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Review
Radiation effects in polyethylene and n-alkanes

G. UNGAR
Ruder Bošković Institute, P.O.B. 1016, 41001 Zagreb, Yugoslavia

The effect of high-energy radiation on n-alkanes and polyethylene (PE) are reviewed. The article includes a description of (a) primary radiation events, formation, spatial distribution and decay of free radicals and radical migration mechanisms, (b) formation of cross-links and other stable products, (c) the effects of crystallinity, crystalline modifications and morphology on radiation cross-linking, and (d) radiation-induced changes in the crystal lattice and the destruction of crystallinity at high irradiation doses. An attempt is made to bring together conflicting views on various unsolved problems of the radiation physics and chemistry of these important and much studied substances. Long-chain paraffins are given considerable attention since their radiation behaviour often provides a link between that of PE and its short-chain analogues.

1. Introduction

The behaviour of polyethylene (PE) under the action of high-energy radiation has now been the subject of extensive studies for more than three decades [1, 2]. Due to its high cross-linking yield and low degradation PE has found application in radiation production of such items as heat-shrinkage tubes and films. Radiation cross-linking may also be used to improve the wear and creep resistance of PE objects and the heat resistance of cable insulation. Compared to many other plastics PE is regarded as being resistant to radiation and PE products can safely be subjected to radiation sterilization etc.

Many fundamental aspects of radiation chemistry and physics of polymers have been studied most extensively on PE. Several very good reviews have been written on this subject, most of which cover a wider range of polymers [3–9]. Articles that deal exclusively with PE include those by Salovey (PE single-crystals) [10], Mandelkern [11] and Dole [12]. Much information can be found in the review by Grubb [13]. The present article attempts to give an updated combined survey of the radiation behaviour of PE and longer chain n-alkanes. Particular emphasis is placed on the relation between the physical state (e.g. crystallinity) and radiation chemistry, on the distribution of cross-links and their precursors, free radicals, and on effects on the crystal lattice and loss of crystallinity at high doses. The latter is of interest, for example, in electron microscopy where beam damage to organic materials causes considerable problems [13].

Only radiation chemistry *in vacuo* will be surveyed. Oxidation processes have been specifically reviewed by Dole [14] and the reader is also referred to some more recent studies [15, 16]. Information on mechanical properties of irradiated PE can be found in the review by Lyons and Weir [17] and in some later papers [18–22]. Thermal behaviour of cross-linked PE has been described in [23–32] and that of alkanes in [33, 34].

Of the n-alkanes, those longer than about 15 C-atoms will be considered in more detail. Much information on radiolysis of shorter alkanes can be found in books by Topchiev [35] and Gäumann and Hoigné [36], as well as in more recent articles by Gäumann *et al.* [37, 38], Tilquin, Tilman and Claes [39], Földiak [40], and references therein.

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2. Free radicals

Considerable space will be given here to reviewing the extensive research on formation and decay of free radicals in irradiated PE and paraffins. The reaction mechanisms which have been proposed on the basis of such research will later be compared with other findings about the distribution of the end products, i.e. cross-links.

2.1. Events leading to radical formation

According to Partridge [41] there are about four ionizations and three direct excitations for each hundred electron volts of radiation energy absorbed by saturated hydrocarbons, altogether about seven excitations after complete neutralization of ions, i.e., the *G*-value for excitation is ~7. In long-chain alkanes about two thirds of these (~4.3) are excitations of the C–H bonds. The remaining one third (~2.7) are excitations of the C–C bonds. Partridge concluded that C–H bond excitations are mainly localized, while the C–C excitations move rapidly along the molecular chain. Therefore the C–H bond will break immediately but very few C–C ruptures would have a chance to occur, particularly if the chains are long [40, 41]. The C–C excitons could be trapped by defects, such as double bonds, thus probably inducing various decay reactions of the olefin groups.

If the C–H bond excitations do not have a chance to migrate, it appears that the C–D bond excitations in deuterated n-alkanes may be highly mobile, as proposed by Gillbro and Lund [42, 43]. Upon irradiation of a crystalline perdeutero-n-alkane doped with a small percentage of its protiated analogue these authors observed, using the electron spin resonance (ESR) technique, that the yield of protiated radicals was several hundred times higher than that expected if an equal probability of C–H and C–D bond scission is assumed; this was found to be true for irradiation at 77 K, but not at 4 K or 273 K. The transfer of deposited radiation energy through the deuterated paraffin was thought to occur by exciton migration. The high preference for scission of the C–H bond rather than the C–D bond, was ascribed to the difference in stretching frequencies, that of the C–D bond being too low compared to the time an exciton spends on a molecule.

It should be mentioned, however, that Iwasaki, Toriyama and co-workers [44–46] ascribed the selective formation of protiated radicals in mixed crystals to reactions of thermal D-atoms rather than to exciton migration. The observed suppression of energy transfer at 4 K was considered to be the main evidence against the exciton mechanism (compare with Section 2.3.1). Supporting evidence comes from a recent study on methyl cyclohexane and dimethyl butane [47], where it was found that the exciton transfer efficiency at 4 K does not differ significantly from that at 77 K.

Abstraction reactions of hot as well as thermal hydrogen (or deuterium) atoms:

$$\mathrm{R_1H \rightarrow \dot{R}_1 + \dot{H}} \qquad (1)$$

and

$$\mathrm{R_2H + \dot{H} \rightarrow \dot{R}_2 + H_2} \qquad (2)$$

were considered by Iwasaki and co-workers [44–46, 48] to be the main mechanism for radical pair production (see Section 2.3.1) and for radical site migration (see Section 2.5), as well as for the preferential formation of protiated radicals in mixed crystals, mentioned above. The fact that no trapped H-atoms were detected in alkanes at 4.2 K [49] was attributed to their rapid tunnel abstraction reaction with surrounding molecules. The hot hydrogen mechanism was also favoured by Salovey and Falconer [50].

All the authors mentioned so far have assumed the formation of free radicals by homolytic scission of the C–H bond excited either directly by radiation or by the neutralization of the molecule. However, ionic mechanisms of radical formation have also been considered. Kevan and Libby [51] postulated radical formation prior to neutralization in the solid phase. This would involve an ion-molecule reaction followed by the expulsion of a hydrogen molecule:

$$\mathrm{RH \rightsquigarrow R\dot{H}^+ + e^-} \qquad (3)$$

$$\mathrm{R\dot{H}^+ + RH \rightarrow \dot{R} + RH_2^+} \qquad (4)$$

$$\mathrm{RH_2^+ + e^- \rightarrow \dot{R} + H_2.} \qquad (5)$$

Alternatively, many years ago Weiss [52] proposed that even H_2 expulsion may occur prior to neutralization. Thus, in addition to neutral radicals, t-vinylene groups would also be formed from cation radicals (Equation 3) via the reactions:

$$\begin{array}{l} \mathrm{RCH_2\dot{C}^+H_2R \rightarrow RCH{=}\dot{C}^+HR + H_2} \\ \qquad\qquad\qquad\qquad \big\downarrow + e^- \\ \qquad\qquad\qquad\quad \mathrm{RCH{=}CHR.} \end{array} \qquad (6)$$

Very recently Chappas and Silverman [53] reconsidered this mechanism, modifying it somewhat. According to Silverman, one of the strongest pieces of evidence in support of the Weiss mechanism is the observed $RCH{=}\dot{C}^{+}HR$ ion in PE irradiated at 4 K [54]. However, other mechanisms have also been postulated to account for the appearance of the vinylene cation. Slovokhotova *et al.* [55] ascribed these species to trapping of positive charges by the already present t-vinylene groups.

The ionic mechanism would offer a tenable interpretation for the non-uniform generation of radicals (e.g. in the doped crystals of deuteroparaffins or in cases listed in Section 2.3) via the migration of positive holes. However the ionic mechanism has been rejected by Gillbro and Lund [43] on the grounds that the admixture of an olefin, with a lower ionization potential, did not suppress the energy migration in n-alkanes by means of hole trapping.

Although in favour of the hydrogen trapping mechanism in pure alkanes, Toriyama, *et al.* [46] consider the ionic process to occur in alkanes with added electron scavengers, such as alkyl bromides. They conclude that the contribution from the ion–molecule reaction (Equation 4), and of the corresponding positive hole migration, depends upon the relative ease of the electrons returning to the primary cations.

It should be mentioned that most studies on crystalline alkanes have been performed at low temperatures and that little is known about rapid processes taking place around ambient temperature. A thermoluminescence study on PE by Meggitt and Charlesby [56] produced evidence in favour of positive hole migration, activated by various relaxations in the amorphous and in the crystalline phase. Remarkably efficient energy migration over distances of the order of micrometres has recently been postulated [57] in the long-chain n-alkane crystals at or above room temperature. This energy transfer was invoked in order to explain the finding that cross-linking occurs only in selected disordered areas widely separated from each other (see Section 5.2 and Fig. 8). The nature of the active species is as yet unknown.

2.2. Types of radicals

In PE, three types of radicals have been detected upon irradiation *in vacuo*: those giving rise to a sextet ESR spectrum were found to be secondary alkyl radicals [58–61]

$$-CH_2\dot{C}HCH_2-,$$

the septet spectrum was ascribed to allyl radicals [61–63]

$$-\dot{C}H-CH{=}CH-$$

and, finally, the broad singlet spectrum observed only at high irradiation doses, was attributed to polyenyl radicals [60–64]

$$-\dot{C}H-(CH{=}CH)_n-.$$

At 77 K the radicals are almost exclusively alkyls [65]. They are regarded as the main precursors of cross-links (Section 3.1). Irradiating PE above 320 K gives measurable quantities only of allyls or polyenyl radicals. Between room temperature and 320 K both alkyl and allyl radicals are observed [62]. If a specimen is irradiated at 77 K and subsequently warmed to room temperature, the concentration of allyls increases while the concentration of alkyls is greatly reduced. This is because the allyls, which are stabilized by resonance, are formed from alkyls [62, 63, 65, 66]. Fig. 1 shows the quantitative relation between the two types of radical as a function of temperature.

The *G*-values reported for alkyl radical formation at 77 K are listed in Table I. The most

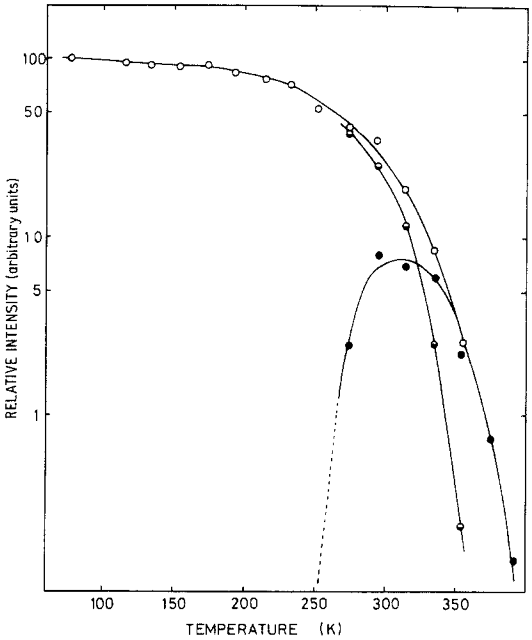


Figure 1 ESR signal intensity arising from alkyl and allyl radicals in irradiated linear PE. ○ total radical, ◒ alkyl, ● allyl. (Reprinted from [66] by courtesy of Marcel Dekker, Inc.)

TABLE I G(alkyl) values

Material	Temperature of measurement (K)	G(alkyl) value	Reference number
Linear PE			
Bulk	77	2.3–3.3	[63, 67]
Single crystals (SC)	77	4.5	[68]
Bulk and SC	77	2.3	[69, 70]
Bulk quenched	77	3.59	[71]
Bulk annealed	77	2.96	[71]
Extended chain	77	2.86	[71]
Branched PE			
Bulk	77	2.5	[63]
n-alkanes			
$C_{10}H_{22}$ and $C_{10}D_{22}$	77	3.1 (± 0.5)	[47]
$C_{10}H_{22}$ and $C_{10}D_{22}$	4.2	4.8 (± 0.5)	[47]
$C_{10}H_{22}$	77	5.4	[43]
$C_{16}H_{34}$	77	5.4	[43]
$C_{16}H_{34}$	77	3.6	[35]
$C_{34}H_{70}$	77	1.8	[63]
$C_{36}H_{74}$	77	1.3	[63]

recent values are those of Gvozdić and Dole [71] who paid particular attention to investigating and reducing the various possible sources of error in G(alkyl) determination. It is possible that certain outstandingly low G-values reported in the literature arose because the specimens were too thin and the appropriate correction for the reduction in absorbed dose was not applied [8, 72].

In irradiated crystalline n-alkanes two types of alkyl radicals have been identified by Gillbro and Lund [43] at low temperatures: the penultimate radical

$$RCH_2\dot{C}HCH_3$$

and the interior radical

$$R'CH_2\dot{C}HCH_2R,$$

where R and R′ are n-alkyl groups. No terminal n-alkyl radical

$$RCH_2\dot{C}H_2$$

has been observed. The yield of penultimate radical was higher than that calculated to result from random C–H bond scission, but this excess could well be accounted for by the isomerization reaction terminal radical → penultimate radical. At the same time the yield ratio of penultimate, interior and terminal radicals in an irradiated liquid alkane, n-hexane, was consistent with random C–H scission, without isomerization taking place.

In contrast to the above is the report by Kimura *et al.* [73] that the radicals in solid n-alkanes are mainly of the interior type with very few penultimate ones. Chappas and Silverman [74] recently claimed to have resolved the controversy in favour of the latter report. Preferential formation of the interior radicals rather than random C–H scission is attributed by Silverman to the ionic mechanism of radical production.

2.3. Spatial distribution of radical formation

2.3.1. Radical pairs

Measurements of the ESR line-width and of the microwave power saturation behaviour have revealed that radical pairs and clusters are formed during irradiation at low temperatures [43, 75–78]. Gillbro and Lund [43] estimated that two per cent of all radicals form in close pairs in n-alkanes at 77 K, whereas at 4 K as many as 40 to 50% are paired. (Iwasaki *et al.* [48] noted the disappearance of closest pairs, 1,3-biradicals, as soon as 35 K, following irradiation at 4 K.) Annealing at higher temperatures caused the decay of more distant pairs. Warming to 77 K produced a drop in local radical concentration within the spur by a factor of about 2.3 in PE, while the total number of radicals decreased by only 20% [79]. Thus it was concluded that about a third of the radicals within a spur recombine, while the rest escape from it when the temperature is increased to 77 K.

It is notable that the concentration of paired radicals in n-decane irradiated at 4 K and subsequently annealed at 77 K remained much higher than in samples irradiated at 77 K [48]. This and other observations led Iwasaki and co-workers [46, 48] to propose that a cage-effect on liberated H-atoms primarily governs the production of radical pairs. Following C–H bond scission the thermal H-atom remains trapped in the vicinity of the parent alkyl radical at 4 K, but travels a longer distance at 77 K. Even at such low temperatures it is still capable of further hydrogen abstraction by quantum tunnelling, thus producing a second alkyl radical. This scheme explains the large fraction of paired radicals at 4 K, and the predominance of isolated radicals upon irradiation at 77 K. Alternative exciton [43] and ionic mechanisms [53] have also been proposed to explain the production of radical pairs (see Section 2.1).

2.3.2. Radical distribution between phases in PE

As will be seen in Section 4.1, cross-links in irradiated PE form preferentially in the amorphous phase or in the fold surface, and to a much lesser extent in the crystal interior. An obvious question to ask is whether this selectivity originates from a preferential formation of radicals in the non-crystalline phase, or whether radicals, formed at random, combine more readily in this phase of higher mobility. The latter possibility implies radical migration to the crystal surface. This section and Sections 2.4 and 2.5 briefly survey the relevant ESR results.

Most older ESR studies [63, 67, 80, 81] concluded that radicals form uniformly throughout the crystalline and non-crystalline regions. However, two subsequent works on single crystals [82, 83] attempted to distinguish between the spectral contributions from the radicals in the interior and at the surface of the crystals. HNO_3-treated samples with the fold surface removed also featured in these studies. The conclusion of both the latter works was that at 77 K alkyl radicals remain trapped preferentially in the fold surface of PE single crystals.

Gvozdić and Dole [71] measured the alkyl radical yield at 77 K in highly crystalline extended-chain PE (ECPE) as well as in remelted and quenched samples of the same material, having a much lower crystallinity. The *G*(radical) values were 2.86 and 3.59, respectively, (see Table I), a small difference considering that the respective "amorphous" fractions in the two samples were 3% and 32%. The authors attribute the lower radical yield in the crystalline material to the cage recombination of H-atoms with their parent alkyl radicals.

In conclusion, there appears to be a slight preference for radical formation in the non-crystalline phase of PE, but this seems insufficient to account for the large difference between the cross-linking yields in the crystalline and amorphous phases (compare with Section 4.1).

2.4. Radical decay in PE: effect of crystallinity

Studies of alkyl radical decay have mainly been conducted after irradiation at 77 K. Subsequently, the decay of the ESR signal was recorded at a higher, usually room, temperature. Unfortunately the large majority of alkyl radicals would have already decayed by the time room temperature is reached [63, 66, 84] so that the available information on decay kinetics relies only on the surviving few per cent of the initial radical population. Mainly those works in which the decay kinetics were related to the polymer morphology will be reviewed below.

As early as the late fifties Lawton *et al.* [85] and Koritskii *et al.* [62] noted that the radicals decay considerably more quickly in branched PE than in linear PE. Comparing different types of PE, Charlesby *et al.* [63] also found that alkyl radical decay at 293 K was accelerated by the increasing degree of branching, i.e. by decreasing crystallinity. Allyl decay, on the contrary, was not affected.

Ormerod [81] studied the alkyl decay in single crystals of different fold periods. The decay rate was found to decrease markedly with increasing crystal thickness. This was consistent with the concept that the radicals produced within the crystals must diffuse to the fold surface to react [69, 86]. Nara *et al.* [84] and Fujumura *et al.* [66] have studied the temperature dependence of radical decay rate following irradiation at 77 K. A stepped curve was obtained. The step at around 120 K corresponds to the decay of radical pairs and the steps at around 200 K and above 250 K correspond to the appropriate relaxation in the amorphous and in the crystalline phase, respectively. Similar stepped decay against temperature curves were also observed with short n-alkanes, the steps being associated with different polymorphic transitions [87].

Kusumoto *et al.* [82] investigated alkyl decay at room temperature in single crystals of PE. The decay process was resolved into two components: fast and slow decay. The slow decay was attributed to reactions of isolated radicals within the crystals and its rate decreased with increasing crystal thickness. The fast decay was independent of crystal thickness and was thought to take place at the fold surface and at crystal defects. The effect of thickness on the slow process was explained in terms of the α-relaxation, the temperature of which increases with increasing crystal thickness. Thus the chain mobility in crystals was considered important and no radical migration to the crystal surface was invoked.

In the work of Dole and collaborators [67, 68, 88] the alkyl decay at room temperature was also resolved into a fast and a slow component. It was concluded that practically all decay takes place in the non-crystalline phase. The fast decaying radicals were those which were already in the amorphous phase at the beginning of the experiment, while the slow radicals had to diffuse from the crystal interior to the surface to react. The marked catalytic action of evolved hydrogen on radical decay was fully recognized. Although the effect of molecular hydrogen had been clearly established long before [89], in most subsequent studies it was not taken into account. The effect of hydrogen will be discussed further in Section 2.5.

Patel and Dole [88] confirmed that the slow decay constant, k_s, diminishes as the single crystals become thicker. The effect was particularly pronounced at higher temperatures. For example, a relatively small increase in fold period, from 11 to 15 nm, reduced k_s by half at 333 K. Like Kusumoto *et al.* [82] these authors adopted the view that activation of the α-process greatly increases radical mobility within the crystals. Contrary to Kusumoto, however, they proposed that the primary effect of increased mobility is a faster diffusion of radicals towards the crystal surface, rather than an enhanced cross-linking in the crystal interior.

This latter conclusion is further vindicated by the recent finding [90] that changing the crystal thickness by 4 nm, as in the experiment of Patel and Dole [88], has an almost negligible effect on the extent of damage to the crystal lattice (see Section 5.1 and Fig. 6). Moreover, the present author [90] also found that raising the irradiation temperature from 313 to 358 K, i.e., into the range of the α-transition, increased the efficiency of radiation-induced lattice damage by only about 50%. This result should be compared with the finding of Dole that a change from 313 to only 333 K already causes a five-fold increase in the slow radical decay rate in 14 nm thick crystals [88].

In conclusion, all the evidence points to radical mobility being higher in the non-crystalline phase than in the crystalline phase. In addition, most authors agree that the radicals decay mainly at the crystal surface. This gives further support to the concept first proposed by Salovey and Keller [86] that radicals migrate to the fold surface to form cross-links (see also Section 4.1).

2.5. Mechanism of radical migration

It is clear that the observed mobility of the alkyl radical site cannot be accounted for only by simple molecular diffusion, particularly not in the crystalline phase. The observed decay of certain close radical pairs at temperatures as low as 35 K [48] best illustrates this point.

It was proposed very early on [91] that the radical site in PE migrates via a series of hydrogen abstraction reactions, either intra- or intermolecularly:

$$-CH_2-\dot{C}H-CH_2- \rightarrow -\dot{C}H-CH_2-CH_2- \quad (7)$$

and

$$\begin{array}{ccc} -CH_2-\dot{C}H-CH_2- & & -CH_2-CH_2-CH_2- \\ & \rightarrow & \\ -CH_2-CH_2-CH_2- & & -CH_2-\dot{C}H-CH_2-. \end{array} \quad (8)$$

Dole and Cracco [92] suggested that molecular hydrogen may be accelerating the radical migration. Ormerod [89] obtained conclusive evidence for this hypothesis by showing the second-order decay constant, k (in g radicals^{-1} sec^{-1}), to be a linear function of H_2-pressure and to obey the relation:

$$k \times 10^{-23} = 1.1p + 0.2, \quad (9)$$

where p is the H_2 pressure (in mm Hg). The pressure of hydrogen, which builds up during irradiation of PE in a closed container, often reaches substantial pressures if large doses are applied. The entire radical decay may then involve interaction with hydrogen. However, the cross-linking efficiency, as measured by the solubility of irradiated polymer, is not affected by the presence of hydrogen gas (see also [12]).

Ormerod [89] suggested that radical transfer occurs via a three-body complex:

$$\dot{R} + H_2 + RH \rightarrow (\dot{R} \ldots H\text{—}H \ldots HR) \rightarrow RH + H_2 + \dot{R}. \quad (10)$$

The alternative mechanism would be a two-step process involving free H-atoms:

$$\dot{R} + H_aH_b \rightarrow RH_a + \dot{H}_b; \quad (11)$$

$$\dot{H}_b + RH_c \rightarrow H_bH_c + \dot{R}. \quad (12)$$

The latter mechanism was considered unsatisfactory because if free H-atoms were present, the combination with alkyl radicals

$$\dot{H}_b + \dot{R} \rightarrow H_bR \quad (13)$$

would often take place in preference to the combination reaction

$$\dot{R} + \dot{R} \rightarrow RR. \quad (14)$$

This would then manifest itself as both a reduction in gas pressure above the PE sample, and a reduction in cross-linking, when hydrogen gas is introduced into the irradiation ampule. However, neither of these two changes were observed [92].

According to Equation 9 radical decay still takes place even at zero hydrogen pressure. This was considered by Ormerod [89] to occur by the rather slow H-abstraction mechanism (Reaction 7 or 8).

The catalytic effect of hydrogen even now remains unclear; Patel and Dole [88] claimed H_2 gas to be completely insoluble in freeze-dried PE single crystals, and yet it still had a pronounced effect on both fast and slow alkyl decay (see Section 2.4). The authors suggested that the radicals are being transferred through the crystal by the non-catalysed H-abstraction process. Consequently, the catalysis of the slow decay is being effected merely by increasing the radical concentration gradient at the crystalline–amorphous interface.

The experimental evidence for radical migration in crystalline n-alkanes is listed next. Disappearance of radicals from spurs by mutual combination or by escape from spurs at low temperatures has already been mentioned in Section 2.3.1. Iwasaki *et al.* [48] reported a pronounced process of radical isolation during three hours of annealing crystalline n-$C_{10}D_{22}$ at 200 K. The total number of radicals decreased by 40%, which was attributed to recombination of distant pairs. In a long-chain olefin, n-$C_{35}H_{70}$, Charlesby *et al.* [63] could detect the conversion of some alkyl radicals into allyls even at 195 K, following irradiation at 77 K. In the same study the decay rate in saturated n-$C_{34}H_{70}$ and n-$C_{36}H_{72}$ at room temperature was found to be less than the overall decay rate in PE. However, so far it has not been investigated how the decay rate in crystalline alkanes compares with the slow decay in the crystalline phase, of PE. A study of the effect of hydrogen on the decay in alkane crystals has not been reported either.

The question of whether the migration of alkyl radical sites is intra- or intermolecular (Reactions 7 or 8) is still a matter of controversy. Waterman and Dole [65] calculated that intermolecular migration is more likely in the crystalline phase of PE. Seguchi and Tamura [93] also favoured intermolecular transfer when correlating radical decay rate with crystal size. Subsequently Shimada *et al.* [94] claimed to have produced more direct evidence in favour of this conclusion. They followed alkyl radical decay both in single crystals of PE and in the PE-urea complex in which PE chains are kept isolated in separate urea channels. The decay in the urea complex was very slow and even at 380 K it was still barely occurring. However, the validity of Shimada's evidence has been questioned [74] on the grounds that there must be at least two radicals in a chain for intramolecular termination to become at all possible. This would require higher radiation doses than the 1.1 Mrad employed by Shimada *et al.*

Hama *et al.* [95] made experiments with a series of irradiated n-alkane diols, $HO(CH_2)_nOH$, where $n = 6$ to 12. Thermal annealing led to conversion of secondary alkyl radicals into end radicals $\text{—}CH_2\dot{C}HOH$, and exposure to ultra-violet light reversed this process. At the same time the total number of radicals did not decrease, i.e., no recombination occurred. From the latter observation and from some other evidence the authors concluded that migration occurred along the chains rather than intermolecularly. However, it should be mentioned that the dose used in their study was only 0.4 Mrad, which gives, e.g. in octane diol, one radical in about 5000 molecules if G(radical) is taken as 4 (see Table I). Hence, the fact that little or no combination occurred during the interior-to-end radical conversion cannot be taken as an unambiguous proof of intramolecular migration taking place. In conclusion, the question of inter- or intramolecular radical migration still lacks a definite answer.

3. Permanent chemical changes

The exposure of PE and long-chain alkanes to high-energy radiation *in vacuo* results in the following chemical changes: cross-linking, main-chain scission, evolution of hydrogen and formation of main-chain unsaturation, i.e. trans-vinylene (—CH=CH—), diene (—CH=CH—CH=CH—) and polyene groups. Where vinyl (—CH=CH_2) groups are already present, as in commercial linear PE, they become rapidly destroyed on irradiation. In spite of extensive research the mechanisms of some of these reactions remain unclarified. A survey of the main effects will be given here, as well as some current views concerning the reaction mechanisms.

3.1. Cross-linking

It is generally accepted that cross-linking occurs mainly by recombination of two free radicals. The *G*-value for cross-linking in PE is initially about 1 [96, 97] but increases with dose [97]. *G*(cross-link) values for long-chain n-alkanes are listed in Table II. These results will be considered more closely in Section 4.2.

A direct proof that cross-linking is a radical reaction was obtained for polypropylene [102] where the reaction is very slow. Thus, by admitting a radical scavenger (methyl mercaptane) into polypropylene at room temperature immediately after irradiation at 77 K it was possible to completely prevent cross-linking. The use of radical scavengers in long-chain n-alkanes was only partly successful. Salovey and Falconer [98] irradiated n-heptadecane in the presence of iodine. 80% and 35% of cross-linking was suppressed by the scavenger in the molten and crystalline alkane, respectively. In crystalline short-chain n-alkanes from butane to octane, between 30%

TABLE II *G*(cross-link) values in long-chain n-alkanes

n-alkane	State of aggregation (crystalline subcell)	Irradiation dose (Mrad)	Measurement method	*G*	Reference number
$C_{16}H_{34}$	crystalline (triclinic)	4	GC	1.6*	[50]
	liquid	4	GC	1.7*	[50]
$C_{17}H_{36}$	crystalline (orthorhombic)	4	GC	1.13*	[98]
	liquid	4	GC	1.63*	[98]
$C_{20}H_{42}$	crystalline (triclinic)	4–50	GC	0.9*	[99]
			GPC	1.0*	[99]
	liquid	4–20	GC	1.5*	[99]
			GPC	~1.5*	[99]
$C_{22}H_{46}$	crystalline (triclinic)	150–800	GPC	0.7†	[100]
	liquid	300	GPC	2.0†	[100]
$C_{23}H_{48}$	crystalline (orthorhombic)	150–800	GPC	0.7†	[100]
	liquid	300	GPC	1.3†	[100]
$C_{35}H_{72}$	crystalline (orthorhombic)	0 (extrapolated)	GPC	1.4*	[101]
	liquid	0 (extrapolated)	GPC	1.8*	[101]
$C_{36}H_{74}$	crystalline (orthorhombic)	0 (extrapolated)	GPC	1.1*	[101]
	crystalline (orthorhombic)	4–50	GPC	~0.8	[99]
$C_{40}H_{82}$	crystalline (orthorhombic)	219	GPC	0.95†	[100]

**G*(dimer)

†*G*(link), calculated from the weight ratio, W_1 = (monomer)/(monomer + dimer + trimer + . . .) and applying Flory's relation [105] $W_1 = \exp(-2q)$, from which q, the average number of cross-links per initial molecule, is obtained.

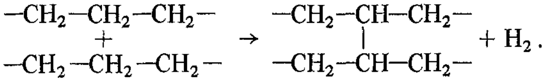
and 50% of dimerization was found to occur immediately, possibly by a non-radical mechanism, at temperatures below 140 K [39, 103]. This has been deduced from experiments where the irradiated crystals were dissolved in a radical scavenger at temperatures sufficiently low to prevent any combination of trapped radicals before dissolution was completed. The dissolved dimers, detected by gas chromatography, were attributed to the "immediate" cross-linking process taking place during irradiation. On the other hand, dimer formation in liquid paraffins is thought to occur entirely through bimolecular radical termination [104].

The most widely used method for quantitative determination of cross-links in polymers is to measure the dose required for incipient formation of insoluble gel ("gel point") and, at higher doses, to determine the gel and sol fractions. This method, based on statistical considerations, was developed successively by Flory [105, 106], Stockmayer [107, 108], Charlesby [3, 109–111], Saito [112–114] and Inokuti [115, 116]. According to this approach an infinite polymer network can form as soon as there is one cross-linked unit per weight average molecule. The theory [115–117] also makes provision for chain scission if this occurs simultaneously with cross-linking.

Since a more direct method for cross-link determination in polymers is lacking, solubility measurement so far remains the most accurate technique, in spite of its obvious draw-backs. One such drawback is the fact that the statistical treatments mentioned above assume random cross-linking, i.e. that each chain segment has an equal probability of linking. However, as will be pointed out in Section 4.1, preferential cross-linking can take place in the amorphous phase of semicrystalline polymers. Also, the method neglects intramolecular cross-links, although their numbers can be very high in certain polymer configurations, e.g. in single crystals [10, 69, 86]. Furthermore, in its original derivation [105–108] the theory assumes that no rings can form, i.e. that any two chains can be cross-linked to each other at only one point. At present, alternative approaches to the gelation problem are being sought which make use of the percolation statistics previously developed for magnetic phase transitions [118–120].

Cross-links can be determined by other methods not based on solubility or molecular weight measurement. They involve determination of equilibrium swelling, or measurement of the elastic modulus of the molten network [121]. Recently the pulsed nuclear spin-resonance technique was applied to assess the number of cross-links in molten networks [122]. At present, however, there is no satisfactory method for direct determination of the absolute number of cross-links, irrespective of their distribution. A promising technique is measuring the number of tertiary C-atoms by ^{13}C nuclear magnetic resonance (NMR). The NMR band expected for cross-links in PE has been established [123, 124] from a specially-synthesized "H-shaped" model compound. At the moment there are still experimental problems associated with applying this technique to PE due to the low mobility in the cross-linked polymer [125].

Stoichiometrically, the formation of a cross-link is accompanied by the evolution of one H_2 molecule:



$$\begin{array}{c} -CH_2-CH_2-CH_2- \\ + \\ -CH_2-CH_2-CH_2- \end{array} \rightarrow \begin{array}{c} -CH_2-CH-CH_2- \\ | \\ -CH_2-CH-CH_2- \end{array} + H_2. \qquad (15)$$

More hydrogen is produced by double-bond formation. It has been argued on several occasions whether or not the following material balance is valid for PE:

$$G(H_2) = G(X) + G(\text{t-vinylene}) + 2G(\text{diene}), \qquad (16)$$

where $G(X)$, G(t-vinylene) and G(diene) are the G-values for the formation of cross-links, t-vinylene groups and diene groups, respectively. Good agreement has been reported by Kang *et al.* [97] after extrapolating the G values to zero dose. However, the accord could have been fortuitous, as argued by Mandelkern [11]. At 308 K the G-values determined by Kang *et al.* were: $G(X) + G(\text{t-vinylene}) + 2G(\text{diene}) = 1.0 + 2.4 + 0.5 = 3.9$, while $G(H_2)$ was 3.7.

The effect of crystallinity and crystal structure on cross-linking will be surveyed in Sections 4.1 (for PE) and 4.2 (for paraffins).

3.2. Unsaturation

The dose dependence of the trans-vinylene $\left({}^{R}_{H}\!\!>C=C<\!\!{}^{H}_{R}\right)$ concentration in PE was described by Dole *et al.* [126] as agreeing with zero-order formation accompanied by first-order decay. The rate of vinylene formation is almost independent of temperature down to 77 K [85, 96]. The mechanism and the products of decay have not yet been fully clarified. However, efficient energy transfer is obviously required for its activation. From the vinylene concentration and the decay rate Partridge [41] estimated that vinylene elimination is approximately 700 times faster than the rate of activation calculated on the assumption of no energy transfer. The decay was considered by Partridge to result from migratory C–C bond excitons. Alternatively, it was suggested [127, 128] that t-vinylene groups decay in a direct reaction with molecular hydrogen:

$$CH{=}CH + H_2 \rightarrow CH_2{-}CH_2 . \qquad (17)$$

Supporting evidence for Reaction 17 was the finding [128] that hydrogen, like t-vinylene, also complies with combined zero-order formation and first-order decay kinetics, with a constant ratio $[H_2]/[\text{t-vinylene}]$ for a given temperature. However, a large discrepancy remains between the high activation energy of Reaction 17 and the observed zero activation energy of t-vinylene decay. Detailed studies of olefin groups in irradiated PE were also performed by Slovokhotova and collaborators [55] who found evidence from infrared spectroscopy studies for ionic reactions of the t-vinylene groups.

Proposed mechanisms for t-vinylene formation include a path *via* either a methylene diradical [41] or a path which starts from an intramolecular pair of radicals separated by three CH_2 groups.

By comparing the vinylene yields in PE single-crystals of different fold periods, as well as the yield in a pure crystal core with fold surfaces etched away, Patel [129] concluded that vinylene groups form preferentially within the crystal core. The same also applies to conjugated diene groups.

The decay of terminal vinyl groups ($R{-}CH{=}CH_2$), which are present in most linear polyethylenes, is described as being of second order [130, 131] or first order [132, 133]. The reaction is highly dependent on temperature. It seems to require diffusion of vinyl chain ends. Its rapid occurrence at room temperature is readily explained by the finding of Keller and Priest [134] that about 90% of vinyl groups in PE single-crystals are located at the fold surface, and thus are highly mobile. The vinyl decay was found to occur faster in molten PE than in solid PE [130, 135]. On the other hand, room-temperature irradiation of two samples with different degrees of crystallinity, 0.69 and 0.82, respectively, gave identical vinyl decay rates [133]. It should be added that in this last experiment the extents of vinyl decay were only the same provided that the free radicals in the more crystalline sample had been annealed-out prior to exposure to air. Otherwise this sample showed less vinyl decay. Incidently, the importance of completing the reactions of trapped radicals appears to support the view [135] that vinyl groups decay by reacting with free radicals. Section 4.1 will briefly consider the contentious relationship between vinyl decay and cross-linking.

3.3. Chain scission

The chain scission yield in PE is again a controversial issue. The well-known Charlesby–Pinner relation [117] has been used most often to determine simultaneously the extents of scission and cross-linking. Quite an appreciable degree of chain rupture *in vacuo* has been postulated in the past to explain the unattainability of 100% gel in PE even at high irradiation doses. Subsequent works give less importance to scission. Kang *et al.* [97] quote G(scission) as 0.19 and 0.26 at 308 K and 393 K, respectively. Budzol and Dole [130] report values between 0.2 and 0.4 in the melt at 428 K. Patel [136] reported formation of 100% gel with an irradiation dose of about 250 Mrad, when using partly fractionated PE. The low molecular weight portion, which takes longest to gel, was removed prior to irradiation. According to Mandelkern [11], who irradiated a number of different molecular-weight fractions at 406 K, the dose dependence of sol fraction does not indicate any scission, irrespective of whether irradiation is performed in the crystalline state or in the liquid state.

The main problem with determining the scission yield in PE lies in the difficulty of separating its small effect on molecular weight from the overwhelming effect of cross-linking. A promising, but so far only preliminary, experiment has been reported by Sugimoto *et al.* [137]. By irradiating the urea–PE complex, in which polymer chains were kept isolated from each other, these authors succeeded in completely preventing cross-linking. As a result a slight decrease in molecular weight occurred upon irradiation, which was attributed to chain scission. However, the authors suspected that in this preliminary experiment some oxidative degradation might have taken place. Further developments of this work may be expected in the future.

TABLE III G(C–C scission) values in long-chain n-alkanes

n-alkane	State of aggregation	Irradiation temperature (K)	Irradiation dose (Mrad)	G	Reference number
$C_{16}H_{34}$	crystalline	277	4	0.25	[50]
	liquid	292	4	0.50	[50]
$C_{17}H_{36}$	crystalline	277	4	0.25	[98]
	liquid	297	4	0.52	[98]
$C_{23}H_{48}$	crystalline	274	75	0.27	[139]
	crystalline	274	200	0.24	[139]
$C_{32}H_{66}$	crystalline	306.5	200	0.28	[139]

Chain scission yields in paraffins are usually determined from fragment analysis using gas chromatography. In short alkanes, such as n-heptane, G(scission) was reported as being 1.20 [35] and 0.88 [104] in the liquid, and 0.66 [35] in the solid state. However, with increasing chain length the G-value decreases [138] and appears to reach a fairly steady value of around 0.25 for solid-state radiolysis, see Table III [50, 98, 139]. This G-value links up reasonably well with the G-values mentioned above of 0.19 and 0.26 for PE, reported by Kang *et al.* [97].

In addition to cross-linking and chain scission, irradiation of normal alkanes in the liquid state produces branched molecules. These contain between n and $2n$ carbon atoms, where n is the carbon number in the original molecule [35, 50, 104]. Branching is produced by combination of a shorter scission radical with a parent, n carbon atom, radical. Only a few branched molecules are produced in the solid state. This is the result of efficient cage recombination of radicals produced by the C–C bond scission. The cage effect also accounts for the lower G(scission) values in the solid state, compared with those measured in the liquid state [50, 107, 108].

4. Effect of crystallinity and molecular arrangement on cross-linking

4.1. Polyethylene

Already in 1958 it had been proposed by Lawton *et al.* [85] that cross-linking in irradiated PE takes place preferentially in the amorphous phase. Salovey and Keller [86] reported the surprising observation that the gel dose for solution-grown single crystals was ten times higher than that for bulk material. These early findings clearly showed the importance of physical state on network formation.

Salovey and Keller [86] also found that the gelation behaviour of single crystals is strongly dependent on interlamellar contact: the better the contact the more gel is formed for a given radiation dose. The idea was put forward that there is no major difference in the overall number of cross-links but that the majority of cross-links formed in loose crystals are intramolecular, and hence ineffective in network formation. It was also concluded that the links form mainly within folds at crystal surfaces, thus producing small carbon rings within the chains. Intermolecular links, effective in gel formation, are mainly formed between adjacent lamellae and can thus arise only if the crystals are in close enough contact. These ideas were confirmed and extended by both above authors and their co-workers [69, 70, 140–142]. See also the review by Salovey [10].

Further and more direct evidence for the above suggestions came from the work of Patel and Keller [143]. Single crystals were used, the fold surfaces of which had been removed by ozonization. Thus, isolated chain segments were left with a carboxylic group at each end. After the dicarboxylic acid crystals had been irradiated, the products were analysed by gel permeation chromatography (GPC). Cross-linking products, i.e., dimer, trimer and other soluble oligomers of the original dicarboxylic acid, were detected as more or less discrete peaks in the GPC spectra. The spectra showed that the G-value for cross-linking in the crystal core is much lower (0.25) than in the whole polymer, or, for that matter, in crystalline n-alkanes. (In n-$C_{40}H_{82}$ irradiated under identical conditions G(cross-link) = 0.95, see [100].) Moreover, the yield of cross-linked material was found to be independent of the original dicarboxylic acid length. The interpretation of these results was that cross-linking takes place almost entirely at the crystal surface, thus confirming the previous conclusions.

In another experiment [144] ozonization was carried out after the folded-chain crystals were irradiated with doses of up to 400 Mrad. Complete degradation to uncross-linked dicarboxylic acid was achieved. Since only the lamellar surface was accessible to ozone it must have contained the cross-links. The scarcity of cross-links inside the crystal lattice was attributed to carbon atoms on adjacent chains being too far apart (0.41 nm at least) for interchain C–C bonds (0.154 nm) to form (see also Fig. 5).

Using an elastic continuum model, Guiu and Shadrake [145] have calculated the strain energy of a cross-link within the crystal lattice as being 2.45×10^{-19} J. Ungar [100] has correlated this value with the experimental decrease in enthalpy of fusion, ΔH_f, in irradiated PE and obtained a G(cross-link) value of 0.6 in the crystalline phase. This G-value would represent only the upper limit since the decrease in ΔH_f is caused not only by the increase in lattice enthalpy, but also by a decrease in entropy of melt due to cross-linking [30]. However, even this overestimate is substantially lower than the overal G-value of 1.5 reported for PE at moderate irradiation doses [97].

In melt-crystallized bulk PE the gelation behaviour was found to depend greatly on the mode of crystallization: in quenched samples gelation efficiency was higher than in slowly-cooled material of higher crystallinity [17, 31, 135, 146, 147]. This finding again gave support to the early suggestion by Lawton *et al.* [85] that cross-linking takes place preferentially in the amorphous phase. Recently, Dole and Gvozdić [148, 149] compared gel formation in a sample of extended-chain PE (ECPE) (of crystallinity 0.93) with that in a sample of the same material that had been remelted and quenched (of crystallinity 0.68). About twice as high an irradiation dose was needed to form gel in the ECPE sample. For comparison, the amount of free radicals produced in ECPE was only 20% lower than that in the quenched sample [71] (compare with Section 2.3.2).

The intriguing question remains as to whether the differences in gel formation arise from differences in the total number of cross-links, or merely from different cross-link distributions. In the case of single crystals there is considerable evidence, including the effect of interlamellar contact, which favours the latter idea; the concept of "effective" intermolecular cross-links and "ineffective" intramolecular cross-links is well documented. In the case of bulk PE the situation is less certain, particularly with regard to ECPE. In moving from a less-crystalline quenched material, to a more crystalline material one would have to fit an increasing number of cross-links into a decreasing amorphous phase in order to keep the total number of cross-links constant. Arriving at ECPE where there is practically no amorphous phase an increased cross-link concentration within the crystal lattice would have to be assumed if all the radiation-produced radicals were to be used up in cross-linking (the slightly lower radical yield in ECPE, see above, is in this case only of secondary importance). The actual observation is, however, just the opposite, i.e., for a given dose the least damage to the crystal lattice is produced in ECPE (see Section 5.1 and Fig. 6). Therefore it appears that the total number of cross-links does depend to a certain extent on the degree of crystallinity. There is reason to believe that in highly-crystalline PE some free radicals may be lost in reactions other than cross-linking.

Other experiments of relevance to this section include the work of Budzol and Dole [130]. These authors recorded an increase in cross-linking efficiency in molten PE. G(cross-link) was found to be between 1.4 and 1.6 in the melt at 428 K. The solid-state value extrapolated to the same temperature was only 1.18.

In contrast to these latter findings are the publications by Mandelkern and co-workers (see review by Mandelkern [11]). Amongst other findings they report that the transition from the solid to the liquid state causes a sharp decrease in cross-linking efficiency. The interpretation given is in terms of a promotive effect of vinyl groups on the reaction of cross-linking. Since the vinyl end-groups are diluted in the melt, but are concentrated in the non-crystalline phase in the solid polymer [134], their interaction would be enhanced in the solid state. However, repeating these type of experiments, Dole and co-workers obtained results which contradict those of Mandelkern (see the recent review by Dole [12]).

Finally, the effect of crystallinity on radiation cross-linking should not be taken as a specific feature of PE. Patel [150] reported an even more pronounced crystallinity effect in a polydiacetylene which could be prepared both in fully-crystalline and in fully-amorphous forms. The gelation irradiation dose was 50 Mrad for the former, and only 3 Mrad for the latter.

4.2 Alkanes

First, it is perhaps profitable to briefly consider alkane crystallography. Crystals of long-chain n-alkanes are built up of stacked layers of straight-chain molecules. The chains are either perpendicular or tilted with respect to the layer plane. In contrast with single crystals of PE, pure alkanes. Crystalline-alkanes exist in a number There is no disordered phase in pure un-irradiated alkanes. Crystalline-alkanes exist in a number of polymorphic forms which are reviewed in [151–153]. For the present purposes it will suffice to mention that there are three basically different modes of packing of neighbouring methylene groups in the so-called sub-cells. (a) The orthorhombic sub-cell is the most common and is identical to that in PE; the planes of the zig-zag carbon backbones are nearly perpendicular to each other in the nearest-neighbour molecules. (b) In alkanes with the triclinic sub-cell the zig-zag planes of all molecules are parallel. (c) In n-alkanes shorter than $C_{40}H_{82}$ the so-called "rotator" phase exists in an interval of a few degrees below the melting point; its sub-cell is often, but not always, hexagonal [153, 154] and the molecules exhibit extensive rotational and translational motion.

A considerable amount of information on the radiation behaviour of short alkanes, including the effects of temperature and state of aggregation, can be found in the monograph by Topchiev [35]. The longer chain alkanes have been investigated in greatest detail by Salovey and his co-workers [10, 50, 98, 99, 101]. Amongst other techniques, these authors employed gas chromatography for the quantitative analysis of radiolytic products of n-$C_{16}H_{34}$ and n-$C_{17}H_{36}$. The G-values for formation of the respective dimers, C_{32} and C_{34}, are listed in Table II together with the corresponding values for other long alkanes reported so far. Since alkane C_{40} seems to be the upper limit of applicability of gas chromatography, n-$C_{20}H_{42}$ was the longest alkane whose cross-linking products were studied by this method [99]. For longer alkanes gel permeation chromatography (GPC) has been used [99, 101, 120, 155]. The GPC method has the additional advantage in that it can measure high molecular weight products, i.e., trimers, tetramers etc.

The data given in Table II show that irradiation of the liquid produces a greater degree of cross-linking than does irradiation of the solid. Further, as far as G(cross-link) is concerned, for alkanes longer than about C_{20} it does not seem to matter whether the irradiated crystals are orthorhombic or triclinic. The same has been shown for PE, which also sometimes contains a triclinic fraction [156]. On the other hand, G(cross-link) becomes much higher if an alkane is irradiated in the "rotator" phase in which case it may even exceed the liquid-state value [32, 100]. As determined from the heat of fusion, the G-values for n-$C_{32}H_{48}$ irradiated at 274 K (orthorhombic-phase), 315 K ("rotator"-phase) and 326 K (liquid-phase) are in the ratio 1:2.5:1.75.

It should be mentioned that the latter finding is not the only example of the high reactivity of the "rotator" phase. Shibasaki and Fukuda [157] found recently that γ-ray induced polymerizability of a long-chain vinyl compound, octadecyl acrylate, increases substantially upon phase transition from the triclinic to the hexagonal "rotator" modification of the crystalline monomer. Similarly, large differences in radiolytic behaviour were found in 1-bromo-adamantane irradiated in both the ordered and the orientationally-disordered crystal modification [158].

At higher doses the term "solid-state irradiation" becomes inadequate for alkanes irradiated at or above ambient temperature. As shown recently [34, 57], at higher irradiation dose levels a cross-link-rich amorphous (liquid) phase forms alongside the existing crystalline phase which contains monomer only, see Section 5.2. Further cross-linking takes place primarily in the new liquid phase. One obvious consequence of this is an overall non-randomness of reaction statistics. Indeed, GPC analysis of irradiated $C_{40}H_{82}$ has shown [100, 120] that once a molecule is cross-linked its chance for further cross-linking increases much more than would be predicted from a purely random introduction of links [105, 106]. That is, for a given total fraction of cross-linked material the amount of trimer and higher oligomers is higher than expected, and the amount of dimer is lower than expected.

However, a deviation from random cross-linking statistics has also been found in certain alkanes when irradiated in the liquid state, i.e., above the melting point. A larger than expected amount of trimer etc. for a given dimer fraction was observed in $C_{22}H_{46}$ and $C_{23}H_{48}$ [100]. Furthermore, even at an irradiation dose as low as 50 Mrad, an inexplicably large trimer peak was found in the GPC spectrum of melt-irradiated $C_{36}H_{74}$; no such large trimer peak was seen for $C_{35}H_{72}$ [101]. These deviations from the theoretical distribution of cross-linked products deserve further investigation. This is needed especially in view of the obvious implications for cross-linking statistics in polymers where such rigorous tests of the theory are not possible.

5. Radiation damage to the crystal lattice and loss of crystallinity

5.1. Polyethylene

Although cross-linking occurs primarily outside the crystal core (see Section 4.1) at high radiation doses the lattice in PE becomes progressively distorted, crystallinity is reduced and finally, at doses between 3 and 4 Grad is destroyed completely [32, 159–162]. Fig. 2 shows the decrease in crystallinity in bulk PE as measured by X-ray diffraction. To reach doses as high as a couple of gigarads several months of ^{60}Co γ-irradiation are usually required, but electron beams, for example, such as are used in electron microscopes, are capable of delivering equal dosages within a few minutes [13]. It has been observed that lowering the temperature increases the radiation resistance of both PE [164] and alkane [165] crystals, but this increase in resistance is only 3-fold between room temperature and 18 K in the case of PE [164].

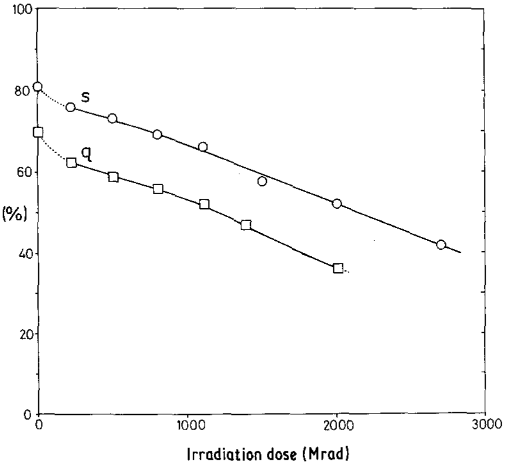


Figure 2 Decrease in X-ray crystallinity (method of Hermans and Weidinger [163] against radiation dose for slowly cooled (s) and quenched (q) bulk PE irradiated at 313 to 318 K [100].

The continuous amorphization accompanied by orientational disordering of molecular chains in PE crystals manifests itself in a thinning of the crystal lamellae and an increase in their area. This has been observed both by electron microscopy (EM) [166] and by measuring macroscopic dimensions of irradiated single-crystal mats [167].

It is generally believed [32, 160, 162, 168–170] that cross-links are by far the most severe radiation-induced defects in the crystal lattice and that they are mainly responsible for its destruction. The possibility that t-vinylene groups play a significant role is ruled out by the fact that their concentration reaches saturation between 400 and 600 Mrad [129, 171] whereas the greatest effect on the lattice occurs above this dose range (see below).

A number of electron and X-ray diffraction studies [32, 160, 168, 169, 172, 173] have recorded appreciable changes in the orthorhombic unit cell dimensions when heavy irradiation doses are applied: the *a* parameter increases substantially, the *b* parameter changes only little, while the *c* parameter (chain axis) contracts somewhat, see Fig. 3. The *a*/*b* ratio tends towards $\sqrt{3}$, which is the value characterizing the hexagonal lattice. The width of the reflections increases overall [100, 162, 170, 173–175] so that the higher orders disappear completely above 1000 Mrad. Yet the low order reflections 1 1 0 and 2 0 0 do not broaden as much as might be expected from the large changes in interplanar spacings. In some instances the line broadening was resolved into separate contributions from the limited crystal size and from lattice distortion. It was discovered that, initially, the average lateral size of the crystallites actually increases somewhat [173]. This unusual effect has been attributed by Čačković *et al.* [173] to an early destruction of smallest crystallites, thus shifting the average size to larger values.

Development of fully hexagonal crystal symmetry in room temperature irradiations usually coincides with, or is forestalled by, the complete disappearance of crystallinity. However, reflections from a true hexagonal lattice have been observed, during high-temperature EM irradiation of PE single crystals, first by Orth and Fischer [162] and subsequently by some other investigators [169, 176]. Recently, a clear first-order orthorhombic–hexagonal phase transition was

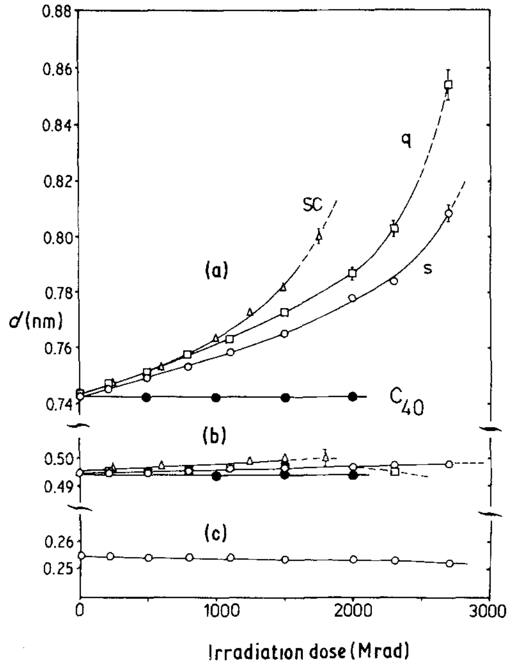


Figure 3 Dose dependence of unit cell parameters *a*, *b* and *c* measured at 293 K for PE single-crystals (SC; △), quenched bulk PE (q; □) and slowly cooled bulk PE (s; ○) and for alkane n-$C_{40}H_{82}$ (●) irradiated at 313 to 318 K. The crystal long spacing in PE samples was 13.8 nm for SC, 23 nm for q, and 33 nm for s (after [32, 34]). *c*-parameter values are those for the slowly cooled sample.

attained simply by warming up samples which had been γ-irradiated at room temperature [32]. Thus, the physical properties of the new hexagonal phase could be studied. The transition was fully reversible. Fig. 4 shows the melting and the orthorhombic → hexagonal transition temperature for linear PE of three different crystal morphologies as a function of radiation dose.

The highly disordered hexagonal modification is of considerable interest on its own as it represents a state of aggregation between the classical crystalline and amorphous state. It is less ordered than the hexagonal "rotator" phase in n-alkanes but more ordered than the conventional liquid crystalline states. Current experiments being conducted on irradiated bulk PE [177] show that the temperature interval of stability of the hexagonal phase increases with increasing hydrostatic pressure, which indicates that this phase is probably of the same nature as the hexagonal modification which appears in unirradiated PE at pressures above about 4 kbar [178] (for a recent review on this modification see [179]). The "rotator" phase in alkanes, on the contrary, disappears at high pressures [180, 181].

Several models have been proposed for the lattice configuration around a cross-link in the orthorhombic crystal modification: the two linked chains and the surrounding lattice were assumed to become elastically distorted [182, 183], see Fig. 5, or, alternatively, the formation of a kinked conformation which brings the two chains closer together at the cross-link point was suggested [173]. However, the observed changes in lattice parameters in irradiated PE (Fig. 3) have not so far been adequately interpreted. It may be appropriate to point out here that increasing the temperature [184, 185], or introducing methyl branches into the crystal lattice [186–188], gives rise to exactly the same changes in unit cell parameters as does introduction of cross-links. It therefore seems most likely that the local configuration of the particular defect has no direct bearing on the changes in average cell parameters. Rather, it appears that any larger atomic displacement, and thus perturbation of the crystal potential field,

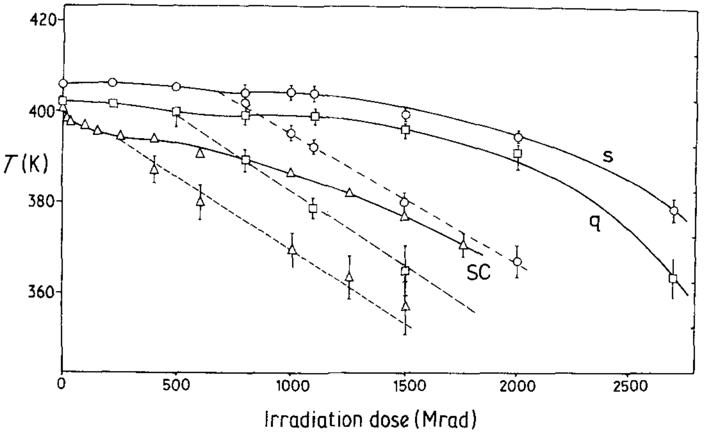


Figure 4 Melting (solid lines) and orthorhombic → hexagonal transition temperatures (broken lines) for linear PE, using the same samples. Samples s, q and SC, as in Fig. 3 [32].

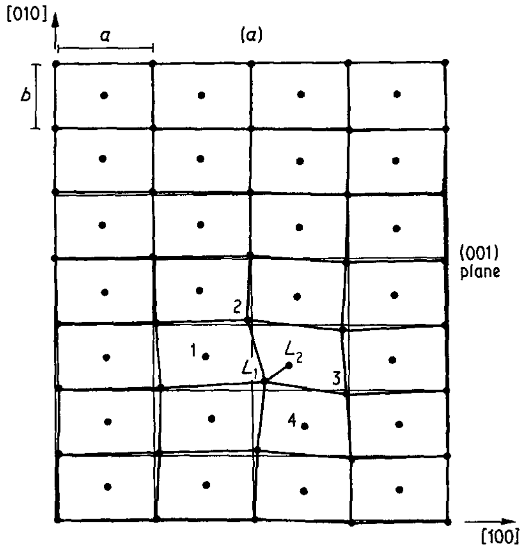


Figure 5 Distortion of the PE lattice as viewed on the (0 0 1) plane containing the cross-link. Dots represent the chain axes. Cross-linked chains are denoted L_1 and L_2. (Reprinted from [157] by courtesy of the Royal Society).

results in an increased motion of the chains. This proposal is supported by broad-line NMR studies which revealed a substantial increase in lattice mobility in irradiated PE [160, 189]. Rotational motion would make the molecular potential envelope more cylindrical, which would naturally result in the observed tendencies towards hexagonal symmetry and an expansion of the unit cell.

It has been suggested in the past that the destruction of crystallinity in PE may occur by a gradual progression of cross-linking from the fold surface towards the interior of the crystals. The assumption was that it would be easier for the cross-links to form in the distorted lattice near the already cross-linked surface layer than in the virgin crystal interior. The observed greater lattice distortion and earlier loss of crystallinity in thinner crystals (Fig. 3) would appear to support this view. Recently Yoda and co-workers [170, 190] analysed the 0 0 2 diffraction-line profile in irradiated PE. They reported that the coherent diffraction length along the chain axis in the crystals decreases continuously with irradiation. Moreover, they concluded that "the range amorphized in the chain direction of the crystallites is the same for larger and smaller crystallites" [190]. If their assertion were correct then, for a given dose, the relative decrease in crystallinity of a sample, $\Delta X/X_0$, would be inverseley related to the average crystal thickness, L. Thus

$$\frac{\Delta X}{X_0} = \frac{l}{L}, \tag{18}$$

where ΔX is the decrease in crystallinity, X_0 is the initial degree of crystallinity and l is the average thickness of the amorphized layer, assumed in [190] to be constant for a given irradiation dose. Thus, the above assertion of Yoda and Odajima can be tested simply by measuring the decrease in crystallinity for a number of identically irradiated samples with different L-values. Such a test has recently been performed by the author [90] who determined the straightforward decrease in heat-of-fusion, $(\Delta H_f^0 - \Delta H_f)/\Delta H_f^0$, as a measure of $\Delta X/X_0$. The result, however, disagreed with the conclusion of Yoda and Odajima, as is shown in Fig. 6a. The experimental data are represented in Fig. 6a by individual points; the broken line gives the dependence expected from Equation 18 (for constant l) fitted to the observed $\Delta X/X_0$ values for PE single crystals with $L = 14.2$ nm. The largest discrepancy occurs, of course, for the thickest extended-chain crystals where Equation 18 predicts a decrease in crystallinity of only 1%, as compared to the 22% decrease observed. In Fig. 6b the relative increase in unit cell parameter a is also shown for comparison as it is one of the best single indicators of any changes in the lattice. There is a clear effect of crystal thickness, but it is not very marked, the increase in a being only doubled for a 30-fold reduction in crystal thickness. In conclusion, if cross-linking indeed proceeded from the fold surface this could only account for a fraction of the overall lattice damage, the major part stemming from a more or less random formation of cross-links within the crystal core.

Recently, a new interpretation of the observed increase in radiation resistance with increasing crystal thickness (Figs 3 and 4) was proposed [32]. According to it, cross-linking in the crystal lattice, and the final destruction of crystallinity, are greatly accelerated when the highly-mobile hexagonal crystal modification is approached: for example, note the sharp final drop in melting temperatures at highest irradiation doses in Fig. 4. The tendency towards hexagonal symmetry appearing earlier in thinner crystals was described in terms of the mutual relationship between the free energies of the orthorhombic and the hexagonal phases. In unirradiated material these are already closer to each other in thin crystals than in thick crystals (compare with the theoretical work by Hoffman

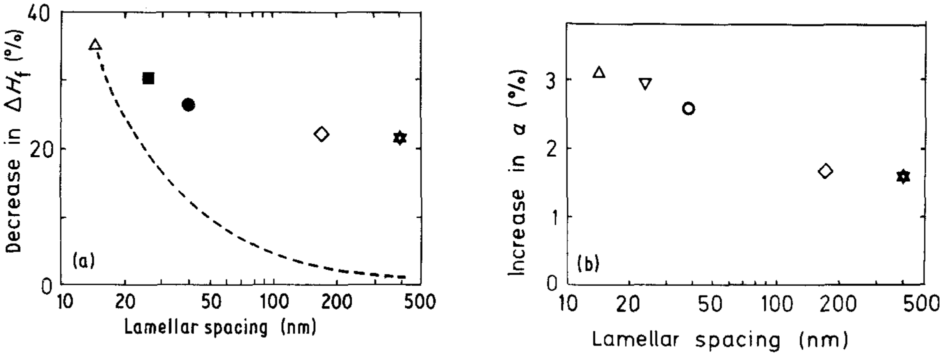


Figure 6 (a) Per cent decrease in heat-of-fusion, $100 \times (\Delta H_f^0 - \Delta H_f)/\Delta H_f^0$, after γ-irradiation dose of 800 Mrads at 358 K for a number of samples with different lamellar spacings, L. Here L approximates the crystal thickness. (b) Corresponding increase in a parameter of the unit cell. Samples are of linear PE in the form of single crystals (△), annealed single crystals (▽), quenched bulk (■), slowly cooled bulk (○ and ●), extended-chain crystals annealed at high pressure (◇) and extended-chain crystals crystallized at high pressure (☆). Room-temperature irradiation gives analogous behaviour with all effects smaller by about one third in absolute values. The broken line in (a) shows the behaviour predicted by Equation 18.

[191]). Thus, a lower concentration of cross-links is required in the former to bring about the hexagonal transition, and hence the final accelerated destruction of crystallinity occurs earlier in thinner crystals. The finding that the orthorhombic–hexagonal phase transition in alkanes more than doubles the cross-linking efficiency [32] strongly supports this latter concept.

5.2. Alkanes

In spite of the identical local atomic arrangements in crystals of PE and orthorhombic n-alkanes, and in spite of the apparent equivalence in their radiation chemical behaviour, the way in which crystallinity in alkanes is destroyed by radiation differs completely from that in PE. As described in the preceeding section, the lattice in PE becomes progressively more distorted with increasing irradiation dose so that the amorphization takes place in a continuous fashion. On the contrary, practically no change in either lattice spacing or line width can be observed in γ-irradiated alkanes [34] (Fig. 3), even though the diffraction intensity and the heat-of-fusion decrease more steeply than in PE. The difference between the irradiation behaviours of PE and alkane crystals was first pointed out by Orth and Fischer [162] who could record no change in the position or width of electron diffraction spots during EM irradiation of n-$C_{28}H_{58}$ crystals. The observed behaviour was attributed to the cross-link-induced crystal defects being of the quasithermal type. The long-range order would thus remain preserved in alkane crystals, whereas the same cross-links introduced in the crystals of PE would produce paracrystalline distortion.

Ahmad and Charlesby [33] measured the melting-point depression and the decrease in heat-of-fusion in γ-irradiated n-$C_{36}H_{74}$ and compared these data with G(cross-link) values from the literature. They concluded that one cross-link destroys a crystalline volume equivalent to that of one molecule. Cross-linking was regarded to occur at random, inducing isolated local amorphization within an appreciable radius around each cross-link. However, since a dose of 1000 Mrad already produces, on average, almost 1 cross-link per molecule, this mechanism fails to explain the observation of the authors themselves that even a dose of 2000 Mrads still leaves the X-ray diffraction rings sharp.

A detailed investigation of the process of crystallinity destruction in alkanes has recently been undertaken by employing both γ-ray [34, 100] and EM-beam [57, 100] irradiation. The crystals were studied by a combination of X-ray and electron diffraction, thermal analysis, gel permeation chromatography (GPC) and EM imaging. As a result, it was established that the preservation of a constant position and width of the diffraction maxima in irradiated n-alkanes is due to a large-scale separation of the material into a well-ordered crystalline phase and a fully amorphous phase. Even at low irradiation doses an amorphous, or liquid, phase appears which contains the cross-linked molecules. With further irraadiation this amorphous phase increases and the crystalline phase decreases in proportion but remains almost completely free of cross-links. For sufficiently low irradiation dose rates (γ-irradiation) a nearly complete phase equilibrium is maintained during irradiation. Absorption of large radiation doses over short periods of time (electron irradiation) can, on the contrary, lead to substantial lattice distortion in alkanes. The distortion is then of the same type as that observed in irradiated PE. Its extent depends on three factors: larger distortion occurs (a) if alkane molecules are longer, (b) if the irradiation temperature is lower, and (c) if the irradiation dose rate is higher. Thus, for example, at liquid nitrogen temperature the crystal lattice in all electron-irradiated alkanes undergoes qualitatively the same changes as those seen in PE, i.e., most notably, the unit cell expands greatly, primarily along the *a* axis. This indicates that at low temperatures cross-links accumulate even in the lattice of alkane crystals.

The effect of chain length on unit cell dimensions during room-temperature EM irradiation is illustrated in Fig. 7. The irradiation behaviour of the crystal lattice in n-tetranonacontane ($C_{94}H_{190}$) is almost identical to that of PE single crystals (not shown in Fig. 7). At the other extreme, n-$C_{28}H_{58}$ shows only small, although noticeable, changes in lattice parameters. With decreasing irradiation dose rate less distortion occurs for a given total dose. Consequently, in ^{60}Co γ-irradiated alkanes up to at least C_{40} practically no distortion occurs. For comparison, the does rate of the γ-irradiation in Fig. 3 was over 3000 times lower than that used in the electron irradiation experiment in Fig. 7.

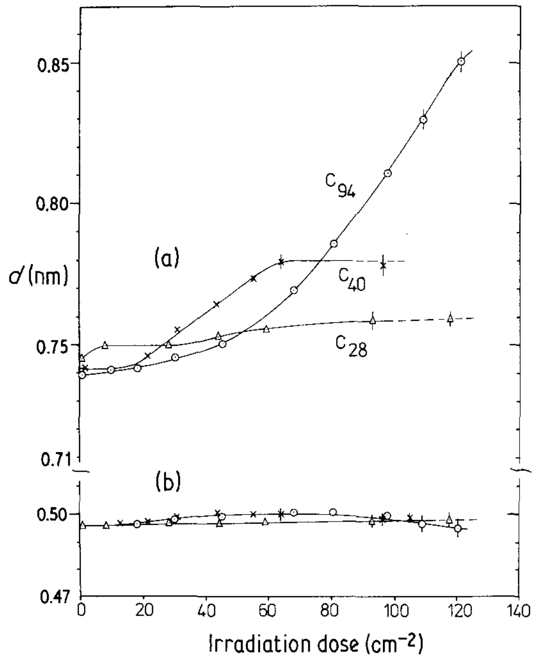


Figure 7 Irradiation dose dependence of orthorhombic lattice parameters *a* and *b* for alkanes $C_{28}H_{58}$ ($\triangle$), $C_{40}H_{82}$ (x) and $C_{94}H_{190}$ (o) exposed to the electron microscope beam at room temperature. Current density = 100 mA m^{-2}, roughly equivalent to 2.5 Mrad sec^{-1}. (At approxmiately 100 C m^{-2} faint hexagonal lattice reflections appear in C_{28} and C_{40} (not shown here). (After [57]).

Phase separation in irradiated alkanes being established, the question arises as to whether the cross-links form within the crystalline phase and subsequently become excluded from it, or whether cross-linking is confined to the already existing liquid phase. A partial answer was provided by direct EM observation of images produced by diffraction contrast [57]. In a range of alkanes radiation was found to create round non-diffracting regions within the crystalline lamellae. These regions were identified as "droplets" of liquid-like material, rich in cross-links (see Fig. 8). An observation that foreshadowed these findings was the appearance of minute "black patches" in dark-field images of a crystalline alkane, reported in a short note by Petermann and Gleiter several years ago [193].

With increasing exposure to the EM beam the "droplets" in alkane crystals were found to grow at the expense of the crystalline phase. Eventually they take over all of the crystal. An important observation [57, 100] is that droplets appear only

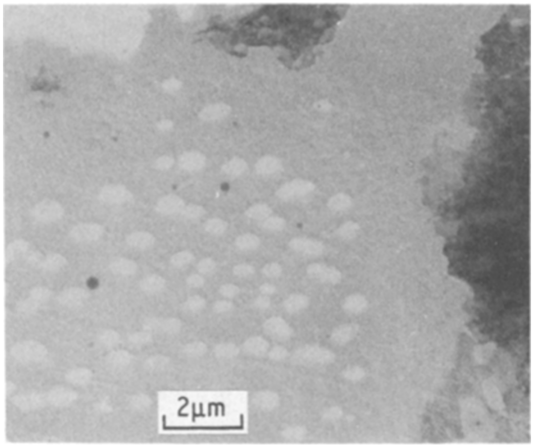


Figure 8 Bright-field EM image of a n-$C_{40}H_{82}$ crystal after irradiation for 3 min in the electron microscope at 330 K, 24 degrees below melting point. The bright non-diffracting patches are the amorphous "droplets" which appeared during irradiation. The same crystal is also shown after a longer exposure in [192].

in those cases where there is little change in lattice spacings, that is in $C_{28}H_{58}$ at or above room temperature and in $C_{40}H_{82}$ above 313 K. In spite of the high molecular mobility in alkane crystals [194] it is obvious that the extremely rapid formation of widely-separated amorphous regions during irradiation is incompatible with a diffusion through the crystal and a coalescence of whole cross-linked molecules. Consequently it was concluded [57] that, at least in the cases where "droplets" were observed, cross-linking takes place primarily within the completely amorphous phase. It was concluded further, by extrapolation to lower dose rates, that γ-irradiation at room temperature would result in practically all cross-linking taking place in the amorphous phase even in longer alkanes such as C_{40}. Accordingly, the crystalline phase would remain almost free of defects throughout the entire course of irradiation, as is actually observed (Fig. 3). Certain GPC data on molecular-size distribution in γ-irradiated alkanes [100, 120] also comply with this latter concept (compare with Section 4.2).

A clear implication of the observed "droplet" formation is an unusually long-range and rapid migration in active sites in alkane crystals, as already indicated in Section 2.1. While the primary deposition of radiation energy must be uniform, cross-linking is still confined to amorphous domains separated from each other by as much as several micrometres. Once nucleated, the "droplets" grow in size but not in number. Thus it was concluded that they serve as effective sinks for the active sites within the surrounding crystal lattice in a radius of up to several micrometres. The nature of the active species and their migration mechanism have not yet been identified. Manifestations of this mechanism have not been observed in very long alkanes like C_{94} or in PE single-crystals, at least not in such a clear-cut form, even when the irradiation temperature was brought close to the melting point.

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