Irradiated Polyethylene IV—Free Radical Decay*

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Free radical decay was measured in linear polyethylene over the temperature range of 50° to 125°C. The radicals were formed by β- and γ-ray irradiation and their concentrations determined by e.s.r. techniques. Decay rates were measured in nitrogen, air, oxygen, and vacuum environments. The decay reaction which takes place by radical recombination can be resolved into two parts, one more rapid than the other. The rapid reaction takes place in an amorphous region or in a metastable crystalline one which is formed during irradiation; the latter region can become amorphous following a melting–solidification excursion and is, therefore, latently amorphous. The kinetics for the rapid reaction is second order, but tends toward first order as the dose and temperature are increased. The decay-rate constant values are dependent on the total radical concentration and the amount of metastable material. The slow decay reaction takes place in the crystalline region. Its rate-constant values can be related to vinyl-group decay and to the metastable material content. The effects of dose and temperature on the activation energies indicate that these energies can also be correlated with the metastable material. Variations in reaction order for the rapid decay reaction are accounted for with the aid of relationships in which the second-order decay constant is dependent on the decay time and the diffusion coefficient.

FREE radical formation studies of polyethylene have shown that the methylene radical which possesses a sextet electron spin resonance (e.s.r.) spectrum is formed almost exclusively at −195°C[1–10]. At room temperature or in its vicinity, however, a radical possessing a septet e.s.r. spectrum is formed which is believed to be the allyl radical[1–3,6–8,10] The extent to which each radical is present depends largely on the temperature, the dose, and the type of polyethylene.

The decay of these radicals has been the subject for a number of studies in recent years[4,5,8,11–17]. In general, the studies were conducted in the temperature range of −196° to +77°C. Therefore, they cover the decay of the methylene as well as the allyl radical. Although these investigators are in general agreement that decay occurs by radical recombination, details differ concerning the decay mechanism. Thus the question exists whether the kinetics is first or second order. Loy[5] indicates that second-order kinetics prevails. His results suggested a non-random distribution of radicals. Lawton, Powell and Balwit[4,11] found a pairwise first-order-decay process which was dependent on the type of radical, temperature and matrix. Charlesby and Libby[8] and Ormerod[15] used second-order kinetics to account for the decay of both radicals. They found the radical stabilities to be dependent on the physical and chemical properties of the polyethylene. Smith and Jacobs[12], who also favour a second-order kinetic reaction, assume radical recombination in the spurs as well as expansion of the spurs; both reactions are assumed to be enhanced by the presence of hydrogen and

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by pre-irradiation history. Cracco, Arvia and Dole[13,14] suggest a first-order process for radical decay in the spurs. They and Ormerod[15] studied the influence of hydrogen and the manner in which it affects radical migration. Kashiwabara[16], who assumes second-order kinetics, found a temperature correlation between the decay and the mechanical dispersion patterns. Geymer and Wagner[17] provide good correlation between calculated and experimental rate constants for a second-order diffusion model.

In the present study, the decay of the allyl radical was investigated over a temperature range of 50° to 125°C for a single dose of 28·5 Mrad and a dose range of 0·057 to 27·4 Mrad for a single temperature of 70°C. The second-order radical recombination process assumed for the decay reaction correlated well with our data and is in agreement with the results of others[5,8,12,15,17]. Evidence was obtained that radical decay in irradiated linear polyethylene takes place largely in a crystalline region and in a latently amorphous region, a product of the radiation process and representing a metastable state, which becomes amorphous following a melting–solidification excursion.

The kinetics indicate that decay takes place through rapid and slow second-order reactions. To explain the existence of the two decay reactions, the possibilities considered were that the presence of oxygen provides an alternate decay mechanism or that the presence of amorphous and crystalline phases provides different radical recombination rates in a diffusion-controlled reaction. The second turns out to be correct.

Our evidence for the morphological basis is in terms of the response of the initial radical concentration, the decay constant values, and the activation energies to temperature, radiation dose and the degree of crystallinity. Evidence for a diffusion mechanism is shown through the dependence of the decay-rate constant on dose, the metastable polymer, vinyl and initial radical concentrations.

In addition, it was found to what extent variations in certain parameters determine the values of decay constants, and that variations in the reaction order may be interpreted in terms of a diffusion-dependent, second-order reaction.

EXPERIMENTAL METHODS

A $\frac{3}{16}$ in., void-free, linear polyethylene rod was used for the radical decay studies. Most of the studies were conducted with rods prepared from Marlex 50 (density=0·96, melt index=0·9) which was supplied by Allied Resinous Products, Inc. It is listed as Resinol Type F polyethylene. Several experiments were conducted with other Phillips-type polyethylenes possessing melt indices of 0·2, 0·74 and 2·6. These were obtained from the Grace Chemical Company.

Electrons from a 2 MeV van de Graaff accelerator were used as one of the radiation sources for generating the free radicals. The 1 cm wide beam was expanded vertically to 9 cm. The polyethylene rod and an attached blue cellophane dosimeter were scanned horizontally by the beam every two seconds to provide a uniform incident dose to the sample and dosimeter. The samples were irradiated in air and cooled with a continuous airstream. Temperatures were maintained at 20° to 25°C. The dose rate was approximately 4 Mrad/min.

DuPont No. 300 MSC blue cellophane was used as a dosimeter. It was calibrated by plotting the calculated delivery doses versus optical-density change. These values were verified with a calibrated ionization chamber. The energy absorbed by the rods was 67 per cent of the incident energy.

A number of evacuated samples were irradiated with γ-rays at room temperature. A cylindrical ^{60}Co rod was used which provided approximately 0·17 Mrad/hour.

Free radical concentrations were measured with a Varian Model 4500 X-Brand EPR Spectrometer. Absolute radical concentrations were not determined. Instead, it was assumed that the concentrations were proportional to the peak-to-peak amplitude of the largest line in the derivative form of the spectrum. The five-line spectrum of the allyl radical did not change during the course of the measurements. A coal sample was used as a relative standard. The microwave power supplied to the cavity was 10 mW.

The irradiated samples were placed in a specially constructed variable-temperature cavity whose operation is similar to the Varian V 4547 assembly. The e.s.r. measurements were begun about 30 seconds after radiation was completed. No more than three minutes was required for sample-temperature equilibration in the cavity. Temperatures were maintained within ±0·5 deg. C. Nitrogen, air and oxygen were used as flow gases in the cavity.

RESULTS AND DISCUSSION

Kinetics

The effects of temperature and radiation dose on the decay rate were investigated. In all cases where nitrogen was used as a flow gas, two decay reactions were evident, one much more rapid than the other. These are shown in *Figure 1* (top), where a representative second-order plot of the reciprocal radical concentration (in arbitrary units) versus time is provided. The linear relationship which follows the more rapid decay reaction suggests that second-order kinetics is operative in this portion of the decay reaction. Kinetics of this order might be anticipated for a recombination reaction where a distribution of radicals approaching uniformity is present. At the higher temperatures of this study, where the decay reaction is more rapid, decay could be followed conveniently over a tenfold variation in concentration. No deviation from second-order kinetics was observed for the slow reaction. Decay curves of the type shown in *Figure 1* (top) have also been noted in polyethylene by others[5, 12] at lower temperatures.

The radical concentrations involved in the rapid decay reaction were determined by extending the linear plot for the slow reaction, *Figure 1*, and determining the differences in radical concentration between the experimental and extrapolated values for equivalent times. The latter values are indicated by the dashed line in *Figure 1*. The rapid decay reaction also follows second-order kinetics for samples receiving radiation doses in the 0·057 to 9·02 Mrad range. The 18·4 to 27·4 Mrad range, however, provides data which tend to follow first-order kinetics. A representative second-order plot for the rapid decay reaction is shown in the lower plot of *Figure 1*. This series of experiments involving the effect of dose on the rate constant was conducted at 70°C.

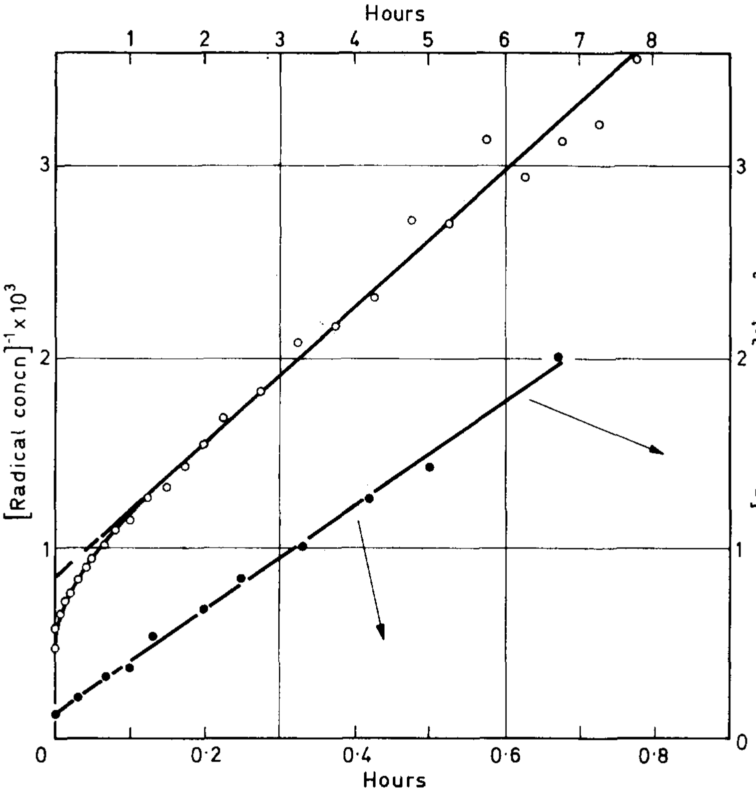

Figure 1—Second-order relationship for radical decay, 90°C, O–O, total radical concentrations. ●–●, radical concentrations in the rapid decay process. Dose 28·5 Mrad

The plot in *Figure 1* is based on the integrated form of the second-order rate expression, i.e. the reciprocal radical concentration versus time. Another method for evaluating the adequacy of the second-order kinetics involves the following form of the second-order rate equation.

$$\{d[R]/dt\}/[R]^2 = k_1 \qquad (1)$$

where [R] denotes radical concentration, t is time, and k_1 is a decay constant.

A plot of $\{d[R]/dt\}/[R]^2$ versus time should provide a line parallel to the abscissa whose intercept at the ordinate is the value for k_1. *Figure 2* shows plots for measurements conducted at several temperatures. The $d[R]/dt$ values were obtained from tangential slopes of R versus time plots. *Figure 2* emphasizes the adequacy of the second-order relationship for the slow decay process.

Peroxy and methylene radicals

Possible reasons for the existence of two decay reactions would include the effect of residual oxygen and the effects of a multiphase material on the recombination reaction. The effect of oxygen was examined at 90°C by allowing the decay reaction to take place in a stream of air or oxygen rather than nitrogen. Second-order plots of these experiments are shown in *Figure 3*. It is evident that air increases the rates of both reactions.

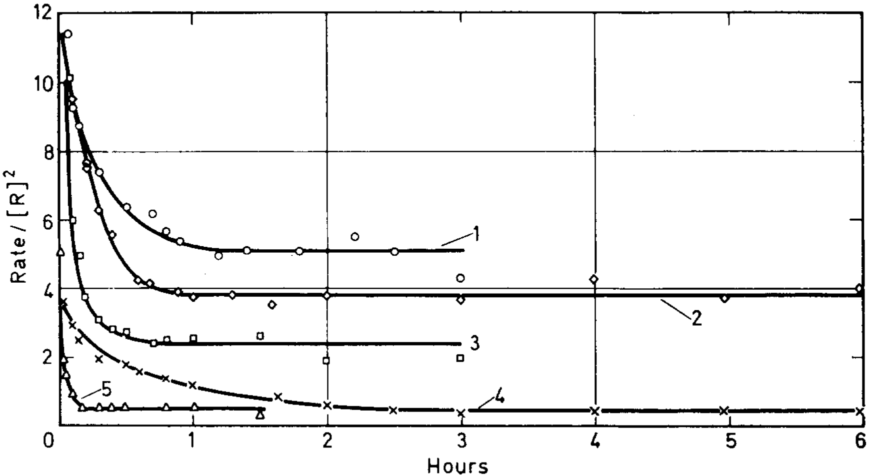

Figure 2—Evidence for the second-order character of the slow decay process

	Rate/[*R*]^2, (*radical-h*)$^{-1}$	*Temperature, °C*	*Dose, Mrad*
1	$\times 10^3$	70	0·057
2	$\times 10^4$	70	1·54
3	$\times 10^3$	118	28·5
4	$\times 10^4$	70	27·4
5	$\times 10^2$	125	28·5

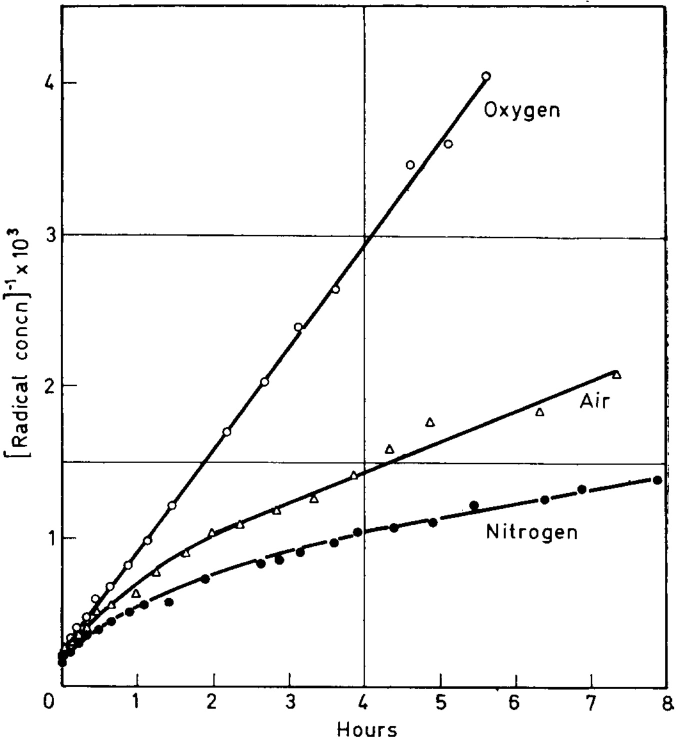

Figure 3—Comparative effects of nitrogen, air and oxygen on radical decay (90°C). Dose 28·5 Mrad

In the presence of oxygen, only one decay reaction is evident, however, and it is more rapid than those in nitrogen or air. The apparent single reaction in the presence of oxygen and its second-order characteristics suggests a reaction involving oxygen and two radicals to form a peroxide, ROOR.

The possibility that the rapid reaction is due to the presence of oxygen is considered unlikely for the following reasons. If it were due to oxygen, the presence of a small amount of oxygen (as in air) would increase the fraction of radicals in the rapid reaction. This was not observed, however. Also, there would be some evidence of the peroxy radical in the observed spectra. No spectral evidence was found, however, at room temperatures or higher, even though the radiations were performed in air.

The reaction of radicals with oxygen in polyethylene to form peroxy radicals has been reported by Abraham and Whiffen[18], Loy[5], and Ohnishi, Sugimoto and Nitta[10]. The absence of the radicals in the present study is due, in part, to their relative instabilities in the 50° to 125°C temperature range, the use of polyethylene rod rather than film, and the absence of oxygen in the decay environment. These conclusions are based on the results of Ohnishi *et al.*[10], who found the half-life time of the peroxy radical to be 20 minutes at room temperature, and the requirement that film rather than bulk polyethylene be used to obtain sufficient peroxy radicals for observation.

It is assumed that the allyl radical is the only radical encountered in this study. The possible presence of the methylene radical in the spectra was considered; it was not observed, however, at any of the elevated temperatures of the present study. At room temperature it was evident only for doses below 1 Mrad; even then, it decayed very rapidly. Furthermore, the estimated 12 kcal/mole activation energy for methylene radical decay[19], and its rapid decay at room temperature, suggest that very little if any of this radical exists in the temperature range of the present study. (To detect methylene and peroxy radicals, conditions for obtaining highly resolved spectra were used, e.g. low scanning speeds to enhance spectra detail, and reduction of the incident microwave power supply to 0·5 mW to minimize saturation broadening.)

Oxygen and its influence on the decay process were also studied by irradiating and permitting decay of the samples under vacuum. The decay curves under this condition were similar to those in *Figure 1*. This result, and the additional consideration that a large percentage of the radicals had reacted before the decay study commenced, suggest that a good portion if not all of the residual oxygen had reacted before the measurements. Thus, oxygen does not appear as a probable cause for the existence of the two decay reactions.

A consideration of measurable quantities that might be influenced by the presence of different phases in the polyethylene, however, suggests that the existence of the two decay reactions is due to the presence of a crystalline phase and one which is less ordered. The measured quantities, i.e. free radicals and decay constants, are related to morphology in the following sections.

Effect of dose and temperature on radical concentration

The distribution of radicals which decay in either the rapid or slow reactions suggests a correlation between this distribution and the quantity of polyethylene designated as amorphous or crystalline. The suggestion is based on the assumptions that the rapid and slow decay reactions take place in different regions of the polymer and that the radicals initially formed by radiation are uniformly distributed.

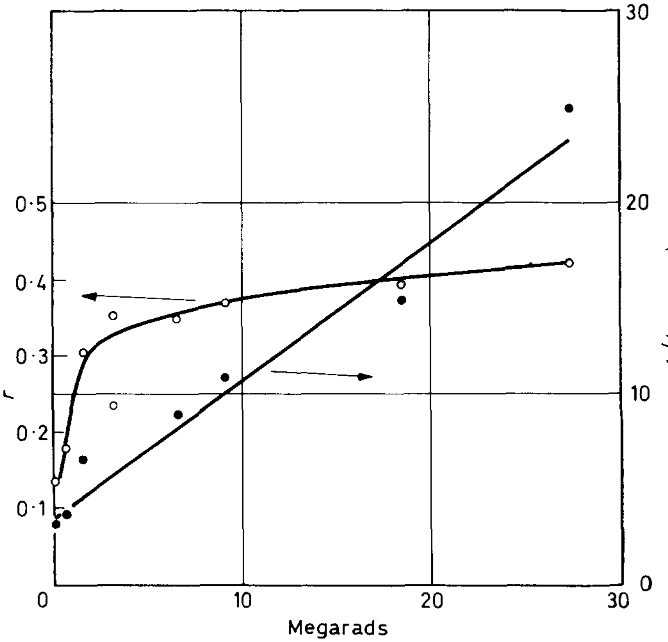

Figure 4—Variation of the radical concentration fraction with radiation dose in the rapid decay reaction (70°C). Dose 28·5 Mrad

The distribution was determined from a plot of the fraction r versus dose (*Figure 4*), where r is R_{10}/R_{T0}; R_{10} is the initial radical concentration for the rapid decay reaction, and R_{T0} is the total initial radical concentration. This fraction increases rapidly for the first few Mrads and levels off following additional radiation absorption. *Figure 4* (open circles) shows that the fraction r has a lower limiting value of about 0·1 to 0·13. As the dose increases, r at first increases sharply and then slowly in the 0·35 to 0·42 fraction range.

The character of the curve can be explained in terms of the fraction of material designated as amorphous which is present in linear and in highly branched polyethylenes and the second-order character of the radical decay reaction. The following relationship is used.

$$-\mathrm{d}\,(r_{\mathrm{max.}}-r)/\mathrm{d}D=k_2\,(r_{\mathrm{max.}}-r)^2 \tag{2}$$

where $r_{\mathrm{max.}}$ is the limiting value for R_{10}/R_{T0}, D denotes radiation dose, and k_2 is a constant.

It is assumed in equation (2) that the volume fraction of polyethylene which will contain R_1 radicals is proportional to this radical concentration, a limiting volume fraction exists, and that the decay of this volume fraction with respect to dose is proportional to the square of the volume fraction.

The basis for the square relationship is assumed to be the following. Some radicals had decayed before the initial measurements of this study. This early decay is associated with radicals which are in very close proximity in the spurs and the decay which takes place at lower temperatures[4, 5, 8, 11–16]. The decay kinetics of these radicals is, presumably, the same as that found in this study, i.e. second order. Although these radicals are not uniformly dispersed when considering the spurs in which they exist, their concentrations may be considered proportional to volume because of the large volume fractions referred to in this study. Thus, the decay of the volume fraction is also second order.

Integration of equation (2) gives

$$1/(r_{\max.}-r)-1/(r_{\max.}-r_0)=k_2D \tag{3}$$

where $r_0=R_{10}/R_{TO}$ at zero dose. The plot of $1/(r_{\max.}-r)$ versus dose, shown in *Figure 4* (solid circles), provides the linear relationship implied in equation (3). A value of $r_{\max.}=0{\cdot}46$ is assumed. The intercept value of r_0 equal to 0·17 would indicate that the polymer volume in which the rapid decay reaction takes place is 17 per cent of the total volume. The value is of interest since it corresponds approximately to the amount of material in Marlex 50 which has been designated as amorphous[20, 21].

The apparent limiting value for $r_{\max.}$ corresponds to another value associated with the amorphous region—the limiting fraction of amorphous material which is formed as the number of methyl-group branches increases[22]. These data were used to determine $r_{\max.}$, so $r_{\max.}$ may be associated with the possibility that the crosslinks which are the product of radical decay act as branches in non-linear polyethylene. These correlations of the radical fractions with the fraction of amorphous material suggest that the rapid decay is taking place in the amorphous region.

The effect of temperature on R_{10}/R_{TO} was also determined. The increase in R_{10}/R_{TO} with temperature can be associated with a decrease in the crystalline fraction as the temperature increases, and is consistent with observation[23]. *Figure 5* also shows the effect of temperature on R_{TO}. The temperature at which a change in slope occurs, 80°C, is the same temperature at which fusion begins[21]. R_{TO} decreases rapidly to a small fraction of the value at 80°C. This rapid decrease takes place because R_{TO} is largely R_{10}. The latter radical, being in the amorphous phase, decays rapidly at the higher temperatures. These results emphasize the relationship between R_{10}, R_{TO} and phase.

Effect of dose on rate constants

From a study of the relationships between dose and decay-rate constants, it is possible to show that the rate constants have properties similar to diffusion constants and to obtain parameters related to these constants. The effect of dose on decay-rate constants is shown in *Figure 6*, where

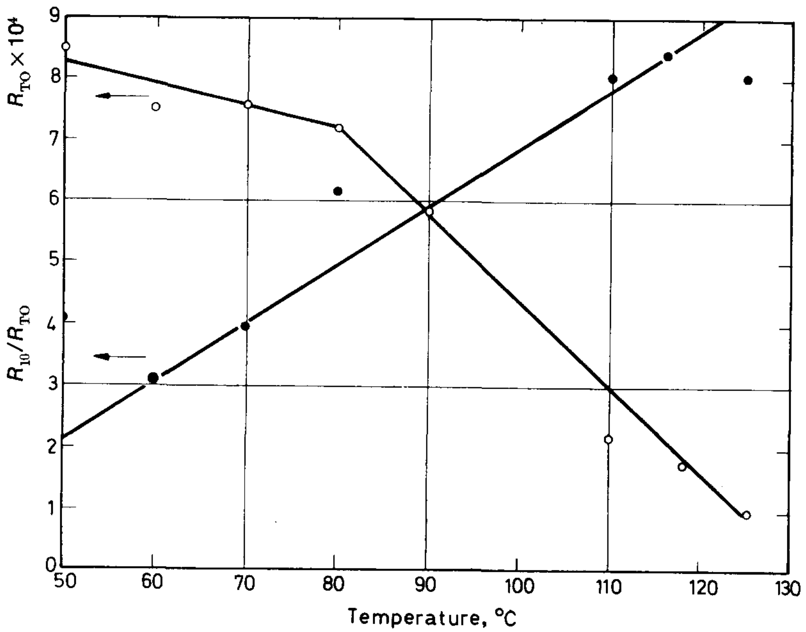

Figure 5—Effect of temperature on the total initial radical concentration (○–○) and radical concentration fraction in the rapid decay reaction (●–●). Dose 28·5 Mrad

rate constants and reciprocal rate constants are plotted against dose. The linear relationship for $1/k_{22}$ versus dose, where k_{22} is the second-order rate constant for the slow decay process, suggests the possibility that the rate constants are related to diffusion constants. This evidence is based on other studies of diffusion in polymer systems[24–26] which have provided similar linear reciprocal relationships between the diffusion constant and the molecular weight of the diffusing material or the number of crosslinks in the polymer.

Effect of crystallinity on the rate constant

A diffusion-regulated reaction in a crystalline matrix should be dependent on the structural condition of the crystalline phase. This is illustrated in *Figure 7* for plots of k_{11} and k_{22} versus the percentage of crystallinity in Marlex 50. The data cover the temperature range of 50° to 125°C. Crystallinity data provided by Charlesby and Callaghan[21] for un-irradiated Marlex 50 were used. It is believed that the 28·5 Mrad dose that the specimens received did not affect the crystallinity significantly[23,27]; therefore, crystallinity data for un-irradiated Marlex 50 is appropriate.

A linear relationship is evident in *Figure 7* for the slow decay reaction constant k_{22} over the entire temperature range studied and for the rapid decay constant k_{11} up to 110°C, suggesting a correlation between crystallinity and decay rate. The linear relationship is not interpreted to indicate that the rate constant is dependent on the amount of crystallinity, however. The continued decrease in decay-rate constants, after the crystalline content

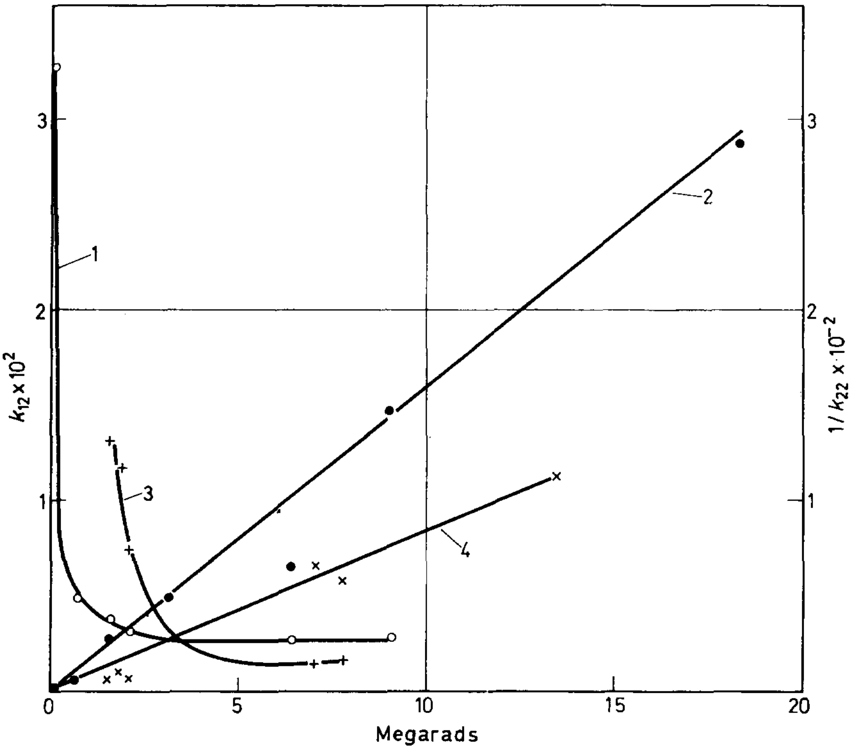

Figure 6—Effect of radiation dose on decay constants (70°C). 1, k_{12}; 2, $1/k_{22}$ (irradiated in air). 3, k_{12}; 4, $1/k_{22}$ (irradiated in vacuum)

becomes almost constant below 80°C, opposes this conclusion. Instead, the correlation between crystallinity and rate constants reflects a correlation between the changing structural condition or deterioration of the crystalline phase during fusion and the rate constants.

The changing crystalline condition occurs in the 80° to 137°C melting range and can be correlated with low-molecular-weight diluents, chain ends, etc., which modify the crystal structure and lower the melting point. The increase in the rate constant values, therefore, reflects radical decay in crystallites which have been modified by heat. The lower temperature linearity for k_{11} indicates that the rapid decay reaction is also dependent on the crystalline condition.

The results in *Figure 7* would appear to imply that k_{11} and k_{22} become zero at 83 per cent crystallinity. The apparent anomaly is due to the small values for the decay-rate constants relative to the ordinate scale. Although the percentage of crystallinity does not change appreciably below 80°C, the decay-rate constants continue to decrease. An exploded view of *Figure 7* in the vicinity of 83 per cent crystallinity would show a curve with values of k below 80°C forming a line parallel to the ordinate.

Relationship between vinyl-group decay and k_{22}

Another relationship, that between the decay constants and vinyl-group

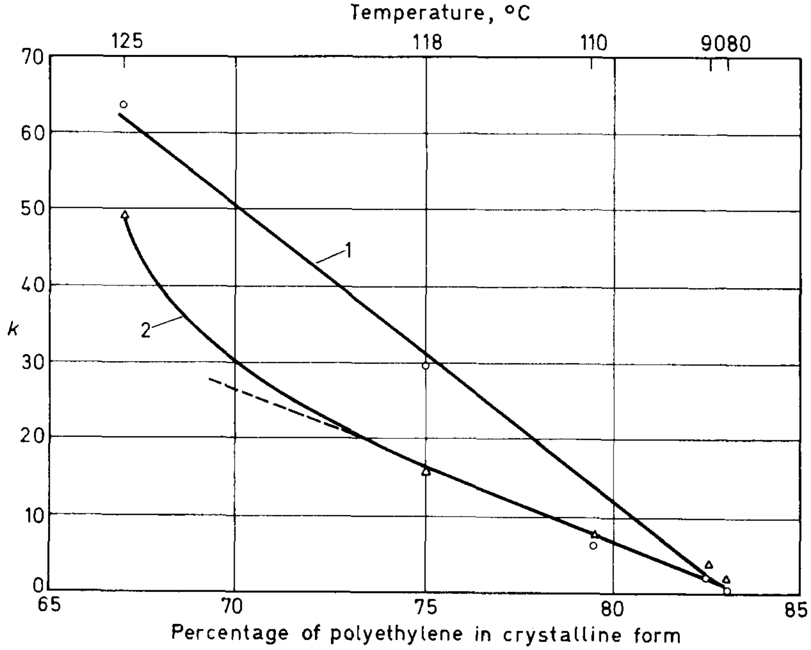

Figure 7—Effect of the percentage of crystallinity in polyethylene on the decay rate constants, 1, $k_{22}\times 10^4$; 2, k_{11}. Dose 28·5 Mrad

decay, provides evidence that the decay reaction is diffusion regulated. Allyl radicals whose decay is the object of the present study originate from the vinyl groups initially present in Marlex 50 and from vinylene groups which are formed during radiation[28]. In the lower dose range, allyl radicals are formed largely from vinyl-group dimerization[28]. It is therefore not surprising that the decay of these radicals with respect to time is related to the decay of the vinyl groups with respect to dose. The relationships are discussed in this section.

In a previous publication[28], it was shown that vinyl-group decay is second order and governed by the equation

$$1/[\mathrm{Vi}]-1/[\mathrm{Vi}_0]=k_3D \tag{4}$$

where [Vi] is the concentration of unreacted vinyl groups and $[\mathrm{Vi}_0]$ is the initial vinyl concentration.

Equation (4) is related to the decay-rate constant through equation (5), which is realized from *Figure 6.*

$$1/k_{22}=r\,D \tag{5}$$

where r is a proportionality constant. The desired relationship is obtained by combining equations (4) and (5):

$$1/[\mathrm{Vi}_0-\mathrm{Vi}]=1/[\mathrm{Vi}_0]+r\,k_{22}/k_3\,[\mathrm{Vi}_0]^2 \tag{6}$$

Equation (6) is a linear expression between the reciprocal of the vinyl groups which have reacted and k_{22}. Validity for equation (6) is shown in a plot of $1/[Vi_0 - Vi]$ versus k_{22}, *Figure 8*. This gives the required straight line with the correct intercept[28] at $1/[Vi_0]$, $1{\cdot}05 \times 10^4$ g/mole. Two sets of data are plotted in this figure; the crosses are the rate constants from specimens irradiated with γ-rays in vacuum, the open circles are rate constants for specimens irradiated with electrons in air. The latter plot is extended with an interpolated rate constant (solid circle) obtained from *Figure 6*.

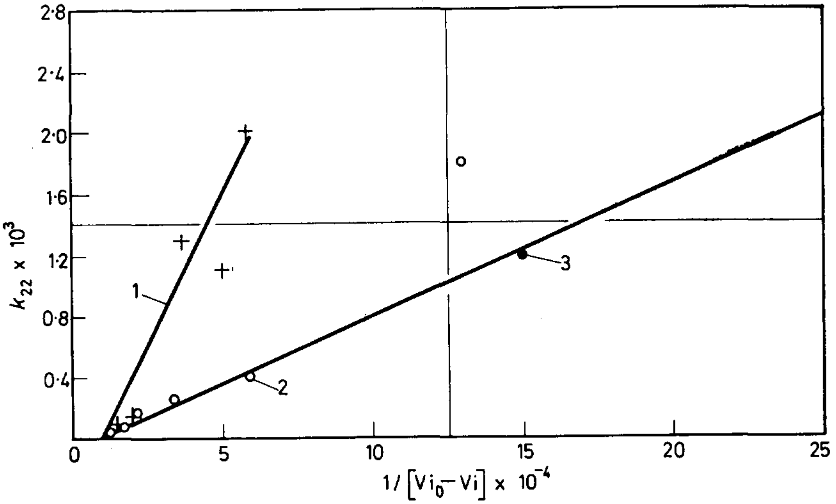

Figure 8—Relationship between slow decay rate constant and vinyl group decay. 1, irradiated in vacuum; 2, irradiated in air (experimental points); 3, irradiated in air (points interpolated from *Figure 6*)

A possible explanation for the relationship between reacted vinyl groups and k_{22} may be found in the assumption that the radical decay reaction is a diffusion process. Thus, factors which would influence diffusion would also influence the decay rate. It is also reasonable to assume that some radical decay had taken place before the measurements were made in this study, especially among those radicals in close proximity. Radical decay results in crosslinks, and they in turn reduce the diffusion rate[24]. Thus, it may be expected that reacted vinyl groups would be related to radical decay.

Parameters related to k_{22}

It has been shown that k_{22} is related linearly or inversely to dose, crystallinity, and vinyl-group decay. In this section, a combined relationship between all these quantities will be shown and a new decay constant, independent of the above quantities, will be defined.

To show this relationship, a useful parameter is introduced which relates the decay constants with dose and radiation-generated amorphous material. It was originally described by Williams, Matsuo and Dole[27]. They showed

Table 1. Parameters affecting the radical decay constant values (70°C)

Dose, Mrad	R_{TO}, *radicals-arb. units*	$[Vi_0\text{-}Vi]$ *mole/g*	ϕ_A	k_{22} *(radical-h)*$^{-1}$	k_{22}' *vinyl group/radical-h*	k_{12} *(radical-h)*$^{-1}$	k_{12}' *radical*$^{-2}$ $\times h^{-1}$
0·057	$0{\cdot}30\times10^{3}$	$0{\cdot}10\times10^{-5}$	1·00	$4{\cdot}05\times10^{-3}$	$0{\cdot}41\times10^{-8}$	$3{\cdot}26\times10^{-2}$	9·8
0·64	2·25	0·80	1·06	1·80	1·53	0·495	10·5
1·54	2·75	1·64	1·18	0·386	0·74	0·370	8·6
3·05	4·00	2·95	1·48	0·248	1·08	0·315	8·5
6·48	5·85	5·00	1·58	0·156	1·23	0·270	10·0
9·02	6·55	5·80	1·69	0·068	0·67	0·285	11·0
18·4	7·45	7·50	1·99*	0·035	0·52		
27·4	7·85	8·20	2·22*	0·041	0·75		

*These values for ϕ_A were obtained from an extrapolated linear plot of ϕ_A (room temperature irradiation) versus $(\text{dose})^{1/2}$ (see ref. 27). The 140°C irradiation data also provided a linear relationship between ϕ_A and $(\text{dose})^{1/2}$.

that doses up to 12 Mrad do not affect the percentage of crystallinity. However, when the irradiated samples were permitted to undergo a melting and solidification excursion, the amorphous content of the polyethylene increased, indicating that a metastable material was produced. Infra-red techniques were used to measure the relative amorphous content.

This information is relevant to the present study since k_{22} is dependent not only on vinyl-group decay but on this metastable material. This correlation is indicated in the constant values for k_{22}' in *Table 1*, obtained from the empirical relationship

$$k_{22} = k_{22}'/\phi_A[\text{Vi}_0 - \text{Vi}] \tag{7}$$

where k_{22}' is a decay constant and ϕ_A refers to relative changes in the amorphous material content which are realized after the melting and solidification excursion[27]. Therefore, k_{22}' represents a parameter which is more characteristic of the diffusion properties of the polymer. Equation (7) obviously does not cover the entire dose range since ϕ_A and $[\text{Vi}_0 - \text{Vi}]$ can be equal to zero, thereby providing an infinitely high value for k_{22}, but the relationship is applicable for the approximate dose range covered in *Table 1*.

Although the values for k_{22}' are scattered, equation (7) is significant, since k_{22}' shows no trend for the 99-, 82- and 2·22-fold ranges in values for k_{22}, $[\text{Vi}_0 - \text{Vi}]$ and ϕ_A, respectively, over the 480-fold range in dose. This information indicates that radical mobility in the polymer is reduced in part by vinyl-group decay and by an increase in ϕ_A.

It might be anticipated that ϕ_A, being directly related to amorphous material content, would be directly related to k_{22}. However, the irradiated material represented by ϕ_A does not become amorphous until it is heated above the melting point and cooled. Therefore, another property related to ϕ_A must govern its association with k_{22}.

A corresponding empirical relationship is suggested for k_{12} (the second-order rate constant for the rapid decay reaction), R_{TO} (the initial radical concentration), and ϕ_A

$$k_{12} = k_{12}'\phi_A/R_{TO} \tag{8}$$

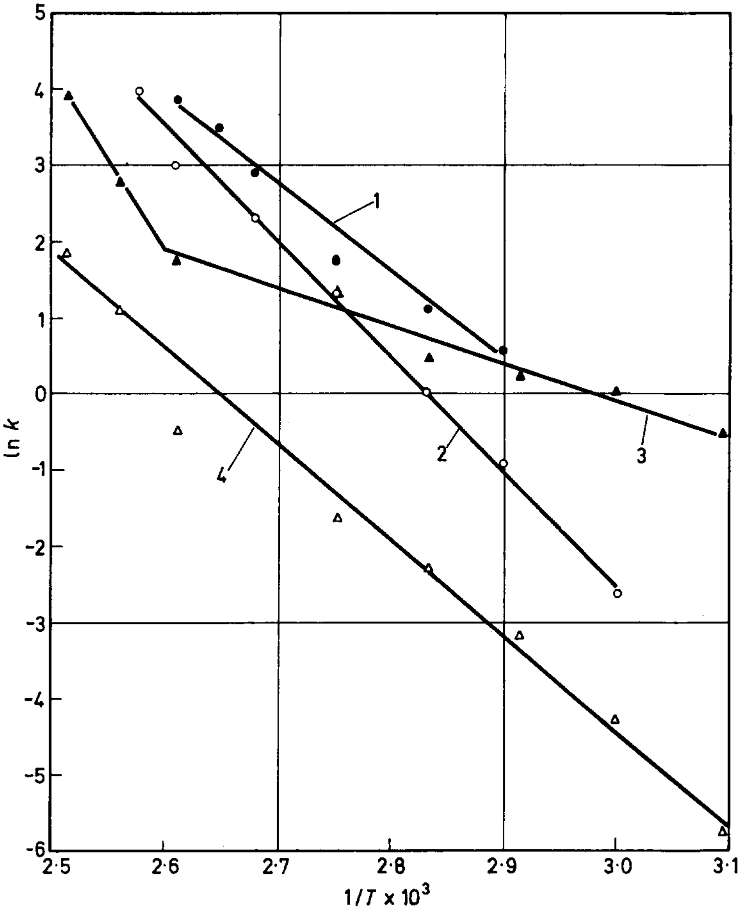

Figure 9—Arrhenius plot of decay rate constants. 1, k_{11} (0·9 Mrad). 2, $k_{22} \times 10^3$ (0·9 Mrad). 3, k_{11} (28·5 Mrad). 4, $k_{22} \times 10^3$ (28·5 Mrad)

Reasonably constant values for k_{12}' are realized (*Table 1*) for the 158-, 21·8-, 11·5-, and 1·69-fold ranges in dose, R_{TO}, k_{12} and ϕ_A, respectively.

Activation energies

A consideration of the activation energies for the decay reactions is instructive, since it emphasizes the role of matrix condition in radical decay and provides evidence for an additional radical decay process in molten polyethylene. The activation energies were determined from the Arrhenius relationship by plotting the logarithms of the decay-rate constant values against the reciprocal absolute temperatures (*Figure 9*). The values are given in *Table 2*.

A discontinuity occurs in the ln k_{11} versus $1/T$ plot at 110°C for samples receiving 28·5 Mrad. This is the temperature at which the crystalline content of Marlex 50 begins to decrease rapidly with temperature[21]. The discontinuity may be interpreted in terms of another radical decay mechanism

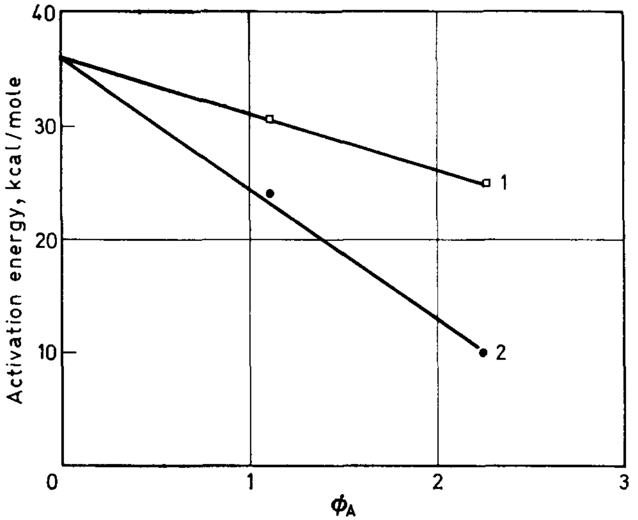

Figure 10—Relationships between the activation energies and the relative metastable material content of polyethylene. 1, k_{22} activation energies; 2, k_{11} activation energies

whose activation energy and frequency factor make this mechanism predominant above 110°C.

The correlations of the rate constants with both crystalline and amorphous phase conditions and with the percentage of crystallinity, discussed in the previous sections, suggest that a similar correlation should exist between the activation energies and the phase condition. This correlation is evident in *Figure 10* where the activation energies are plotted against ϕ_A, the relative metastable material content.

Table 2. Activation energies for radical decay in irradiated Marlex 50

Dose, Mrad	*Rate constant*	*Temperature range, °C*	*Activation energy, kcal/mole*
0·9	k_{11}, h^{-1}	72–110	23·1
0·9	k_{22}, (radical-h)$^{-1}$	60–115	30·4
28·5	k_{11}, h^{-1}	50–110	9·8
28·5	k_{11}, h^{-1}	110–125	45
28·5	k_{22}, (radical-h)$^{-1}$	50–125	24·8

Figure 10 points to several conclusions. (1) The activation energies for both k_{11} and k_{22} have a common activation-energy value at $\phi_A = 0$. (2) This common value provides evidence not only for relationships between the activation energies and the amount of metastable material generated by the radiation process, but also that the relationships are linear. (3) The rapid and slow decay reactions take place in material having a common pre-irradiation origin which was 100 per cent crystalline, i.e. $\phi_A = 0$. The initial value for ϕ_A provided by Williams *et al.*[27] is 1·0; however, this corresponds to the amorphous content of pre-irradiated material which

is nominally 83 per cent crystalline. (4) The intercept at $\phi_A=0$, 36 kcal/mole, represents the activation energy for radical decay in 100 per cent crystalline material. (5) The amorphous material associated with k_{11} may represent material which has received more radiation and therefore more crystalline damage.

The sharp decrease in the activation energy for k_{11} with respect to ϕ_A and dose is consistent with the observation that diffusion and the activation energy for diffusion are dependent on the crystallinity of the polymer[24].

Effect of polymer molecular weight on radical decay

Radical decay was studied in polymers possessing melt indices of 0·2, 0·74 and 2·6, to determine the effect of molecular weight on the rate of radical decay. A correlation between melt index and molecular weight for linear polyethylenes was not found. However, from information obtained for low-density polyethylenes[29], it was estimated that this range of melt indices covers a factor of less than two in number-average molecular weight.

The values for k_{11} and k_{22} obtained from these Phillips-type linear polyethylenes are given in *Table 3*. No trend in the variation of rate constant with melt index is indicated, but a trend would not be anticipated if it is assumed that diffusion in the polymer is dependent on segmental rather than molecular motion.

Table 3. Effect of melt index on decay rate constants (90°C)

Melt index	*Dose, Mrad*	k_{11}, h^{-1}	k_{22}, $(radical\text{-}h)^{-1}$
0·20	31·5	2·18	$3{\cdot}78\times10^{-5}$
0·74	31·5	2·86	4·52
2·6	31·5	2·45	3·41

Variation in reaction order

The information which this study has yielded, together with information from other studies, permits an extension of the preceding general thoughts concerning some aspects of the mechanism for radical decay in polyethylene. The disparity in opinions concerning reaction order probably results from the fact that the mechanism is more complex than indicated here and in other studies. Also, the ability to resolve the decay kinetics into two segments which can be correlated with the material phase does not imply that the phase boundaries are sharp. Instead, it is more probable that diffuse gradients exist and that the decay rates in the diffuse regions are intermediate to those considered fast and slow. More appropriate relationships for the decay process would therefore take into consideration the gradient and treat the slow and fast decay reactions and the change in reaction order as extenuating observations of a general decay process. A generalized relationship of this type which shows how the reaction order changes with time and temperature is given below.

Information obtained in this study shows that temperature and dose influence the reaction order. Both of these factors also influence the condition of the metastable region in the temperature and dose range of this study. Thus, an increase in dose and/or temperature makes this region less ordered, increases the decay rate, and tends to lower the reaction order.

Theoretical studies related to combining entities which are not uniformly distributed have been made by Waite[30] and Antonov-Romanovsky[31]. These authors show that second-order kinetics prevails when the combining entities are relatively far apart and tend toward a uniform distribution. When the entities are not uniformly distributed and the entity pairs are close to their capture radius, then the second-order constants tend to decrease with time and, under initial conditions, the kinetics assumes apparent first-order properties.

The relationships presented by Waite[30] show explicitly how temperature, dose and proximity of the radicals influence the reaction order. The rate equation for radical decay can be presented in the form

$$-\mathrm{d}\,[\mathrm{R}]/\mathrm{d}t = K\,[1 + r_0/(\pi\mathcal{D}t)^{\frac{1}{2}}]\,[\mathrm{R}]^2 \qquad (9)$$

where K is the rate constant, r_0 the capture radius, and $\mathcal{D}$ the diffusion coefficient for polymer segments containing radicals. For extended time periods, equation (9) takes on the usual second-order-kinetics form. Initially, a second-order rate constant k, where

$$k = K\,[1 + r_0/(\pi\mathcal{D}t)^{\frac{1}{2}}] \qquad (10)$$

will not be constant but will decrease with time, thereby providing an apparent first-order character for the kinetics.

The dependence of k on the diffusion coefficient, equation (10), explains the dependence of the reaction order on dose. Increasing the dose will decrease $\mathcal{D}$ (*Figure 6*), and $(\pi\mathcal{D}t)^{\frac{1}{2}}$ will become smaller and tend to influence k over a longer period of time. This effect was observed in the present study; for small doses (where $\mathcal{D}$ is large) the rapid decay reaction was second order because $r_0/(\pi\,\mathcal{D}t)^{\frac{1}{2}}$ was small. It became first order, however, with increasing dosage because $\mathcal{D}$ became correspondingly smaller.

First-order kinetics was observed by Lawton *et al.*[4] and by Cracco *et al.*[14] over the temperature range of −71° to 41°C. The kinetics which prevailed over the entire decay measurement period may be credited in part to the close proximity of the decaying radicals, as suggested by them, and to small values for $\mathcal{D}$ which exist under these conditions.

SUMMARY

Free radical decay in polyethylene can be described in terms of two decay reactions, one more rapid than the other. Their relative decay rates are dependent on the condition of the matrix. In the temperature and dose range of this study, radicals were found to exist in a crystalline and in a metastable region formed during irradiation.

The decay-rate constants are dependent on vinyl-group decay, the initial radical concentration, the crystalline condition, and the fraction of metastable material present in the polymer.

The activation energies are correlated with the metastable material content of the polymer and decrease with increasing dose. Evidence for an additional radical decay reaction above 110°C was obtained from activation-energy data.

The variation in reaction order with dose and temperature in the rapid decay reaction is explained with the aid of a second-order decay constant which is dependent on the time and the diffusion coefficient.

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