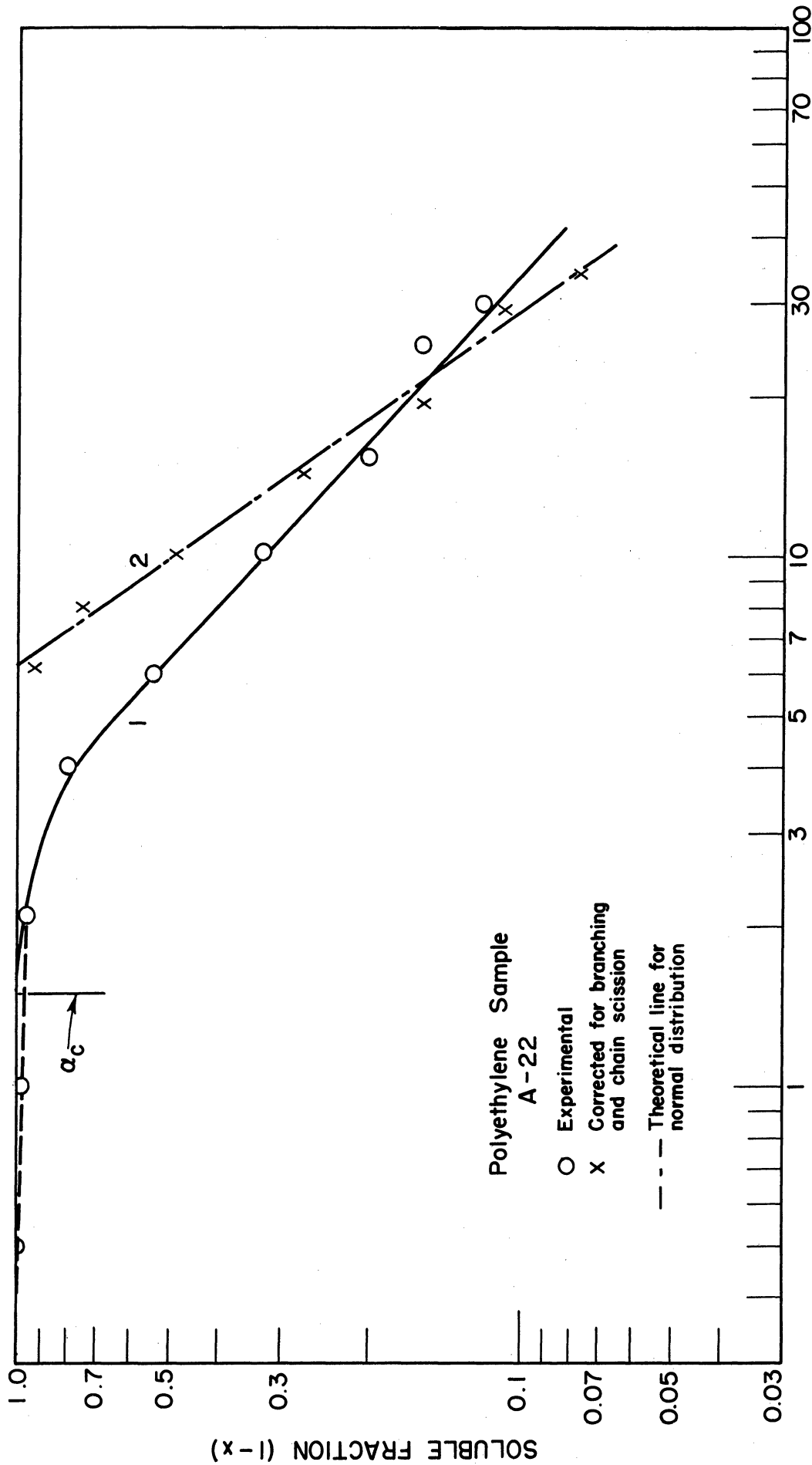


Fig. 6. A typical solubility curve for irradiated polyethylene (A-22).

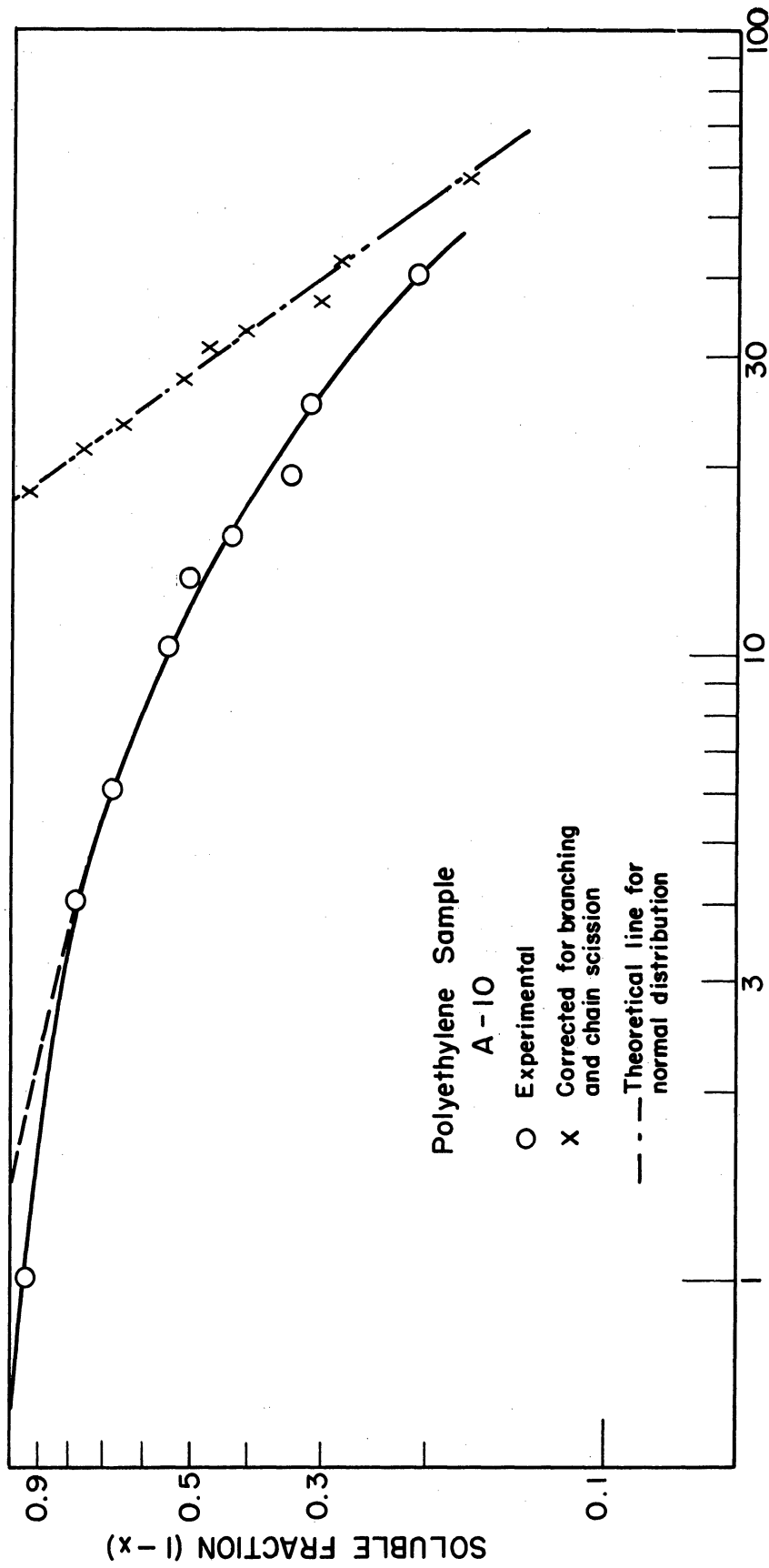


Fig. 7. A typical solubility curve for irradiated polyethylene (A-10).

TABLE XIX

MOLECULAR WEIGHT DISTRIBUTION DATA DERIVED FROM SOLUBILITY CURVES OF IRRADIATED POLYETHYLENE

Sample	$\bar{M}_w$ , x 10 <sup>-5</sup>	$\bar{M}_n$ , x 10 <sup>-4</sup>	$\bar{M}_w/\bar{M}_n$ , observed	$\bar{M}_w/\bar{M}_n$ , comparison	Comments
I <sup>a</sup>	--	--	8	6 <sup>b</sup>	Solubility fraction data from reference 45.
II <sup>a</sup>	--	--	10	8 <sup>b</sup>	
III <sup>a</sup>	--	--	10	12 <sup>b</sup>	
IV <sup>a</sup>	--	--	4	5 <sup>b</sup>	
A-5L	--	--	--	--	Preliminary measurements indicated broad distribution.
A-10 <sup>d</sup>	9.0 20.2	0.44 0.47	20 43	13 <sup>c</sup>	Presence of high-M tail discounted in calculations.
A-22	8.4	1.4	6	7 <sup>c</sup>	Presence of high-M tail discounted in calculations.
A-34	0.5	0.36	14	(Narrow) <sup>c</sup>	Pronounced high-M tail discounted in calculations.
PE-1005	≥6.4	1.6	≥40	--	A "best" value for $M_w/M_n$ might be 70.
PE-1405	--	--	--	--	High-M tail.
PE-1503	--	--	--	--	High-M tail.
PE-2205	1.26	1.01	1.25	--	High-M tail.
TD-385	2.1	1.2	17	--	
DYNH	1.58	1.66	9.5	--	Relatively narrow distribution except for a high-M tail (discounted).

<sup>a</sup>Data obtained from Ref. 45; raw data were only approximate.

<sup>b</sup>Values from Ref. 44;  $M_w$  from gel curves,  $M_n$  from osmotic measurements quoted.

<sup>c</sup>Values given in duPont information bulletin (Ref. 48).

<sup>d</sup>The two sets of data arise from different extrapolations; see text.

TABLE XX

SOLUBILITY DATA FOR IRRADIATED POLYETHYLENE

PE-1503		Blend 7		PE-1405	
Dose, rep x 10 <sup>-6</sup>	Soluble Fraction	Dose, rep x 10 <sup>-6</sup>	Soluble Fraction	Dose, rep x 10 <sup>-6</sup>	Soluble Fraction
0.085	0.973	10.0	0.687	0.085	0.990
0.5	0.963	15.0	0.595	0.50	0.990
	0.972			1.0	0.981
	0.932	20.0	0.361		
1.0	0.991	30.0	0.354	1.8	0.99
	0.935			2.1	0.99
	0.964				
1.8	0.938			4.0	0.994
	0.946			6.0	0.978
2.1	0.978			6.5	0.95
	0.967				
4.0	0.979			10.2	0.78
	0.932			15.4	0.57
6.0	0.951				
	0.961				
7.8	1.00				
	0.937				
10.2	0.843				

culated using osmotic data given in the paper. In one case, sample II, the value of  $\bar{M}_n$  calculated by our method was closer to the osmotic value than was Baskett's value; on the other hand, with sample III, the value found for  $\bar{M}_n$  did not agree with the osmotic value.

ASL: Because of the relatively high content of carbon black, few measurements were made on this sample. However, a broad distribution was indicated by the preliminary measurements.

A-22 (99-100% soluble): The extrapolation is not as difficult as in some other cases because of the steep slope of the right-hand portion of the curve. If the effect of the high molecular weight tail is ignored, a "best" value of 6 may be estimated for  $\bar{M}_w/\bar{M}_n$ . Although this ratio is close to the approximate value supplied by the du Pont Company,<sup>47</sup> the absolute values of  $\bar{M}_w$  and  $\bar{M}_n$  are in disagreement with the du Pont values\*—300,000 and 45,000, respectively. No reason for this discrepancy is apparent.

A-10 (98% soluble): With a very broad distribution as exists with this sample, extrapolation is very difficult. Two possible extrapolations are evident in Fig. 7, and results of these alternatives are presented in Table XIX. Again, the values of  $\bar{M}_w/\bar{M}_n$ , at least for one extrapolation, is fairly consistent with the value supplied by the du Pont Company.

A-34 (99% soluble): This sample appears to have a broad distribution, contrary to the data supplied by the du Pont Company. In particular, a pronounced high molecular weight tail was observed.

Poly-Eth 1005 (100% soluble): The solubility curve for this sample resembles the curve for A-10. A very broad distribution of molecular weights must exist for the "best" value for the ratio  $\bar{M}_w/\bar{M}_n$  would be approximately 70.

Poly-Eth 1405 (99% soluble): Although more solubility data at high doses would be required to complete the study of this sample, acceptance of all the existing data would suggest a fairly narrow distribution.

Poly-Eth 1503: For some reason the data obtained were difficult to reproduce. Since this polymer was fairly soluble even after a dose of  $1 \times 10^7$  rep, both  $\bar{M}_w$  and  $\bar{M}_n$  must be relatively low.

Poly-Eth 2205 (99.8% soluble): Again, the presence of a high molecular weight tail is obvious. If, however, this tail is ignored, the distribution of most of the polymer appears to be fairly narrow, at least for polyethylene.

\*These values were supplied through the courtesy of Dr. Billmeyer, Polychemicals Department, E. I. du Pont de Nemours and Company.

TD 385 (99% soluble): The solubility data imply a moderate breadth for the molecular weight distribution.

DYNH (99% soluble): If the presence of a high molecular weight tail is discounted in calculations, the distribution should be fairly narrow.

These results illustrate the advantages and disadvantages of this technique. In a general way, the method reveals whether or not a polymer sample has a broad or narrow distribution of molecular weights. This is true whether or not one wishes to include a high molecular weight tail in considering the breadth of distribution. Once some experience has been gained, the technique is relatively easy to use, although very precise determinations of gel fractions are necessary when the solubility is close to infinite.

The determination of absolute values of  $\bar{M}_w$  and  $\bar{M}_n$ , however, still is uncertain. The reason why good absolute values of  $\bar{M}_n$  are obtained in some cases and not in others is not clear. Undoubtedly there are many uncertainties in the method used, such as the conversion of dose to degree of crosslinking, the choice of  $\beta$ , the accurate determination of gel fraction, etc. But these errors might be expected to affect all values of  $\bar{M}_n$ ; thus the source of error does not appear to be a consistent one.

## CONCLUSIONS

1. Examination of the curve relating the soluble fraction of irradiated polyethylene to dose can reveal useful information about the breadth of the molecular weight distribution. Although precise determination of the ratio  $\bar{M}_w/\bar{M}_n$  may be difficult if the distribution is broad or if a high molecular weight tail is present, at least a qualitative indication of the breadth may be obtained.

2. It appears possible to obtain reasonable estimates of the absolute value of  $\bar{M}_n$  in some cases, but not in others. However, even if the estimate of  $\bar{M}_n$  is in error, the ratio  $\bar{M}_w/\bar{M}_n$  seems to agree reasonably well with the ratio determined from measurements of light-scattering and osmotic pressure, at least in the few cases for which such data were available.

## III. MISCELLANEOUS STUDIES

### A. Mooney Viscosity Measurements on Polyethylene

## INTRODUCTION

Complex relationships exist between such physical properties of polyethylene as the following: melt index, intrinsic viscosity, molecular

weight, molecular weight distribution, and degree of branching. At present, measurements of melt index and intrinsic viscosity are routine; measurements of the other properties listed are, however, tedious and difficult. Unfortunately, because of the influence of these latter properties, two samples of polyethylene having the same melt index (and perhaps the same intrinsic viscosity as well) may have quite different characteristics. To see if such samples could be differentiated by means of simple methods, it was decided to study the viscosity, measured with a Mooney viscometer, of several samples of polyethylene having the same melt index.

#### EXPERIMENTAL

The following samples were studied: Poly-Eth 1005 (Nat B, Lot 3643), Poly-Eth 1205 (Nat B, Lot 3756), Poly-Eth 2205 (Nat B, Lot 3019), Poly-Eth 2405 (Nat B, Lot 2466), and Poly-Eth 1008.5 (Nat B, Lot 3161). Preliminary measurements were made using pellets; later molded sheets were used.

The Mooney viscometer was obtained from Scott Testers, Inc.; the large rotor was used in these experiments. Cellophane was used between the polymer and metal surfaces.

For the pellet experiments, the viscometer was operated at 280°F—this temperature being high enough for molding the most viscous polymer. After the sample had remained in the closed mold for 10 or 15 minutes, the motor was started; after 1.5 minutes, gauge readings (which did not change much thereafter) were recorded. Samples were examined for scoring after each run to be sure the slippage had not occurred along the mold faces.

For the sheet experiments, pellets were molded into 1/8-inch sheets at 300°F and 30,000 pounds for 10 minutes, released while hot, and then quenched; these sheets were cut into pieces approximately 2 x 2 inches, and introduced into the viscometer mold chamber, which was, in this case, heated to 240°F. After 5 minutes the mold was closed; 25 minutes later the motor was started, and gauge readings were recorded periodically over a period of 3 hours. As before, samples were examined for scoring after each run.

#### RESULTS AND DISCUSSION

Results of the preliminary pellet experiments at 280°F are given in Table XXI. Although the scale readings are inconveniently low, differences between the samples are evident.

In an attempt to obtain larger scale readings and hence larger differences in scale readings for different samples, the temperature of operation was lowered to 240°F. At this temperature it was necessary to use layers of molded sheets for the sample. Results are given in Table XXII; a typical curve

TABLE XXI

## MOONEY READINGS FOR POLYETHYLENE AT 280°F

Sample: pellets  
 Time for reading: 1.5 min  
 Temperature: 280°F  
 Molding time: 10-15 min  
 Large rotor

Sample	Trial <sup>a</sup>	Scale Units	
		Mooney Reading	Average Reading
PE-1005	1	7.8	7.6 ± 0.2
		7.8	
	2	7.5	
PE-1205	1	2.6	3.0 ± 0.5
		2.6	
	2	3.5	
		3.5	
PE-2205	1	3.8	3.3 ± 0.8
		3.8	
	2	2.5	
		3.0	
PE-2405	1	7.9	7.3 ± 1.3
	2	6.0	
		8.6	
PE-1008.5	1	1.5	2.0 ± 0.5
		1.5	
	2	2.5	

<sup>a</sup>Each trial refers to a separate charging of sample.



TABLE XXII

MOONEY READINGS FOR POLYETHYLENE AT 240°F

Sample: 6 1/8-in. sheets  
 Time for reading: variable  
 Temperature: 240 ( $\pm 1$ )°F  
 Molding time: 30 min  
 Large rotor

Sample	Trial	Mooney Reading, Scale Units				
		2 min	10 min	30 min	2 hr	3 hr
PE-1205	1	--	--	--	24.0	--
	2	32	28	25.5	22.5	21.8
	3	24.6	24.2	22.6	22.0	22.0
	4	42	33	29.0	24.5	--
	5	41.5	30.5	27.1	22.3	21.5
	Avg		35 $\pm$ 10	28.9 $\pm$ 5	26 $\pm$ 3	23 $\pm$ 1.5
PE-1005	1	14.9	14.8	14.3	13.5	13.2
	2	16.4	15.7	14.5	13.0	12.8
	Avg	16 $\pm$ 1	15.2 $\pm$ 0.5	14.4 $\pm$ 0.1	13.2 $\pm$ 0.3	13.0 $\pm$ 0.2
PE-2205	1	15.1	14.0	12.8	12.0	11.9
	2	15.1	14.7	13.8	13.0	12.8
	Avg	15.1	14.3 $\pm$ 0.4	13.3 $\pm$ 0.5	12.5 $\pm$ 0.5	12.4 $\pm$ 0.5
PE-2405	1	15.3	14.2	12.8	11.3	11.0
	2	15.0	14.1	12.7	11.2	10.9
	Avg	15.1 $\pm$ 0.2	14.1 $\pm$ 0.1	12.7 $\pm$ 0.1	11.2 $\pm$ 0.1	11.0 $\pm$ 0.1
PE-1008.5	1	3.5	3.2	3.3	3.2	3.2
	2	3.2	3.1	3.3	3.1	3.1
	Avg	3.3 $\pm$ 0.2	3.2 $\pm$ 0.1	3.3	3.2 $\pm$ 0.1	3.1 $\pm$ 0.1

is given in Fig. 8. Except for trials 2 and 3 (Poly-Eth 1205), which were made while the technique was being mastered, the experimental precision of the average values of scale reading was generally  $\pm 0.5$  scale units. Although at 2 minutes large differences between the rather imprecise data for Poly-Eth 1205 and Poly-Eth 1005 exist, differences between data for Poly-Eth 1005, Poly-Eth 2205, and Poly-Eth 2405 are not apparent. However, at longer times, the precision of data for PE 1205 and PE 1005 improves, and slight but significant differences between data for PE 1005, PE 2205, and PE 2405 appear. The cause of this spreading out at long times is not clear.

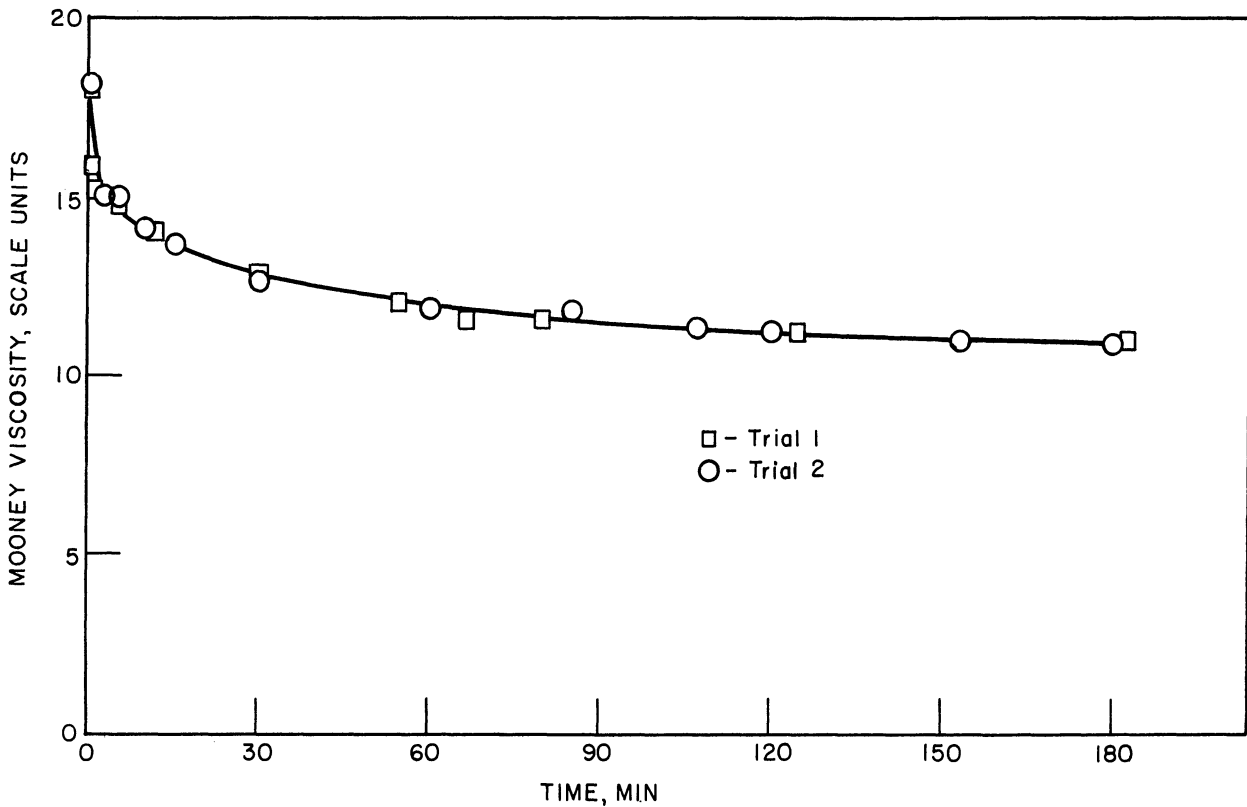


Fig. 8. Dependence of Mooney scale readings for polyethylene on time.

Results of the two sets of experiments do not agree. Possibly there is a difference in temperature dependence of the shear behavior of the samples. However, the data for the sheet experiments are probably the more reliable.

In any case, the Mooney viscosity values of polyethylene samples having the same melt index are different. These differences might be related to a property such as the degree of branching, and could be useful in the routine characterization of polyethylene.

#### CONCLUSIONS

The following conclusions may be drawn:

1. The Mooney viscometer can be used to differentiate between samples of polyethylene having the same melt index.

2. So far, best precision (deviation from the average about  $\pm 0.5$  scale units) and best differentiation may be obtained by using layers of molded sheets as samples, a molding time of 30 minutes, a long reading time (say, 30 minutes, or longer), and a temperature of  $240^{\circ}\text{F}$ .

## B. Synthesis of Cyclohexanone Oxime Using Gamma Radiation

### INTRODUCTION

For some years, it has been known that aliphatic hydrocarbons such as n-heptane or n-hexane may be nitrosylated by nitrosyl chloride under the influence of light (that is, ultraviolet radiation) to form products that may be isomerized to the corresponding ketoximes.<sup>49-52</sup> The nitrosylation of cycloalkanes has also been accomplished using ultraviolet radiation; good yields of cyclohexanone oxime have been claimed for the reaction between cyclohexane and nitrosyl chloride.<sup>53-57</sup>

Because the cost of ultraviolet radiation is, and probably will remain, high, it was decided to study the synthesis of cyclohexanone oxime using gamma radiation, the cost of which will probably decrease eventually.

Results of this investigation are presented below.

### EXPERIMENTAL

Gamma radiation was obtained from either the Co-60 source (3-kilocurie) or the MTR fuel element source.

Unless specified otherwise, reagents were used as received. Nitrosyl chloride was obtained from the Matheson Chemical Company, cyclohexane from the Baker and Adamson Company, and formic acid ("analyzed" grade) from the Baker Chemical Company. In experiments using carefully purified reagents, the cyclohexane was treated with a sulfuric-nitric acid mixture,<sup>54</sup> washed, redistilled (B.P.  $78.5-79.0^{\circ}\text{C}$ ), and dried over Drierite; the infrared spectrum was characteristic of pure (99%) cyclohexane. For these latter experiments, nitrosyl chloride was refluxed gently for 30 minutes, and then fractionated by a procedure outlined by Coleman and others.<sup>57</sup> Hydrogen chloride was prepared by the reaction between concentrated sulfuric acid and hydrochloric acid, and dried by means of concentrated sulfuric acid. Before irradiation, contents of several tubes were degassed (see Table XXIII).

Before charging, cleaned reaction tubes were heated to redness to remove residual organic material.

TABLE XXIII

## PREPARATION OF CYCLOHEXANONE OXIME

Run	Weight NOCl/100 ml Solvent	Temp, °C	Total Dose, rep x 10 <sup>-6</sup>	Weight Product, g	Yield %	Comments
1	2.0	0.0	0.66	--	--	Crystalline product
2	2.0	0.0	0.66	--	--	Crystalline product
3	2.0 <sup>b</sup>	0.0	0.23	--	--	Crystalline product
4	2.9	0.0	0.32	0.07	3.6	Crystals + clear oil
5	2.9	0.0	0.82	0.04	1.9	Crystals + clear oil
6	3.2	-60	0.70	0.48	18	Clear oil
20	1.0 <sup>c</sup>	0.0	2.0	--	--	Little reaction
21	1.0 <sup>d</sup>	0.0	1.8	--	--	Clear oil
22	1.0	0.0	2.0	--	--	Little reaction
23	1.0 <sup>d</sup>	0.0	1.8	--	--	Clear oil
24	1.0	0.0	2.0	--	--	Little reaction
25	1.0	0.0	1.8	--	--	Little reaction
26	1.0	0.0	2.0	--	--	Little reaction
27	1.0 <sup>e</sup>	0.0	0.79	--	--	Clear oil
28	2.0 <sup>c,e</sup>	0.0	0.79	--	--	Clear oil
29	1.0 <sup>c,e</sup>	0.0	0.79	--	--	Clear oil
30	88	--	0.86	--	--	Clear oil
31	8	--	0.86	--	--	Clear oil

<sup>a</sup>Based on amount of nitrosyl chloride charged.

<sup>b</sup>This run consists of supernatant liquid from run 2.

<sup>c</sup>Cyclohexane presaturated with dry hydrogen chloride.

<sup>d</sup>Cyclohexane presaturated with formic acid.

<sup>e</sup>Degassed before irradiation.

Infrared spectra were obtained using a Baird recording spectrophotometer.

## RESULTS AND DISCUSSION

In the preliminary experiments with gamma radiation, tubes containing cyclohexane and small amounts of nitrosyl chloride (1.5 - 3.0%) were irradiated at room temperature; the total dose received by each tube was  $3 \times 10^6$  rep. An oily product was obtained in the tubes, containing 3.0% nitrosyl chloride. However, satisfactory characterization of the oily product was not achieved, although treatment of hydrolyzed product with 2,4-dinitrophenylhydrazine yielded a hydrazone derivative that appeared similar to the hydrazone derivative of cyclohexanone.

Because high yields of oxime are claimed to be favored by irradiation at low temperatures<sup>53</sup> the next set of experiments was conducted at lower temperatures—0 and  $-60^\circ\text{C}$ . Results of these experiments are given in Table XXIII. In runs 1, 2, and 3, the product was crystalline in nature, while in runs 4, 5, and 6, the product consisted of both crystalline and oily, or just oily, material. In all cases, the product was deposited on the walls and bottoms of the reaction tubes. The reaction was continuous; when the product was removed from run 2, further irradiation (run 3) led to the formation of more product. Some of the crystals from run 2 were recovered and recrystallized from petroleum ether. Although it had been expected that this product would be the oxime hydrochloride (M.P.  $148-150^\circ\text{C}$ ), the melting point,  $87-89^\circ\text{C}$ , was very close to the melting point,  $90-91^\circ\text{C}$ , observed for a sample of pure oxime prepared in the conventional manner from cyclohexanone. With runs 4, 5, and 6, yields were determined; these yields, even in run 6, are rather low considering the dose required. Also, yields are not consistent; for example, the yield for run 4 is greater than for run 5, although the dose received was lower.

Attempts were then made to determine, first, the conditions governing the yielding of a crystalline rather than an oily product, and, second, the conditions required for optimum yields. It has been expected that a combination of low temperature, moderately low concentration of nitrosyl chloride, and moderate doses should lead to the best yields of crystalline material. Temperatures of irradiation were accordingly varied between 0 and  $-60^\circ\text{C}$ , the dose between  $1.0 \times 10^6$  and  $2.0 \times 10^6$  rep, and the concentration of nitrosyl chloride between 0.7 and 20.0%. To make sure that any product formed would exist as a hydrochloride rather than as a mixture of oxime and oxime hydrochloride, one sample was saturated with dry hydrogen chloride before irradiation.

Results of these experiments were, however, unsatisfactory; no consistent relationships between the variables were observed, and the results were not reproducible. No reason for this variability was found.

In a final attempt to reproduce the successful experiments described

above, carefully purified reagents were used. Reaction conditions are given in Table XXIII. Although an oily product was obtained in each case, the amount was not as large as the largest amounts found previously. Presaturation of the cyclohexane with dry hydrogen chloride<sup>53</sup> had no apparent effect on the reaction; the concentration of nitrosyl chloride also was unimportant. No evidence of discoloration was observed. Again, satisfactory characterization of the product was not achieved. To avoid the mechanical losses associated with working up the product, infrared measurements were tried as a means of characterization. Unfortunately, the product was soluble only in solvents, such as benzyl alcohol, that absorb too strongly in the infrared regions of interest for identification of appropriate bands.

Because of limited time, the low conversion of this reaction, and the difficulty of identifying the products, work on this problem was suspended.

#### CONCLUSIONS

1. Gamma irradiation, at low temperatures, of a nitrosyl chloride—cyclohexane solution leads to the formation of cyclohexanone oxime (or its hydrochloride).

2. The yields of this reaction are undesirably low; conditions for optimum yields are as yet unknown.

#### C. Fixation of Nitrogen by Gamma Radiation

#### INTRODUCTION

Since the energy of gamma radiation from a Co-60 source is high enough (1.1 and 1.3 Mev) to activate or ionize both nitrogen and oxygen, the possibility of fixing nitrogen by irradiating mixtures of nitrogen and oxygen was considered. It was hoped that nitric oxide could be formed by the initiation of a chain oxidation of nitrogen by gamma radiation either at a lower temperature than is normally required, or under completely different conditions, for example, in the liquid state.

Results of experiments designed to investigate this possibility are reported below.

#### EXPERIMENTAL

Both nitrogen and oxygen were of commercial quality. Other reagents were of ordinary laboratory grades.

Analyses for nitric oxide were made using a Consolidated-Nier mass spectrometer, model 21-201.

## RESULTS AND DISCUSSION

In the first experiment, a mixture of liquid nitrogen and oxygen ( $N_2/O_2 = 2/1$ ) was irradiated at a dose rate of  $1.0 \times 10^5$  rep/hr; the total dose received was  $1.8 \times 10^6$  rep. After irradiation, some of the nitrogen and oxygen was evaporated, and the residue examined in the mass spectrometer. Since only 100 ppm of nitric oxide were found, it seemed clear that no chain reaction, without which the reaction could not be economically feasible, had taken place. Another sample (95% liquid nitrogen and 5% oxygen) was given a dose of  $3 \times 10^6$  rep; again, yields were in the range of parts per million.

Next, in an attempt to increase the efficiency of absorption of gamma radiation, a sample consisting of 98% nitrogen and 2% oxygen was irradiated with  $1.5 \times 10^6$  rep in the presence of silica gel containing a cobalt salt as indicator. Once again, the yield of nitric oxide was almost negligible.

Since the formation of nitrate ions or ammonia by the interaction between pile radiation and dissolved nitrogen and oxygen or hydrogen in the cooling water of the pile is known to occur, the irradiation of (1) gaseous nitrogen plus oxygen (95%  $N_2$ ) and (2) gaseous nitrogen plus hydrogen (95%  $N_2$ )—both in the presence of water—was tried. In addition, a sample of gaseous nitrogen plus hydrogen (95%  $N_2$ ) was irradiated in the presence of aqueous hydrogen bromide, (the bromide being used as a chain carrier). After a dose of  $4.5 \times 10^6$  rep had been received by each tube, the gaseous hydrogen bromide was swept out from its tube and the pH of each liquid was tested; since the liquids were still neutral, it was assumed that the formation of nitrate ions, ammonia, or ammonium ions was negligible.

These results are not surprising, for Harteck and Dondes<sup>58</sup> obtained nitrogen tetroxide from the irradiation of nitrogen-oxygen mixtures in a nuclear reactor only at a high temperature ( $200^\circ C$ ), pressure (20-25 atm) and dose rate ( $3 \times 10^8$  rep/hr). Also Primak and Fuchs<sup>59</sup> claim the radiation yield (analogous to quantum yield) for the production of nitric acid by the irradiation of humid air is unity; in other words, these authors found no evidence for a chain reaction, which would, of course, lead to a radiation yield greater than unity.

Since the radiation-induced reaction between nitrogen and oxygen would be of interest only if yields of nitric oxide would be high (that is, only if a chain reaction existed), no further work on this problem was done.

CONCLUSIONS

It is concluded that the irradiation of a mixture of liquid nitrogen and oxygen produces small quantities of nitric oxide. However, yields are undesirably low; no chain reaction seems to exist. The addition to the liquid mixture of silica gel containing cobalt salts to absorb the radiation or the use of a chain carrier such as hydrogen bromide with gaseous nitrogen and oxygen does not appear to be helpful in obtaining a more efficient reaction.



## APPENDIX

CALCULATION OF MOLECULAR WEIGHTS FROM  
SOLUBILITY DATA OF IRRADIATED POLYETHYLENE

In this appendix details of the calculations used for the determination of molecular weights and distribution in polyethylene are given. The treatment\* is based mainly upon assumptions and considerations used by Baskett, but leads to a numerical calculation of  $\bar{M}_n$  instead of to a calculation by means of the graphical analysis suggested by Baskett (see II, section D, above).

## GENERAL

Two assumptions are made initially: that the polyethylene is branched, and that the polyethylene is subject to chain scission, as well as crosslinking, during irradiation. Curve 1 of Fig. 6 represents a typical experimental solubility curve for such a polymer. If, on the other hand, no branching is present and no chain scission occurs, a curve like curve 2 would be found; this curve corresponds to a linear polymer, having a normal molecular weight distribution (that is,  $\bar{M}_w/\bar{M}_n = 2$ ), that does not undergo scission during irradiation. The basis of this treatment is the correction of the experimental solubility curve for a real polymer for the effects of both branching and chain scission to find the curve for a corresponding hypothetical linear polymer that does not undergo chain scission. From this hypothetical curve, both  $\bar{M}_w$  and  $\bar{M}_n$  for the real polymer are estimated as described below.

## CORRECTION FOR BRANCHING

Let us assume that the experimental branched polymer can be obtained from a linear polymer by adding a certain amount of crosslinking,  $\alpha_0$ . In other words, let us assume that our experimental polymer behaves like a linear polymer that has been subjected to an amount of radiation equivalent to  $\alpha_0$ . To obtain the curve for this linear polymer, we add a constant number to the values for  $\alpha$  in the experimental curve 1 so that the upper portion of the curve becomes a straight line on the log-log plot. It should be noted that with this plot the effect of this correction on the shape of the curve is greatest for the higher soluble fraction portion.

\*This treatment was developed by Mr. W. W. Graessley.

CORRECTION FOR CHAIN SCISSION

Because of the fracture of main-chain bonds by radiation, the lower part of the experimental curve will eventually level off at high doses instead of continuing down as does curve 2 of Fig. 6. Although doses given in Fig. 6 are not high enough for this levelling-off to become evident, the data must still be corrected for the effect of scission. The pertinent formula to use is given by Charlesby,<sup>4,7</sup> and may be expressed as

$$\frac{(1-x)_{\text{observed}}}{(1-x)_{\text{corrected}}} = 1 + \frac{\beta}{2} \left( \frac{\alpha}{\alpha_c + \alpha_0} \right)$$

In this relationship,  $\beta$  is the chain scission parameter (number of bonds broken per crosslink formed; the value of  $\beta$  for polyethylene is given as 0.2).<sup>4,7</sup> The shape of the curve is most affected at the lower end. The final curve obtained after correction should approximate a straight line (curve 2) whose slope is the same as would be predicted for a polymer having a normal distribution and not subject to scission. Thus the corrected points are fitted to a line having the slope equal to the theoretical slope for a polymer of normal distribution and not subject to scission.

DETERMINATION OF MOLECULAR WEIGHT AND DISTRIBUTION

According to the accepted theories of gelation,<sup>21</sup> the weight-average degree of polymerization,  $\overline{DP}_w$ , for the real polymer is found from the intercept of the experimental curve,  $\alpha_c$ :

$$\overline{DP}_w = \frac{1}{\alpha_c} .$$

The more complicated procedure for obtaining the number-average degree of polymerization will now be considered.

First, the weight-average degree of polymerization,  $\overline{DP}_w^0$ , for the hypothetical polymer may be determined from the intercept at infinite solubility of the hypothetical curve (curve 2, Fig. 6):

$$\overline{DP}_w^0 = \frac{1}{\alpha_c + \alpha_0} .$$

This relationship is valid for all types of distribution.<sup>21,44</sup> Assuming a normal distribution, the number-average degree of polymerization,  $\overline{DP}_n^0$ , for the hypothetical polymer is then given by

$$\overline{DP}_n^0 = \frac{1}{2(\alpha_c + \alpha_0)} .$$

We now have a curve for a hypothetical linear polyethylene sample, which upon irradiation is not degraded, but rather crosslinked by an amount  $\alpha_0$ .

To determine the number-average molecular weight of the experimental polymer from the hypothetical polymer, we reverse the procedure used for correcting for the degree of branching. In other words, we add to the hypothetical polymer an amount of crosslinking,  $\alpha_0$  and determine the resulting number-average degree of polymerization.

If an amount of crosslinking represented by  $\alpha_0$  is added to the hypothetical polymer, the number of molecules,  $N$ , is changed according to the following expression:

$$N = N_0 - \text{number of crosslinks,}$$

where  $N_0$  is the number of hypothetical polymer molecules before crosslinking. Then  $\overline{DP}_n$  (for the real polymer) is given by:

$$\begin{aligned} \overline{DP}_n &= \frac{\text{no. of monomer units present}}{N} \\ &= \frac{1}{1/\overline{DP}_n - 1/2 \alpha_0} \\ &= \frac{1}{2\alpha_c + 3/2 \alpha_0} \end{aligned}$$

The ratio of molecular weights ( $\overline{M}_w/\overline{M}_n = \overline{DP}_w/\overline{DP}_n$ ) for the real polymer may now be determined:

$$\frac{\overline{DP}_w}{\overline{DP}_n} = \frac{2\alpha_c + 3/2 \alpha_0}{\alpha_c}$$

#### SAMPLE CALCULATION FOR A-22

First to express our solubility curves in terms of the degree of crosslinking,  $\alpha$ , we must convert the radiation doses to corresponding values of  $\alpha$ . In the absence of other evidence, the conversion must be based on data given by Charlesby.<sup>4</sup> According to Charlesby, exposure of polyethylene to a radiation dose of  $45 \times 10^6$  rep should result in the crosslinking of 0.5% of the carbon atoms present (that is,  $\alpha = 0.005$ ).\* Thus  $\alpha = \text{radiation dose (in rep)} \times 1.11 \times 10^{-10}$ .

Next values of  $\alpha_0$  and  $\alpha_c$  are determined from the solubility graph. For sample A-22,

\*It should be noted that this value is uncertain because of the lack of precise molecular weight data.<sup>16</sup>

$$\alpha_o = 4 \times 10^6$$

$$\alpha_c = 1.5 \times 10^6$$

$$\therefore \bar{M}_n = \frac{14 \times 10^{10}}{1.11 \times (9 \times 10^6)} = 14,000 ,$$

and

$$\bar{M}_w = \frac{14 \times 10^{10}}{1.11 \times 1.5 \times 10^6} = 84,000 .$$

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