

Chlorination of irradiated polyethylene single crystals: 2: XES and e.s.c.a. analysis of irradiated-chlorinated PE

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Chlorination of irradiated polyethylene single crystals was characterized in this study by the X-ray energy spectroscopy and electron spectroscopy for chemical analysis techniques. Results presented show that PE chlorination was extensive, even in unirradiated PE single crystals at 298 K in the dark. The data obtained indicates that PE chlorination consists of a two-step mechanism: (1) a fast uptake which occurs in the first few minutes of chlorine exposure, constituting approximately 50% of total uptake, followed by (2) a slower, approximately first-order rate of uptake. A first-order rate constant of $5 \times 10^{-4} \text{ s}^{-1}$ was estimated for all of the irradiation doses and temperatures studied. The similarity in chlorine uptake trends for both unirradiated and irradiated samples at various temperatures suggests that the rate of Cl_2 diffusion is the rate determining step. Although the magnitude of chlorine uptake increased with increasing irradiation dose, the rate of uptake remained constant. Rapid uptake probably occurred in the amorphous surface zones, followed by a slower step attributable to Cl_2 diffusion into the crystalline regions and subsequent chlorination there.

(Keywords: chlorination; polyethylene; single crystals; X-ray energy spectroscopy; electron spectroscopy for chemical analysis)

EXPERIMENTAL

Details of the PE single crystal preparation, irradiation and chlorination are described in Part 1. From XES analysis, the chlorine content in the PE crystals could be determined by comparison with a reference conducted for polyvinylchloride (PVC). The same scanning microscope SEM-XES apparatus used by Delgado¹ was employed in this study, the main difference being that the specimen area scanned in this case was purposely made much larger, $2.6 \times 10^{-3} \text{ cm}^2$ as compared to an area of $2.2 \times 10^{-7} \text{ cm}^2$ in Delgado's research. Accordingly, the samples in these experiments received less than 15 Mrad dose during the XES analysis. Apparently a dose of 15 Mrad did not significantly damage the specimen; that is, the number of chlorine counts remained within $\pm 2\%$ even after rescanning the same area. Irradiation dose and temperature and chlorine interaction time were varied in order to characterize the chlorination process.

RESULTS AND DISCUSSION

XES analysis

1. Effect of reaction time on the extent of chlorination of irradiated and unirradiated PE single crystals at 298 K

Figure 1 shows the effect of reaction time on the extent of chlorination of unirradiated and irradiated PE single crystals, respectively, at 298 K. These plots were made for

doses of 0, 1, 38, 75 and 600 mrad. The abscissa of these plots, t_{Cl_2} , is the chlorination interaction time, where the chlorine gas was introduced (within one minute after irradiation) at time $t_{\text{Cl}_2} = 0$. The ordinate, X_{Cl} , is the percentage of 'total sites' chlorinated, which was determined from XES analysis on chlorinated PE samples using PVC as a reference. By a chlorination site we mean that each carbon atom (on a PE chain) has (at most) two covalent bonding sites available for reaction with chlorine. In the PE used here, 1 chain traverse = 130 Å and so there are approximately 103 $-\text{CH}_2-$ units or $2 \times 103 = 206$ total possible bonding sites in one traverse. The chlorine uptake values X_{Cl} refer to chlorine which may or may not be covalently bonded. Unbonded chlorine would probably result from molecular chlorine trapped or dissolved in PE. It is unlikely that there was much unbonded chlorine present since any Cl_2 which could diffuse into PE (and not react) during chlorination would probably diffuse out thereafter. In fact, the X_{Cl} values obtained in this work remained constant for samples kept at room temperature or under vacuum for several weeks. Furthermore, several heating experiments were conducted in which chlorinated PE samples were maintained at 333 K for seven days. Samples were heated to determine how much (if any) of a decrease in chlorine content would occur at this relatively high temperature. A C-Cl bond would be unaffected at 333 K, while diffusion of molecular chlorine out of the sample would be considerably enhanced at 333 K, recalling that the α -transition in PE occurs at about 333 K. Since no such changes in X_{Cl} were observed either at 298 or 333 K, the X_{Cl} values reported here refer to carbon-chlorine covalent

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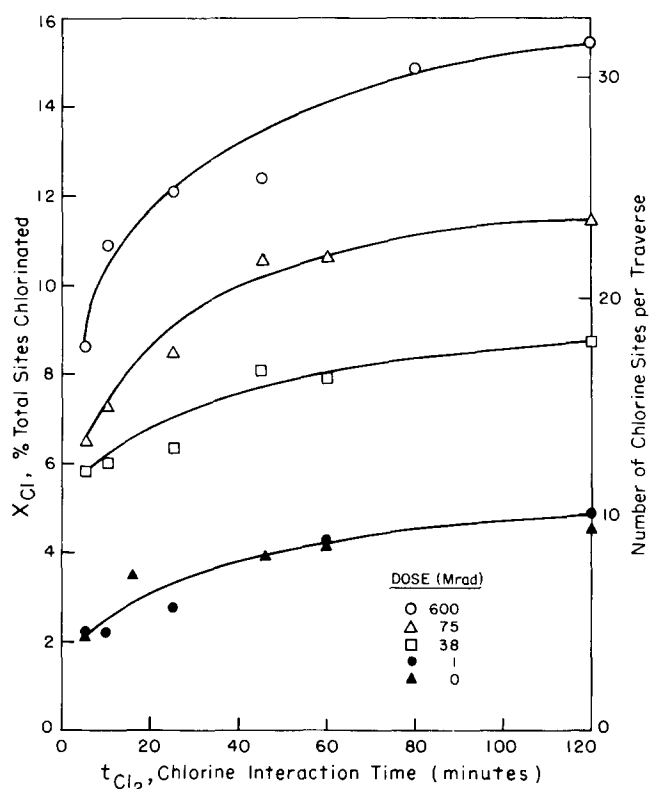


Figure 1 Effect of reaction time on extent of chlorination of polyethylene single crystals at 298 K

bonds. X_{Cl} also refers to the 'total' sites chlorinated because the XES method collects information based on the entire lamella; that is, XES does not distinguish between chlorine located in the amorphous zone and that in the crystalline interior. Chlorine uptake can also be expressed as $N_t(Cl_2)$, the number of chlorine atoms per traverse, which is given by:

$$N_t(Cl_2) = \frac{X_{Cl}}{100} \cdot \frac{(103 - CH_2 - \text{units})}{\text{traverse}} \cdot \frac{2 \text{ bonding sites}}{-CH_2 - \text{unit}} \quad (1)$$

Figure 1 indicates that X_{Cl} varied from 2.2% (for $t_{Cl_2} = 5$ min after a dose = 0–1 Mrad) to 15% (for $t_{Cl_2} = 120$ min after a 600 Mrad dose). $N_t(Cl_2)$ ranged from 4.5 to 31 Cl/traverse for the same t_{Cl_2} dose range. These $N_t(Cl_2)$ values are much higher than the maximum uptake of one chlorine atom/traverse reported by Keller *et al.*¹⁹ in their u.v. light-initiated chlorination experiments on unirradiated PE single crystals at 298 K. The N_t (5 min) and N_t (120 min) values as a function of dose are tabulated below:

Dose (Mrad)	N_t (5 min) No. Cl/traverse	N_t (120 min) No. Cl/traverse
600	17	31
75	13	23
38	12	18
1	4	10
0	4	11

Figure 1 shows that the uptake for the unirradiated and 1 Mrad dose samples is essentially identical. Although the X_{Cl} and $N_t(Cl_2)$ values reported in Figure 1 generally

increase with increasing dose, the observed trends in uptake are similar. Figure 1 also shows that for each dose studied, the chlorine uptake becomes fairly constant after an interaction time of 120 min. Chlorination experiments were conducted for up to 24 h, yielding, X_{Cl} values (not shown in Figure 1) within $\pm 5\%$ of those determined at t_{Cl_2} of 120 min.

The effect of irradiation dose on the extent of chlorination of PE single crystals at 298 K is presented in Figure 2 which is a rearrangement of the data in Figure 1. Four curves are presented in Figure 2, each of which represents a different t_{Cl_2} value, ranging from 5–120 min. Figure 2 shows that, for low t_{Cl_2} (5–10 min), chlorine uptake has a logarithmic dependence on the dose. For $t_{Cl_2} = 45$ and 60 min, there is more scatter in the data, but nevertheless, the trend is similar to that observed at small t_{Cl_2} .

2. Effect of temperature < 298 K on chlorination of irradiated PE single crystals

The effect of the interaction time on the extent of chlorination of PE single crystals at 235 K for 75 and 600 Mrad was studied. Similar trends observed at 298 K in Figure 1 were seen at 235 K, the only difference being that the curves at the lower temperature were displaced downwards. X_{Cl} values at 235 K varied from 4.4–7.2% for $t_{Cl_2} = 5$ –120 min at 75 Mrad to 6–8.6% for the same t_{Cl_2} range at 600 Mrad. The $N_t(Cl_2)$ values at 235 K are given below:

Dose (Mrad)	N_t (5 min) No. Cl/traverse	N_t (120 min) No. Cl/traverse
600	12	18
75	9	15

Figure 3 shows the effect of temperature ≤ 298 K on PE chlorination for t_{Cl_2} of 25 and 45 min for a dose of 75 Mrad. The data in Figure 3 is presented as $\ln X_{Cl}$ vs. $1/T$, obtaining two parallel curves which are approximately straight lines, based on X_{Cl} values for 298, 273 and 235 K for both $t_{Cl_2} = 25$ and 45 min. Although Figure 3 is not an Arrhenius plot, the plot nonetheless suggests that the observed chlorine uptake is an activated process from which an 'apparent' activation energy could be determined from the slope of $\ln X_{Cl}$ vs. $1/T$. Since the plots of Figure 3 are not actually straight lines, the apparent activation energy E_a is reported here as ranging from 0.7

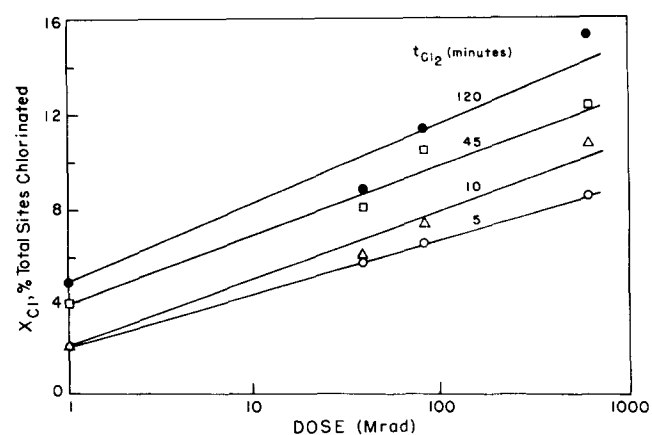


Figure 2 Effect of irradiation dose on extent of chlorination of polyethylene single crystals at 298 K

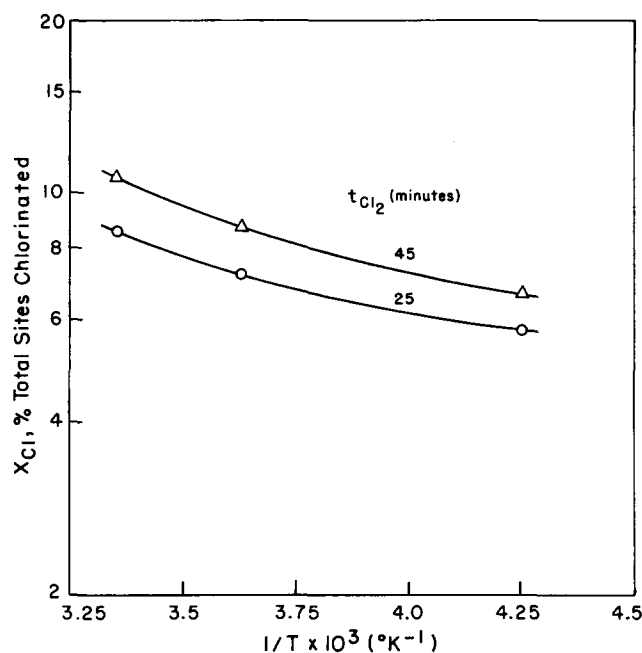


Figure 3 Effect of temperature < 298 K on chlorination of polyethylene single crystals irradiated to 75 Mrad

to $1.1 \text{ kcal mol}^{-1}$ based on the slopes of the tangents for $1/T < 3.6$ and $1/T > 3.6 \times 10^{-3}$, respectively. This relatively low E_a value probably indicates that the chlorine uptake phenomena had a weak temperature dependence.

3. Kinetics of chlorine uptake in PE single crystals

The similarity of the chlorine uptake plots in the preceding Figures suggests that chlorination kinetics for both the unirradiated and irradiated PE single crystals are of the same order. Observed chlorine uptake phenomena consisted of two processes: a fast uptake between 0 and 5 min, and a slower rate of uptake between 5 and 120 min. As discussed in the previous section, it was observed that the maximum chlorine uptake for both the irradiated and unirradiated samples occurred at approximately t_{Cl_2} of 120 min, after which time there were no remaining vacant chlorination sites. As the chlorine gas pressure was maintained at a relatively high value (0.2 Torr) in all experiments, it was not a limiting factor in PE chlorination. A vacant chlorination site is defined as any methylene site ($-\text{CH}_2-$) or free radical site located in regions which are accessible to chlorine. Once a vacant site has been chlorinated, it is considered occupied. If we define $\theta(t_{Cl_2})$ as the fraction of occupied chlorination sites, then $\theta(120 \text{ min}) = 1$. The fraction at any other time is given by:

$$\theta(t_{Cl_2}) = X_{Cl}(t_{Cl_2}) / X_{Cl}(120 \text{ min}) \quad (2)$$

for a given dose. At the end of the fast uptake ($t_{Cl_2} = 5 \text{ min}$), at 298 K, $\theta(5 \text{ min})$ was approximately 0.55 for both the irradiated and unirradiated specimens:

Dose (Mrad)	$\theta(5 \text{ min})$
600	0.56
75	0.56
38	0.65
0 and 1	0.51

and at 235 K, $\theta(5 \text{ min})$ was measured as:

Dose (Mrad)	$\theta(5 \text{ min})$
600	0.69
75	0.61

In other words, over 50% of the total chlorine uptake occurred during the fast uptake process (0–5 min) for all of the doses and temperatures studied here.

Due to difficulty in obtaining X_{Cl} data during the fast uptake process, the following kinetic analysis is concerned with the second, slower uptake process (5–120 min). The rate of (slow) chlorine uptake R_{Cl_2} can be expressed as:

$$R_{Cl_2} = \frac{d\theta(t_{Cl_2})}{dt_{Cl_2}} P_{Cl_2} = K_{Cl} P_{Cl_2} (1 - \theta(t_{Cl_2}))^n \quad (3)$$

or

$$\frac{d\theta(t_{Cl_2})}{dt_{Cl_2}} = K_{Cl} (1 - \theta(t_{Cl_2}))^n \quad (4)$$

where K_{Cl} is the chlorination rate constant and P_{Cl_2} is the chlorine gas pressure. $(1 - \theta(t_{Cl_2}))$ represents the fraction of vacant chlorination sites. The order of the uptake kinetics, n , was estimated by determining which n value best fits the $\theta(t_{Cl_2})$ data, which in this case was $n=1$. For $n=1$, integration of equation (4) gives:

$$\ln(1 - \theta(t_{Cl_2})) = -K_{Cl} t_{Cl_2} \quad (5)$$

Hence K_{Cl} can be estimated from the slope of a plot of $\ln(1 - \theta(t_{Cl_2}))$ vs. t_{Cl_2} . Such plots were made for chlorination of crystals irradiated to 600 and 75 Mrad, and 38 and 0 (and 1) Mrad, at 298 K in Figures 4 and 5, respectively. Figure 6 shows similar plots for chlorination of PE crystals irradiated to 600 and 75 Mrad at 235 K. The slopes of these plots are nearly the same, therefore the rate constant of chlorination K_{Cl} is roughly independent of

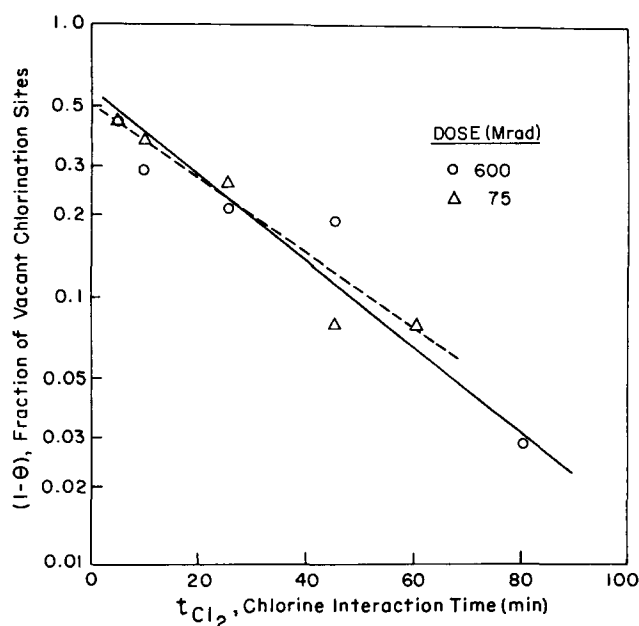


Figure 4 Effect of chlorine interaction time on fraction of vacant chlorination sites in irradiated PE single crystals at 298 K

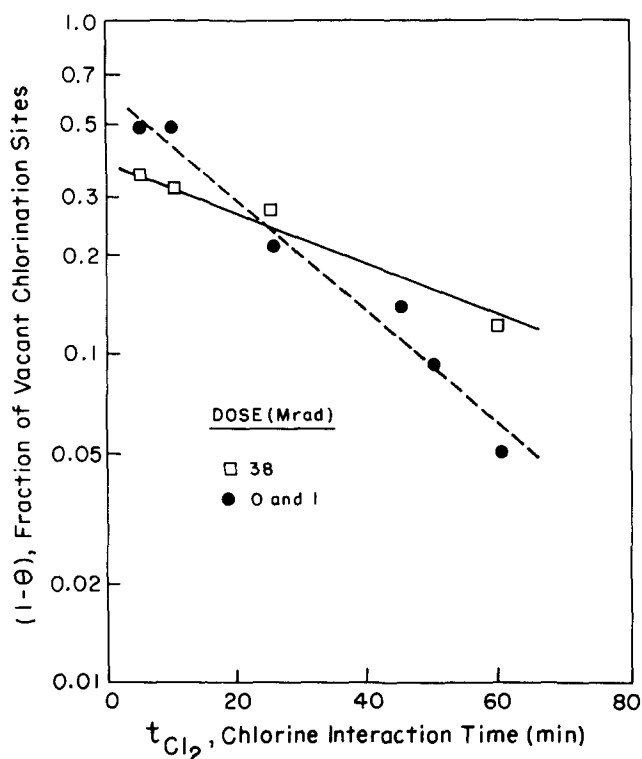


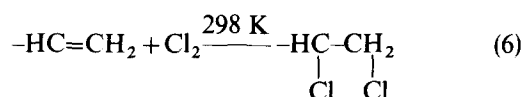
Figure 5 Effect of chlorine interaction time on fraction of vacant chlorination sites in irradiated PE single crystals at 298 K

dose and temperature. The K_{Cl} value thus estimated from the slopes was about $5 \times 10^{-4} \text{ s}^{-1}$.

4. Mechanisms of chlorine uptake in unirradiated PE single crystals

The chlorine uptake data in Figure 1 for 0–1 Mrad dose shows that when chlorine gas came in contact with unirradiated PE single crystals at 298 K, significant chlorine uptake was observed even though chlorination was neither initiated by u.v. light nor by the presence of irradiation-produced alkyl free radicals. Furthermore, the rates of uptake in the unirradiated and irradiated crystals were approximately equal. The following discussion attempts to explain how the unirradiated PE single crystals were chlorinated in this study. There are at least two mechanisms of chlorine uptake that could describe the observed phenomena.

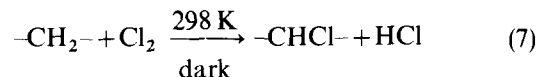
(a) *Reaction of chlorine with double bonds at the PE chain-ends.* The (Marlex 6009 $M_w = 136\,000$) PE used here is reported to have one unsaturated group at the end of each chain molecule ($-\text{HC}=\text{CH}_2$). As the crystals used here had a long spacing $L = 130 \text{ \AA}$, $1(-\text{HC}=\text{CH}_2)/\text{chain-end}$ corresponds to about $1.1(-\text{HC}=\text{CH}_2)/10$ traverses. Since over 90% of the chain-ends in PE single crystals are reportedly located in the amorphous surface zones³, there was about $1(-\text{HC}=\text{CH}_2)/10$ traverses in the amorphous zones which could have readily reacted with chlorine gas via:



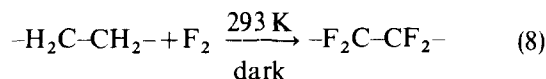
Reaction (6) thus accounts for $N(\text{Chain-end}) = 2 \text{ Cl}/10$ traverses or $0.2 \text{ Cl}/\text{traverse}$. Comparison of $N(\text{Chain-end})$ with the total chlorine uptake in unirradiated PE (where

$N_t(120 \text{ min}) = 11 \text{ Cl}/\text{traverse}$) shows that the uptake due to chlorination of unsaturated chain-end groups was negligible.

(b) *Chlorine uptake via substitution reaction.* In the absence of irradiation-produced alkyl free radical centres, the chlorine uptake in the unirradiated crystals probably proceeded by a chlorine substitution reaction:



This reaction is similar to the fluorination of PE powders at 293 K (in the dark) which was observed by Margrave *et al*⁴



In that study, Margrave did not explain why halogenation occurred without initiators. Thus at this point, it is not known why either reaction (7) or (8) occur.

The observed uptake data for the unirradiated system can be explained by the following analysis. The fast uptake could be due to reaction (7) which occurs first in the amorphous zone. A Cl_2 diffusivity value of $1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 298 K was estimated for low crystallinity PE,⁵ indicating that Cl_2 would have little resistance

* Although Cl_2 diffusivity in PE was unavailable, an estimate of Cl_2 diffusivity in (low crystallinity) PE was made based on comparison of the molecular diameters of Cl_2 (3.7 Å) and CO (3.8 Å). As these molecular diameters are nearly equal, it was assumed that Cl_2 would have about the same diffusivity value as CO ($1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 298 K)⁵

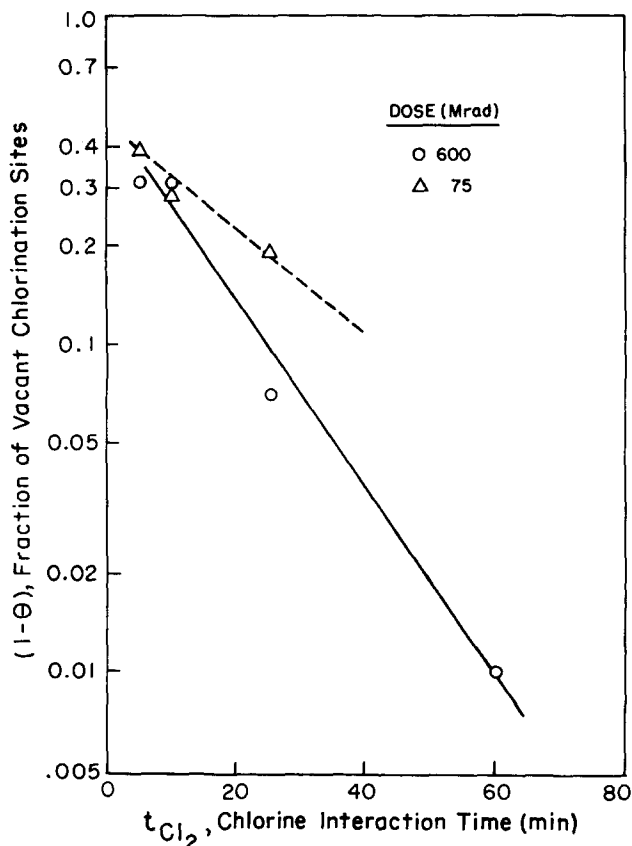


Figure 6 Effect of chlorine interaction time on fraction of vacant chlorination sites in irradiated PE single crystals at 235 K

in penetrating the amorphous surface zone, which is on average estimated to be 13 Å deep. As mentioned previously, over half the chlorination sites are occupied by time $t_{Cl_2} = 5$ min (these sites are probably in the amorphous zones). The slow uptake ($t_{Cl_2} = 5-120$ min) could be due to chlorination which occurs in the crystalline regions. Thus the rate of slow uptake probably reflects the rate of chlorine diffusion into the crystalline region rather than the rate of substitution reaction⁷. The completion of the reaction time $t_{Cl_2} = 120$ min probably indicates that at that time, Cl_2 was unable to penetrate any further into the crystalline regions.

5. Mechanisms of chlorine uptake in irradiated PE single crystals

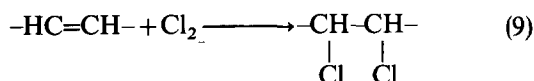
The main difference between the chlorine uptake phenomena in the irradiated and unirradiated samples is that the magnitude of the uptake increases with increasing dose such that $N_r(120 \text{ min}) = 31$ Cl/traverse at 600 Mrad and 298 K compared with $N_r(120 \text{ min}) = 11$ Cl/traverse in the unirradiated PE. There are at least two possible arguments in explaining this increase in magnitude with increasing dose:

(a) At higher doses, the alkyl radical concentration $C_r(D)$ is higher. Therefore there are more radicals with which chlorine could react.

(b) For the dose range used here (1–600 Mrad), the PE density decreases with increasing dose⁶ due to radiation-induced damage to the crystal structure. As the density decreases, chlorine diffusivity increases, resulting in the chlorination of a greater number of sites.

The purpose of the following discussion is to show that argument (b) explains the uptake phenomena in the irradiated samples. Although the unirradiated PE did not experience radiation damage, argument (b), i.e. diffusion of chlorine into PE, also explains the uptake observed in the unirradiated samples.

(a) *Reaction of chlorine with irradiation-produced alkyl radicals.* As mentioned in the e.p.r. results of Part 1 of this study, approximately 70% of the irradiation-produced alkyl free radicals decay via combination during (high dose-rate) irradiation at room temperature. Lawton and Balwitt⁷ estimated that 60% of the radical decay resulted in crosslink formation and the remaining 40% in double bond formation. These double bonds could react with Cl_2 via:

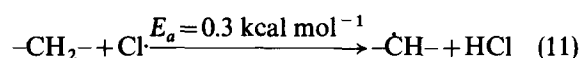
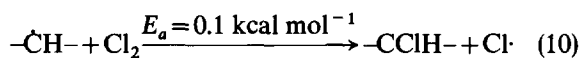


where reaction with one double bond results in the uptake of two chlorine atoms. The following Table shows the number of double bonds (d.b.) formed per traverse (during irradiation) as a function of dose as well as the resulting chlorine uptake which would occur if all of the double bonds formed were available for reaction (many of the d.b. are probably located in inaccessible sites in the crystalline interior) with chlorine.

Dose (Mrad)	No. d.b./traverse	N (d.b.)	
		No. Cl/traverse	N (120 min) No. Cl/traverse (25°C)
600	0.44	0.88	31
75	0.04	0.08	23
38	0.02	0.04	18

Also included in this Table are the $N_r(120 \text{ min})$ values at 298 K which show that chlorine uptake resulting from reaction with these double bonds (d.b.) is a minor effect, constituting less than 3% of the total uptake ($N_r(120 \text{ min})$) at 600 Mrad. Chlorine uptake would also occur via reaction⁶ with double bonds at chain-ends, but as indicated in the previous section, it is also a negligible effect.

The remaining 30% of the alkyl radicals which survive irradiation ('residual' alkyl radicals) decay at a much slower rate, with a half-life of about 4.5 h at 298 K (see Figure 6 in Part 1, ref. 8). These residual radicals would be present immediately after irradiation when Cl_2 was introduced at time $t_{Cl_2} = 0$. Therefore, most of the observed chlorination probably proceeded via the following chain (propagation) reactions:



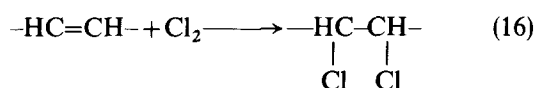
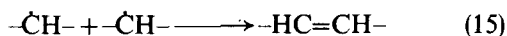
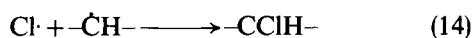
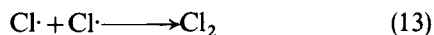
The net result of reactions (10) and (11) is the same as that of the chlorine substitution reaction (7) except that the above reactions occur via free radicals. As the activation energies E_a of reactions (10) and (11) are relatively low, they would be expected to occur quite rapidly. Reactions (10) and (11) suggest that the incorporation of chlorine into the PE could go on continuously without the loss of free radicals; that is, the alkyl radical lost in reaction (10) is regenerated in reaction (11), but probably at a different location. Thus the radical population remains constant during propagation. Keller *et al.*² observed a maximum halogen uptake of only 1 Cl/traverse at 298 K in their u.v. light-initiated chlorination of (unirradiated) PE single crystals. Keller's low uptake can probably be explained by the rapid formation of a relatively thin, highly chlorinated surface layer which inhibits chlorine diffusion into the interior. A more rapid surface uptake could be expected since u.v. initiation forms a population of chlorine radicals which is probably much larger than the alkyl radical site population following irradiation. Although Keller's surface uptake was quite high, the overall chlorination was low compared to this work.

In order to maintain chain reactions (10) and (11) it is necessary that there be a continuous supply of methylene units ($-CH_2-$), each of which consists of (at most) two chlorination sites. The ($-CH_2-$) units are referred to as chlorination sites because they are converted to alkyl free radicals via reaction (11) and then subsequently react with Cl_2 to form a methylene chloride unit ($-CHCl-$) in reaction (10). The uptake data shows that as chlorination proceeds, the number of available chlorination sites (on $-CH_2-$) decreases; that is, the ratio

$$\tau(t_{Cl_2}) = \frac{\text{No. alkyl radicals}}{\text{No. } -CH_2- \text{ units}} \quad (12)$$

increases because the number of chlorination sites decreases due to an increase in the number of methylene chloride units. The number of alkyl radicals remains constant, as seen in chain reactions (10) and (11). Termination would be expected to take place as the number of available chlorination sites approaches 0 or as $\tau(t_{Cl_2})$ approaches infinity. The uptake data of Figures 1 and 2

indicate that termination occurs at approximately time $t_{Cl_2} = 120$ min for all of the doses (1–600 Mrad) studied here. Termination probably consists of the following reactions:



As alkyl and chlorine radical concentrations are approximately equal, the relative frequency of occurrence of the above reactions depends mainly on the mobility of the radical species. A chlorine radical $Cl\cdot$ is much more mobile than an alkyl radical as seen by comparing their diffusivities. Although the chlorine radical diffusivity in PE is unknown, it is probably larger than the diffusivity of molecular chlorine (Cl_2) in PE, which we estimate as $1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 298 K in the amorphous regions. This value is considerably larger than the alkyl radical diffusivity value D_a of $\sim 1 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ at 298 K estimated from the e.p.r. analysis in Part 1 of this work. Thus the reaction of an alkyl radical with a chlorine radical (reaction (14)) would occur more often than the combination of two alkyl radicals (reaction (15)). Furthermore, the unsaturated groups ($-HC=CH-$) produced in reaction (15) would immediately react with the Cl_2 produced in reaction (13), as shown in reaction (7).

(b) *Effect of irradiation-induced changes in the PE crystal structure on extent of chlorine uptake.* For the dose range used here (1–600 Mrad), the major overall effect of high energy-irradiation on PE is an observed decrease in density⁶. As regards PE single crystals, a density decrease indicates an increase in the amorphous content. It is generally believed that this density decrease is due to crosslinking which begins at the fold surfaces and eventually spreads to the crystalline interior. Thus the depth of the amorphous zone increases with increasing dose. As the relationship between the dose and the irradiation-induced increase in the amorphous zone depth has not yet been described quantitatively, the following discussion will be of a qualitative nature.

An increased amorphous zone depth at higher doses would enhance Cl_2 diffusion, resulting in an increase in the number of available chlorination sites ($-CH_2-$ units). As the dose increases, the penetration depth of Cl_2 increases, the number of chlorination sites increases, and so the chlorine uptake values (X_{Cl}) increase. This argument suggests that chlorine uptake would occur via a two step mechanism: a rapid uptake resulting from chlorination in the amorphous zone and a slower uptake resulting from Cl_2 diffusion into the crystalline regions and subsequent chlorination there. As the amorphous zone depth increases with increasing dose, it would be expected that the magnitude of chlorine uptake (X_{Cl}) would increase with increasing dose for constant chlorination time t_{Cl_2} . Since as the chlorination reactions (whether via chlorine substitution or free radicals) are rapid, the rate of the slow uptake R_{Cl} is probably that of Cl_2 diffusion into the crystalline regions. Thus R_{Cl} should be independent of dose. Since R_{Cl} is probably that of Cl_2

diffusion into the crystalline zones, it is also expected that the X_{Cl} values decrease with decreasing temperature due to lower Cl_2 diffusivity at lower temperatures. Termination of the chlorination reactions would be expected to occur when the number of available chlorination sites approaches 0. The number of sites approaches 0 when Cl_2 has diffused to a certain maximum penetration depth in the crystalline regions. The above arguments, in fact, agree very well with the observed PE chlorination phenomena presented in Figures 1–6 for both the irradiated and unirradiated specimens at 298 and 235 K.

The above discussion suggests that the availability of chlorination sites ($-CH_2-$ units) rather than the concentration of irradiation-produced alkyl radicals was the dominant factor in explaining the increase of $X_{Cl}(t_{Cl_2})$ with increasing dose. Although chlorination proceeded via radicals reactions (10) and (11), the low activation energies required for those chain reactions indicates that, given a fixed number of chlorination sites, the same level of uptake would probably eventually occur whether there were 1 or 100 alkyl free radicals initially present. In fact, the e.p.r. analysis showed that within the 2 h time period required for chlorination, only 25% of the residual alkyl radicals had decayed via migration and subsequent combination in the amorphous surface zone at 600 Mrad and 298 K. The remaining 75% of the alkyl radicals were still in the crystalline regions at a time t_{Cl_2} of 120 min. Even if allowance is made for an increase in the amorphous zone depth with increasing dose, it is still likely that most of the residual alkyl radicals were located in crystalline regions which were inaccessible to Cl_2 .

(c) *Analysis of irradiated-chlorinated PE single crystals via e.s.c.a.* Several irradiated-chlorinated PE single crystal samples analysed via XES were also analysed by e.s.c.a. This was conducted on the 75 Mrad irradiated-chlorinated PE single crystal samples and on two of the unirradiated-chlorinated samples. PVC was again used as a reference in determining chlorine content. Sputter etching (removal of sample surface) was conducted on one of the 75 Mrad-irradiated-chlorinated samples in order to measure the chlorine content in regions located at an original depth greater than 30 Å. Figure 7 shows e.s.c.a. spectra obtained for a 75 Mrad-irradiated sample which was chlorinated for 10 min at 298 K. Figure 7 shows presence of carbon (C_{1s} peak), chlorine (Cl_{2p} peak),

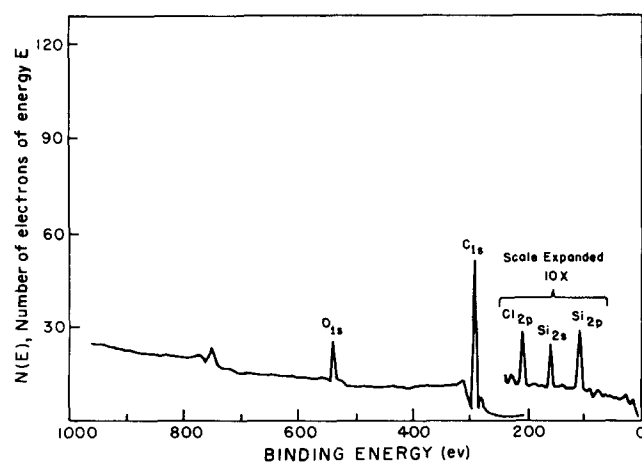


Figure 7 E.s.c.a. spectra of PE single crystals irradiated to 75 Mrad at 298 K for 10 min

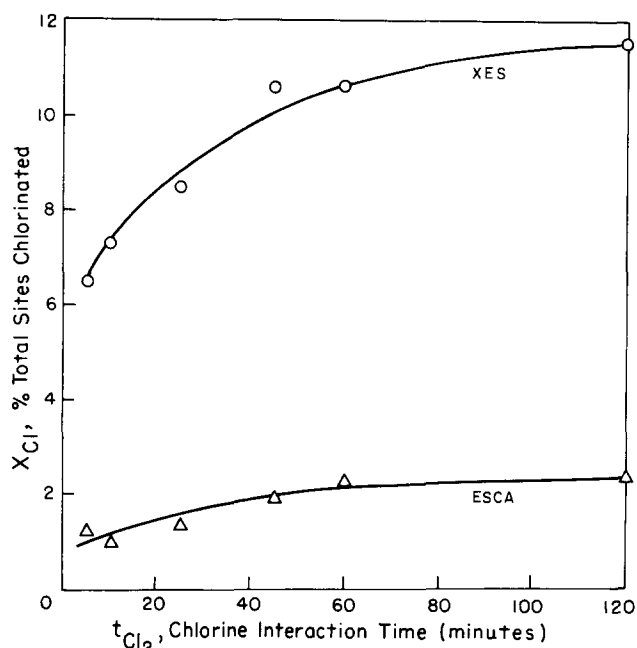


Figure 8 Comparison of chlorine content values determined via XES and e.s.c.a. for irradiated-chlorinated polyethylene single crystals ($D=75$ Mrad, $T=298$ K)

oxygen (O_{1s} peak), and silicon (Si_{2s} and Si_{2p} peaks). The oxygen and silicon peaks are due to contamination. $N(E)$, the ordinate of the e.s.c.a. spectra, refers to the number of electrons detected at a particular energy E . Its scale on the graph can be adjusted by the gain of the instrument. The vertical scale of the silicon and chlorine peaks is ten times greater than that of the oxygen and carbon peaks.

Comparison were made between the ratio of Cl_{2p} and C_{1s} peak heights (Cl_{2p}/C_{1s}) for PVC and those of chlorinated PE in order to determine chlorine content in the chlorinated PE samples. Cl_{2p} peak heights were always expressed relative to C_{1s} peak heights for the same sample as a means of normalizing the data. Recalling that PVC is 25% chlorine by number of sites, it was possible to determine the percentage chlorine content (X_{Cl}) based on e.s.c.a. analysis. Figure 8 shows a comparison of X_{Cl} values obtained for XES and e.s.c.a. as a function of the chlorine interaction time. The X_{Cl} e.s.c.a. plot shows the same trend as that of XES but the e.s.c.a. X_{Cl} values are about five times lower. Values are in the range 1.2–2.5% compared to 6.5–11.5% based on XES for the same t_{Cl_2} range. These comparatively low X_{Cl} e.s.c.a. values probably resulted from surface contamination (e.g. the silicon peak (from diffusion pump oil contaminants) is greater than the chlorine peak in Figure 7) effects as well as the inability of e.s.c.a. to detect the presence of chlorine which was located below the top 30 Å of the sample surface.

Had all the chlorine been present in the top 30 Å of sample surface, then the X_{Cl} e.s.c.a. values would have been of the same magnitude as the X_{Cl} XES values. Two

sputter etching experiments were conducted on the same PE sample (75 Mrad-irradiated and chlorinated) in which ~ 25 and 150 Å of the original surface* was removed from the sample, respectively. After the first etching (~ 25 Å removed), X_{Cl} decreased from 2.3 to 1.9%. After the second etching (~ 150 Å total sample depth removed), X_{Cl} had fallen to 1.3%. These etching experiments indicate that although there is much chlorine present in the amorphous surface zones of the PE single crystals, there is also a significant amount of chlorine located in the crystalline zones. This agrees with the chlorination mechanism presented in the previous section.

CONCLUSIONS

Chlorination of irradiated and unirradiated PE single crystals was characterized by XES and e.s.c.a. analysis. XES measurements showed that chlorine uptake phenomena was similar for both irradiated and unirradiated crystals: a fast uptake in the amorphous zones, accounting for over 50% of total uptake within five minutes reaction times, and a slower approximately first-order rate of uptake having a temperature-independent rate constant of $5 \times 10^{-4} \text{ s}^{-1}$. Since the slow uptake rate constant was observed to be independent of dose and temperature for the ranges studied, the slow uptake probably corresponded to Cl_2 diffusion into the PE crystalline regions. E.s.c.a. was used to remove portions of the surface of irradiated-chlorinated PE single crystals, showing that a significant amount was present in the crystalline interior regions.

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* As the PE single crystals were randomly oriented in the experiments, the sample 'surfaces' which were analysed via e.s.c.a. were not necessarily the crystal fold surfaces. Likewise, the surfaces etched were not necessarily the fold surfaces