Conversion of alkyl radicals to allyl radicals in irradiated single crystal mats of polyethylene

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The decay of alkyl radicals, the conversion of alkyl radicals to allyl radicals and the trapping of allyl radicals in irradiated single crystal mats of polyethylene have been studied by electron spin resonance (e.s.r.). It has been suggested that in the crystal core alkyl radicals react with *trans*-vinylene double bonds and are converted into *trans*-vinylene allyl radicals; at the crystal surface, alkyl radicals react with vinyl end groups and are converted into allyl radicals with vinyl end groups. The decay of radical pairs and the formation of *trans*-vinylene double bonds are discussed.

INTRODUCTION

It has been well established that three types of radicals, i.e. alkyl, allyl and polyenyl are produced in irradiated polyethylene. Alkyl radicals are formed by the irradiation of polyethylene at 77K and are converted to allyl radicals[1,2] when the samples are heated to room temperature. Little is known about the correlation between the decay region of alkyl radicals and the trapping region of allyl radicals.

In the present work, we report the results of an investigation into the decay of alkyl radicals[3], the conversion of alkyl radicals to allyl radicals and the location of allyl radicals in single crystal mats of polyethylene, using the electron spin resonance (e.s.r.) technique. Our results show that allyl radicals are formed both in the crystalline core and at the crystal surface. The formation of allyl radicals from alkyl radicals in the crystalline core and at the crystal surface is correlated with two of the three decay regions of alkyl radicals. The formation of *trans*-vinylene double bonds and the decay of radical pairs of intrachain type are discussed in relation to one of the three decay regions of alkyl radicals.

EXPERIMENTAL

The sample used was high density polyethylene Sholex 6050, in the form of crystal mats prepared by hot-filtering a suspension of single crystals in 0.1% xylene solution at 343K. The samples *in vacuo* at 77K were γ-irradiated from a ^{60}Co source with up to 12.7 Mrad at a dose rate of 0.7 Mrad/h.

E.s.r. measurements were made at 103K with a Varian V-4502 X-band spectrometer with 100 kHz field modulation. Heat treatment experiments to study the decay of alkyl radicals were carried out in the following way. Samples irradiated at 77K were heated to fixed temperatures for 5 min and cooled to 103K in order to take measurements.

RESULTS

E.s.r. spectra of single crystal mats irradiated *in vacuo* at 77K and observed at 103K are shown in *Figure 1a.* The magnetic field was parallel (*Figures 1a, 1c, 1e, 1g*) and perpendicular (*Figures 1b, 1d, 1f, 1h*) to the plane of the crystal mat. When the sample was heated to 263 and 293K, the spectrum altered both in intensity and shape represented by the spectral resolution, as shown in *Figures 1c, 1d* and *Figures 1e, 1f* respectively. The detailed results will be shown later.

Anisotropy of these Figures indicates that alkyl radicals are trapped in a region of regular order, i.e. the crystalline region[3]. The difference spectra obtained by subtracting spectra of *Figures 1e, 1f* from spectra of *Figures 1c, 1d* are shown in *Figures 1g, 1h.* The anisotropy of the spectrum also indicates that the radicals which decay by annealing are present in the crystalline region of polyethylene.

The variation of relative intensity with annealing temperature is shown in *Figure 2.* Three decay regions are observed. The first decay region is below 200K, the second region is from 200 to 260K and the third region is above 260K.

The spectral resolution, at the outer part of the spectrum, $S = b/2a$, as indicated in *Figures 1c, 1d,* and the spectral resolution at the central part of the spectrum, $A = x/y$ as indicated in *Figures 1a, 1b* is shown in *Figure 3.* Around 280K, the spectral resolution at the central part of spectrum A, starts to decrease. This change is due to the conversion of the sextet to the septet components. The resolution of the sextet spectrum is affected by the superimposition of the peak on the sextet spectrum. The septet spectrum is attributed to allyl radicals. Around 300K, the resolution in the outer part of the spectrum, S, also starts to decrease. This change is also due to the conversion of alkyl radicals to allyl radicals.

Figure 4 illustrates the conversion of alkyl radicals to allyl radicals. The number of allyl radicals is calculated by subtracting the intensity of the alkyl radicals from that of total

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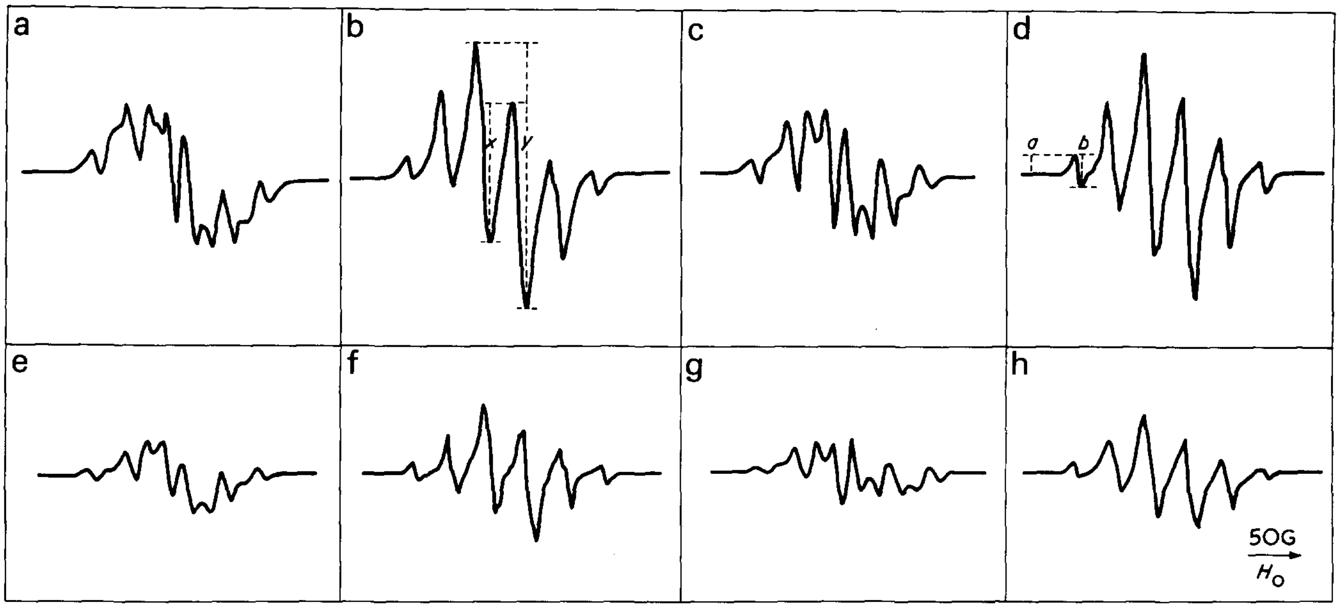


Figure 1 E.s.r. spectra of alkyl radicals produced in a single crystal mat of polyethylene. Observations were carried out at 103K. The magnetic field was parallel (a, c, e, g) or perpendicular (b, d, f, h) to the mat plane of the mat. (a, b) $A = x/y$. The sample was irradiated *in vacuo* at 77K. (c, d) $S = b/2a$. The same sample was annealed at 263K for 5 min and cooled to 103K for measurement. (e, f) Sample further annealed at 293K for 5 min and cooled to 103K for measurement. (g, h) The difference spectra obtained by subtracting spectra (e) and (f) from spectra (c) and (d)

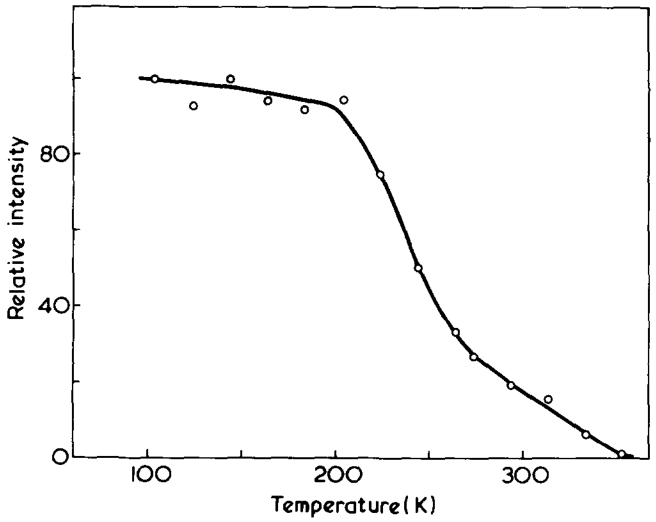


Figure 2 Variation of relative intensity of the spectrum for the single crystal mat of polyethylene irradiated at 77K *versus* temperature of annealing. Observations were carried out at 103K

radicals. Allyl radicals appear around 220K and increase in number to 260K but decrease by annealing at higher temperature with the decrease of the total radicals. The increase of allyl radicals is accompanied by a rapid decrease in the number of alkyl radicals. This result shows that when the sample is irradiated at 77K and annealed at room temperature, alkyl radicals are effectively converted to allyl radicals.

DISCUSSION

Three decay regions of alkyl radicals are observed in *Figure 2.* The first decay region below 200K is correlated with the decay of radical pairs. Radical pairs are observed in single crystal mats of polyethylene[4]. For polyethylene in powder form, the first decay region has been correlated with the decay of radical pairs[5]. The intrachain type of radical pair is observed in drawn polyethylene irradiated at 77K[6,7]. This intrachain type of radical pair should be produced in single crystal mats of polyethylene irradiated at 77K and should be converted to *trans*-vinylene double bonds when the sample is heated to room temperature.

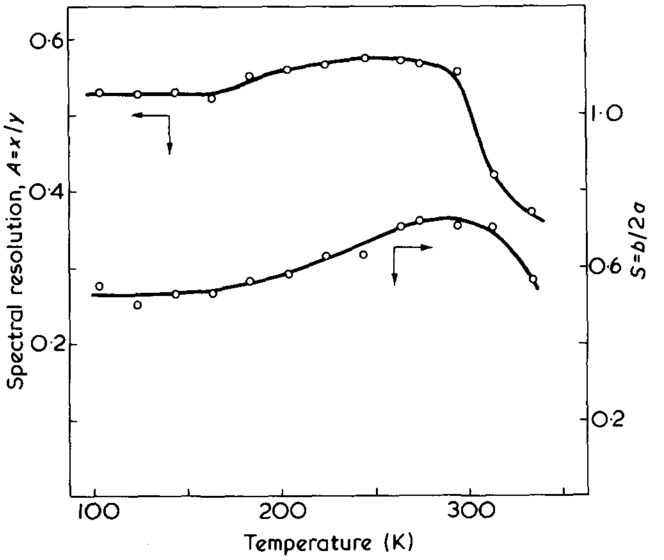


Figure 3 Change of spectral resolution of alkyl radicals produced in the single crystal mat of polyethylene irradiated at 77K *versus* temperature of annealing. $A = x/y$ represents the resolution of the central part; $S = b/2a$ represents the resolution of the outer part (see *Figure 1*)

The second decay region, from 200 to 260K, is correlated with the decay of alkyl radicals trapped in the crystal surfaces. The spectral resolution of both the outer part ($S = b/2a$) and the central part ($A = x/y$) increases in the second decay region as shown in *Figure 3.* This increase indicates that the diffuse component of the spectrum decays, leaving the sharp component. These results support the view that the second region is correlated with the decay of alkyl radicals trapped at the crystal surface.

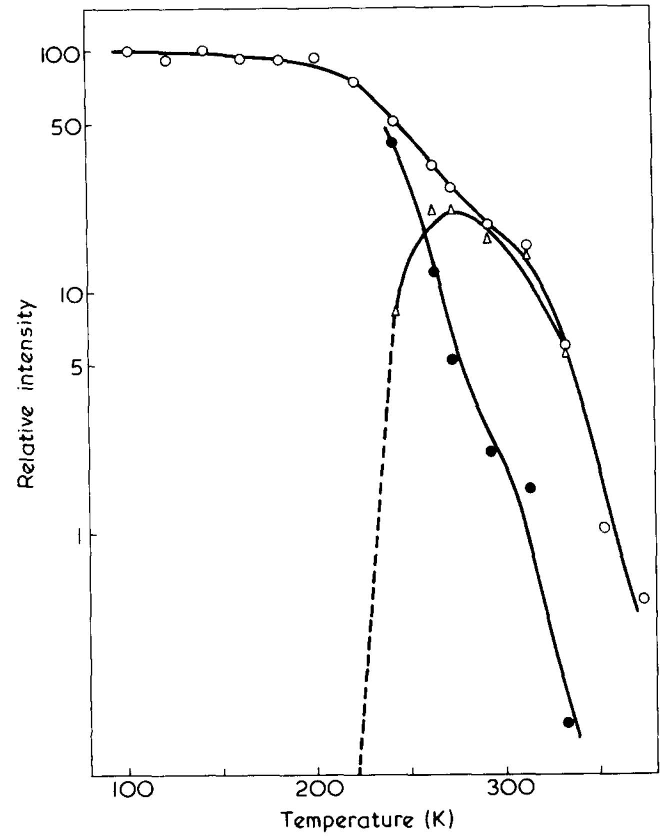
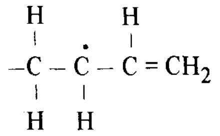


Figure 4 Conversion of alkyl radicals to allyl radicals in the mat irradiated at 77K *versus* temperature of annealing. ○, Total radical; ●, alkyl radical; △, allyl radical

In this decay region some alkyl radicals are converted to allyl radicals by reaction with double bonds. It is reported that allyl radicals are formed both at the crystal surfaces and in the crystal core[2]. When single crystal mats of polyethylene irradiated at 77K and annealed at room temperature were further annealed at 333K for 5 min the spectral shape was not changed[2]. On the other hand, the spectra became sharper when the mats were stored at room temperature for 4 months. These facts agree with the demonstration that allyl radicals are trapped in both the crystalline core and at the crystal surface. The molecular chains of polyethylene are aligned more regularly in the crystalline core than at the crystal surface. Therefore, molecular motions occur and allyl radicals decay only at the crystal surface. Consequently, only the allyl radicals in the crystalline core survive and the spectra become sharper. When the mats are annealed at 333K, molecular motions occur both in the crystalline region and at the crystal surface, and the allyl radicals decay. Therefore the line shape remains unchanged.

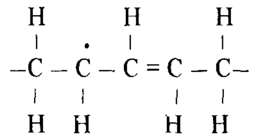
The location of allyl radicals corresponds to that of double bonds because allyl radicals are formed by the reaction of alkyl radicals with double bonds which cannot migrate into the polymer. Keller and Priest[8] reported the location of double bonds in unirradiated single crystals of polyethylene from studies of oxidative degradation using ozone. They found that about 90% of the vinyl end groups are excluded from the crystal lattice and should lie on the crystal surface. Therefore, on the crystal surface, vinyl end groups, which are already present before irradiation, react mainly with alkyl radicals to form allyl radicals of vinyl end type:



$$-CH_2-\dot{C}H-CH=CH_2$$

The third decay region is correlated with the decay of alkyl radicals trapped in the crystal core. The sharp component of the spectrum remains when the diffuse component decays in the second region. This sharp component of the spectrum is correlated with alkyl radicals in the crystal core where molecular chains are more regular than at the crystal surface. As shown in *Figure 1*, the anisotropy is clearly observed in the spectra of radicals which decay in the third decay region.

In the third decay region some alkyl radicals are converted to allyl radicals in the crystal core by reaction with double bonds, which are mostly *trans*-vinylene double bonds, and other alkyl radicals disappear and form double bonds or crosslinks. Patel's[9] findings on the location of double bonds in irradiated polyethylene, based on i.r. measurements, were that the crystal core is the preferred site for the formation of *trans*-vinylene double bonds. Therefore, in the crystal core, *trans*-vinylene double bonds produced by irradiation react with alkyl radicals to form *trans*-vinylene allyl radicals:



$$-CH_2-\dot{C}H-CH=CH-CH_2-$$

The *trans*-vinylene double bonds are produced by the recombination of two alkyl radicals. As shown above, some of the alkyl radicals are trapped pairwise in irradiated polyethylene at 77K. These pairs of alkyl radicals react together to form *trans*-vinylene double bonds, and are converted to allyl radicals by reaction with alkyl radicals when the sample is heated. Three alkyl radicals form one *trans*-vinylene allyl radical.

CONCLUSION

Three decay regions of alkyl radicals were observed in irradiated single crystal mats of polyethylene. The first region is correlated with the disappearance of radical pairs which form mainly *trans*-vinylene double bonds, the second region is correlated with the decay of radicals at the crystal surface and the third region is related to decay in the crystalline region. Allyl radicals are trapped both in the crystalline core and at the crystal surface. In the crystalline core, allyl radicals of *trans*-vinylene type are formed by the reaction of alkyl radicals with *trans*-vinylene double bonds which are produced by irradiation. At the crystal surface, the main reaction is as follows: the allyl radicals with vinyl end groups are formed by the reaction of alkyl radicals with vinyl end groups which are present before irradiation.

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