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ELECTRON SPIN RESONANCE STUDY OF RADICALS IN IRRADIATED POLYETHYLENE

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Electron Spin Resonance Study of Radicals in Irradiated Polyethylene

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In order to elucidate radiation effect in polyethylene, the nature and behavior of radicals produced in polyethylene and the model compound of polyethylene irradiated at 77°K were studied by using electron spin resonance. The structure of radical pairs, which are composed of two radicals produced very closely each other, was investigated in drawn polyethylene and the single crystal of n-eicosane. The radical pairs of intrachain type and interchain type were found in polyethylene and n-eicosane respectively. It was suggested that these two types of radical pairs are the precursors of double bonds and crosslinks respectively.

The thermal decay reactions of radicals themselves produced in irradiated polyethylene were investigated. It was made clear that the short range distances between two radicals play an important role in the decay reaction of alkyl radicals at low temperatures. The trapping regions of radicals were studied and it was clarified that allyl radicals, which are produced by the reaction of alkyl radicals with double bonds, are trapped both in the crystalline and non-crystalline regions.

Keywords: Polyethylene, Radiation Effect, Radicals, Electron Spin Resonance, Radical Pairs, Eicosane, Single Crystal, Thermal Decay, Trapping Region

照射したポリエチレンにおけるラジカルの電子スピン共鳴法による研究

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ポリエチレンにおける放射線照射効果を明らかにする為に，77°Kで照射したポリエチレンおよびそのモデル化合物に生ずるラジカルの性質・挙動を，電子スピン共鳴法を用いて研究した。まず二つのラジカルが極めて近接した場所に生成するラジカル対の構造を，延伸ポリエチレンおよびn－アイコサン単結晶において決定した。ポリエチレンにおいては分子内ラジカル対が，n－アイコサンにおいては分子間ラジカル対が見い出された。これらのラジカル対はその構造からそれぞれポリエチレンにおける二重結合・架橋の先駆体と考えられる。次にポリエチレンに生ずるラジカルそのものの昇温による減衰挙動および存在領域について調べた。その結果低温におけるアルキルラジカルの減衰反応にはラジカル－ラジカル間の距離が大きな要因となることが判った。また，アルキルラジカルが二重結合と反応して生成するとされているアリルラジカルがポリエチレンの結晶・非晶の両領域に存在することが明らかとなった。

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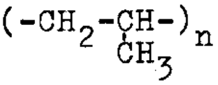
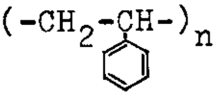
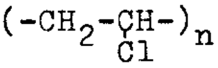
照射したポリエチレンにおけるラジカルの電子スピン共鳴法による研究

（和文要約）

1. 諸　言

ポリエチレンは極めて簡単な化学構造を持ち，また種々の高分子を研究する際の基本的な物質として重要である。例えば表1に代表的な高分子を五種類挙げてあるが，これらはポリエチレンの水素原子をポリプロピレンの場合はメチル基，ポリスチレンの場合にはベンゼン環に置換したものであると言える。このように簡単な化学構造を持ち，高分子において基本的な物質であるので，これまでに種々の情報が蓄積されてきている。

表　1

Polyethylene	$(\text{-CH}_2\text{-CH}_2\text{-})_n$
Polypropylene	 $(\text{-CH}_2\text{-}\underset{\text{CH}_3}{\text{CH}}\text{-})_n$
Polystylene	
Poly(vinyl chloride)	 $(\text{-CH}_2\text{-}\underset{\text{Cl}}{\text{CH}}\text{-})_n$
Polytetrafluoroethylene	$(\text{-CF}_2\text{-CF}_2\text{-})_n$

ポリエチレンの照射効果については，１９４０年代頃から研究が行われ，これまでに次のような事が判ってきている。すなわちポリエチレンに放射線を照射すると水素ガスの発生，架橋の生成，未照射試料にはなかった二重結合の生成，主鎖切断によっておこる崩壊，などが起る。

放射線化学反応によっておこる照射効果を与える反応の中間体として重要なラジカルについては，ＥＳＲによる研究が生成物についての研究と同時期に始められており，これまでにポリエチレンに放射線を照射すると，三種のラジカル，アルキルラジカル（$-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2$），アリルラジカル（$-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}=\text{CH}-$），ポリエニルラジカル（$-\text{CH}_2-\dot{\text{C}}\text{H}-(\text{CH}=\text{CH}-)_n-\text{CH}_2-$）が生成することが判ってきた。このような研究が行われた後にポリエチレンの照射効果についての研究は一般的に一段落したと考えられてきた。照射効果における水素発生，架橋，二重結合等の生成が定性的にも定量的にも研究され，一応つじつまの合う状態となったからである。

これに対し，最近実用的な見地から再評価の必要がでてきた。すなわち原子力発電所が増えてきて，原子炉を動かすための電力を供給したり，制御したりするためにケーブルが必要である。そのケーブルの被覆には高分子材料が使われており，これらは放射線の場において使用さ

れる。放射線計測器にも高分子材料が使われており，これらも当然放射線の場で使用される。このように放射線の場で使用される高分子材料が増加してきているのである。このような理由により，高分子材料に対する照射効果，劣化の研究の要請が高まってきた。

一方１９４０～５０年代には知られていなかったポリエチレンの形態学的知識，情報，構造に関する知識等が得られて情報が豊富になってきた。これらの豊富になってきた情報のうち本報告に関することとしては次の二つが重要である。一つは主鎖軸（ c 軸 ）方向に大体方向のそろった単結晶マットが得られることである。結晶性高分子であるポリエチレンにおいて単結晶が得られることがわかったが，一つの単結晶は電子顕微鏡で見られるような小さな物であり，主鎖軸方向のみをそろえた集合体として，ＥＳＲ測定に使える程度の大きさの単結晶マットが得られる。もう一つはポリエチレンを室温以上で延伸すると，延伸した方向に主鎖軸がならぶことがわかってきた。（延伸ポリエチレン）この場合主鎖軸の配向度は極めて良い。以上のような試料を使うことにより種々の情報を引き出すことができるようになってきた。これらの情報から，高分子の照射効果の研究を更につっこんで再評価する必要がでてきたのである。

互いに極めて近接した場所に捕えられた二つのラジカルの組を一般にラジカル対と呼んでいる。ラジカル対は高分子の照射効果で大きな役割を果たす架橋，二重結合などの先駆体として重要である。それにもかかわらず，ポリエチレンなどの高分子においてラジカル対の存在は近年明らかにされたが，その構造についての知見は全く得られていない。この原因は高分子においては，ラジカル対の構造を決定するために必要な，ラジカル対による $\Delta Ms = 1$ESR スペクトル（通常普通のラジカルのＥＳＲが観測される磁場におけるラジカル対のＥＳＲスペクトル）が，これまでに得られなかったことにある。

これに対し，高分子においても試料になんらかの規則性が与えられるならば，ラジカル対の構造の解析に必要なラジカル対による $\Delta Ms = 1$ESR スペクトルが明瞭に観測されるはずであると考えた。この考えに基づき，ポリエチレンを延伸することにより，高分子では始めて二つのアルキルラジカルからなるラジカル対の構造を決定することに成功した。またポリエチレンのモデル化合物として位置づけられるｎ－アイコサン単結晶においてラジカル対の構造を決定した。

次にラジカルそのものの挙動について調べた。結晶性高分子であるポリエチレンは結晶部分と非晶部分などの領域を持つ。放射線照射により生成したラジカルがどのような領域に存在するかを知ることは，ラジカルの反応およびその結果としての照射効果の理解のために重要なことである。このようなラジカルの存在領域に関する研究は二，三あるが，いずれも一種類のラジカルについての断片的な研究であって，また相互に矛盾している。

本研究においてはポリエチレンにおける重要な二つのラジカル，アルキル，アリル，両ラジカルについて，その存在領域，反応の領域およびアルキル→アリルへの転換の領域について詳細に検討し明らかにした。

2. 照射したポリエチレンおよびそのモデル化合物単結晶におけるラジカル対の構造

固体に放射線が照射されると化学結合が切れて二個のラジカルができる。

$$RR' \rightarrow R\cdot + R'\cdot$$

生成した二つのラジカルの運動エネルギーと，その媒質の"かたさ"に応じて，二つのラジカルが再結合してもとの分子に戻る場合（Geminate recombination）と，一方または両方のラジカルが媒質中を拡散して運動エネルギーを失った所で媒質中に捕捉される場合（Isolated radical）とがある。またある一定の条件の下では，照射されてできる二つのラジカルが，結合距離の数倍の距離のところで対になって安定化すること（Radical pair）もあることが明らかにされてきた。

上に示したラジカル対とは異った機構によって生成するラジカル対もある。放射線照射による結合の開裂により，軽い原子が放出され，この軽い原子の近傍の分子を攻撃して第二のラジカルを作る。このようにして生成したラジカル対が本論文の主題である。ラジカル対を構成する二つのラジカルの間の距離および相互的な配置をラジカル対のＥＳＲ解析により知ることができる。これにより異方性試料の結晶格子の中におけるラジカルの位置をほぼ決定することができる。このことは照射された固体の中における放射線化学反応の素反応の研究にとって新しい可能性を開くものである。

2.1 実験

延伸ポリエチレン試料は沸騰キシレン中に溶解させ，析出させることにより精製した，高密度ポリエチレンの熱プレスシートを，６０℃で１０倍に延伸して得た。この試料において，c軸の配向度は極めて良く，x線の〔００２〕反射から求めた角度分布の半値巾は7°以内である。n－アイコサンの試料はn－アイコサン単結晶の塊から（００１）面にそって切り出した。

照射は７７°Kで電子線又は^{60}Co-γ線によって行った。線量は１５Mradであり，線量率は電子線の場合0.１６Mrad／sec，^{60}Co-γ線の場合0.７Mrad／h であった。ＥＳＲ測定は７７°Kで行った。

2.2 照射したポリエチレンにおけるラジカル対の構造

ポリエチレンの結晶構造を図１に示す。延伸ポリエチレンの延伸方向はc軸に一致している。磁場Ｈｏがc軸に平行な場合の延伸ポリエチレンのＥＳＲスペクトルを図２(a)に示す。中央のスペクトルは孤立アルキルラジカルによるものであり，両側のスペクトルは二つのアルキルラジカルにより構成されるラジカル対によるものである。磁場Ｈｏとc軸とのなす角(γ)を変えるとＥＳＲスペクトルはb（γ＝１０°） c（２０°） d（９０°） のように変化する。この時，両側のＥＳＲスペクトルのそれぞれの中心の間の距離（微細分離d，図２(a)の ⟷ 印）は図３の実測点のように変化している。

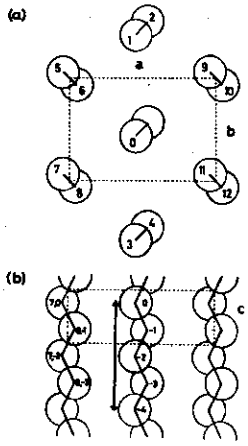


図１　ポリエチレンの結晶構造
(a)（００１）面への投影図
(b)（０１０）面への投影図
⟷ はラジカル対の構造を示す

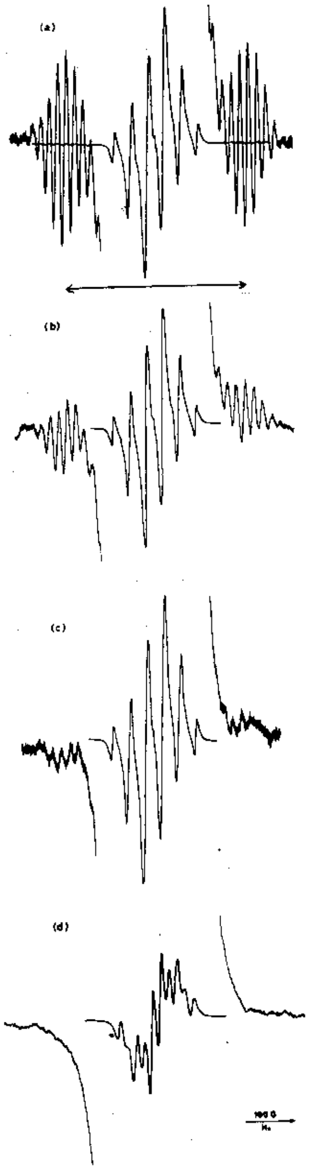


図 2　７７°Kで照射した延伸ポリエチレンにおけるΔMs＝１スペクトルの角度依存性
磁場Hと延伸方向とのなす角γ：(a)０°, (b)１０°
(c)１５°, (d)９０°
両側のスペクトルは２００倍の感度で測定した。
⟷は微細分離を示す

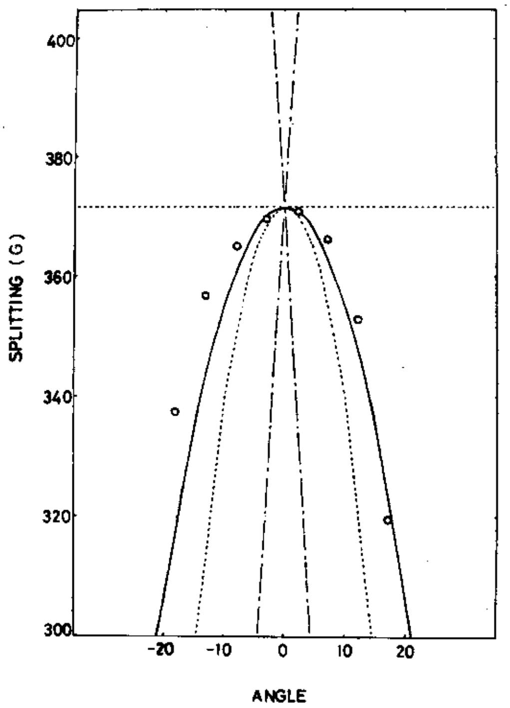


図 3　７７°Kで照射された延伸ポリエチレンにおけるラジカル対によるΔMs＝１スペクトルの微細分離の実測・理論値における角度依存性

○　実測点
――― 理論値Co－C_4，
……… 理論値Co－$C_{7,0}$
－－－ 理論値Co－$C_{8,-1}$
（図１参照）

微細分離dは点双極子近似がなりたつ場合には，次のように表される。

$$d = 3g\beta(1 - 3\cos^2\Theta)/2r^3 \qquad (1)$$

ここで**g**はgテンソル，βはボーア磁子，Θは磁場Ho とラジカル対の二つのラジカルを結ぶベクトル**r**とのなす角である。延伸ポリエチレンに対して図4のような座標軸を取った。Z軸はc軸と一致し，YZ平面はc軸に垂直である。ここで**r**は角度θ，ϕにより規定され，γは磁場Ho とZ軸（c軸）とのなす角である。この座標系において角度Θは

$$\cos\Theta = \sin\theta\sin\phi\sin\gamma - \cos\theta\cos\gamma \qquad (2)$$

と表される。(1)，(2)式を用いてポリエチレンの結晶構造から考えられるいくつかの構造のラジカル対における微細分離の理論曲線を作成し実測値と比較した。この際必要な延伸ポリエチレンの77°Kにおける結晶格子定数は知られていない。そこで，77°Kにおける粉末ポリエチレンの格子定数に，室温における10倍延伸ポリエチレンと粉末ポリエチレンとの格子定数の比を乗じて，延伸ポリエチレンの77°Kにおける格子定数を推定した。

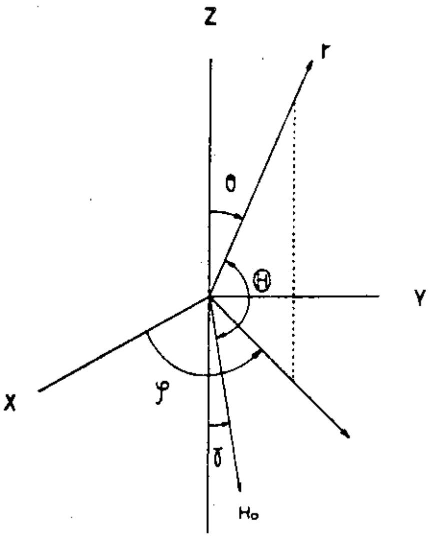


図4　延伸ポリエチレンにおける延伸軸（Z軸）と磁場Ho を関係づける座標軸。磁場はYZ平面内にある

このような解析により実測されたラジカル対は，c軸方向にならんだ二つのラジカルからなる分子内ラジカル対であることが判明した。二つのラジカル間の距離は5.31Åである。このラジカル対は，ポリエチレンを放射線照射した際に生成する二重結合の先駆体と考えられる。

以上のように，ポリエチレンには分子内ラジカル対が存在することがわかったが，この他の実験事実によって，分子内以外のラジカル対の存在も明らかとなった。この分子内ラジカル対以外のラジカル対が延伸ポリエチレンにおいて，ΔMs＝1スペクトルを与えないのは次のような理由によるものと考えられる。ここで用いた延伸ポリエチレン試料はよく配向しているが，非晶又は結晶欠陥領域が試料中に存在するために，c軸に垂直方向にならんだ二つの分子の間の距離には不規則性が存在する。このためΔMs＝1スペクトルの微細分離には分布が生じ，分子間方向（すなわちc軸に垂直な方向）にならんだ二つのラジカルからなるラジカル対のΔMs＝1スペクトルは明瞭には現れない。これに対して分子内ラジカル対の場合には，二つのラジ

カルは共有結合によって固定されており，明瞭なスペクトルを与える。以上のような考察によりn－アイコサン単結晶をポリエチレンのモデル化合物として選び，ポリエチレンではΔMs＝1スペクトルが得られなかった分子間ラジカル対についての情報を得ることとした。

2.3　照射したn－アイコサン単結晶におけるラジカル対の構造

アイコサンの結晶は三斜晶系であって，室温において次のような格子定数を持っている。

$a = 4.281\,\mathrm{\AA}$,　$b = 4.820\,\mathrm{\AA}$,　$c = 25.52\,\mathrm{\AA}$

$\alpha = 91.18°$,　$\beta = 93.53°$,　$\gamma = 107.35°$

77°Kにおける格子定数はx線回析実験を室温以下で行って格子定数の温度依存性を77°Kに外挿することにより得た。こうして得られた格子定数は，$a = 4.18\,\mathrm{\AA}$，$b = 4.70\,\mathrm{\AA}$である。（c，α，β，γは室温におけるそれらと同じであると仮定した）このアイコサン単結晶に対して図5のような座標軸を取った。図5には結晶の（001）面に対する投影を示してある。ここでφはC－Cジグザグ面と，b軸XY面への投影とのなす角であって，これまでデータがないのでESR解析により求めた。

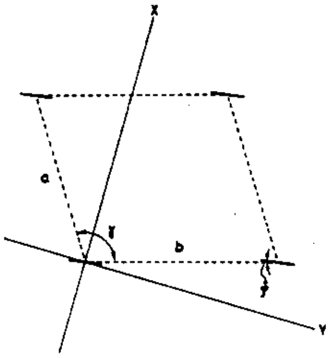


図5　n－アイコサンの結晶構造。（001）面への投影図φはC－Cジグザグ面と，b軸のXY面への投影とのなす角

このように設定した三軸直交系において，YZ平面内にあって，Z軸から－10°，－80°，54°の方向に磁場が向いた場合のESRスペクトルを図6に示す。両側のスペクトルはラジカル対によるものである。このラジカル対の微細分離の角度変化をプロットしたのが図7である。(1)式を用いて考え得る構造を持つラジカル対の理論曲線を作成し理論値と比較した。次にXZ平面においても同様に理論曲線と実測値を比較した。このような方法により見出されたラジカル対の構造を図8に示す。b軸方向に二つのラジカルがならんだ分子間ラジカル対四種，およびa軸方向の分子間ラジカル対一種の存在が明らかとなった。この他にポリエチレンで見出された分子内ラジカル対（図8(c)）の存在も示唆された。

2.2，2.3の結果によりポリエチレンにおいては分子内ラジカル対が，またn－アイコサン単結晶で見い出された分子間ラジカル対はポリエチレンにも存在すると強く示唆される。ポリ

エチレンに存在する分子内および分子間ラジカル対は，それぞれ二重結合，架橋の先駆体と考えられる。

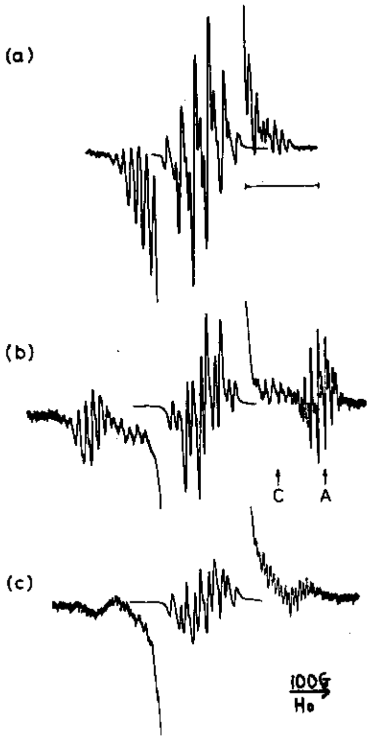


図 6　　77°Kで照射し観測したn－アイコサン単結晶のESRスペクトル
磁場方向はYZ面内においてZ軸から
(a) －10°, (b) －80°, (c) 54°　である
両側のスペクトルは180倍の感度で測定した

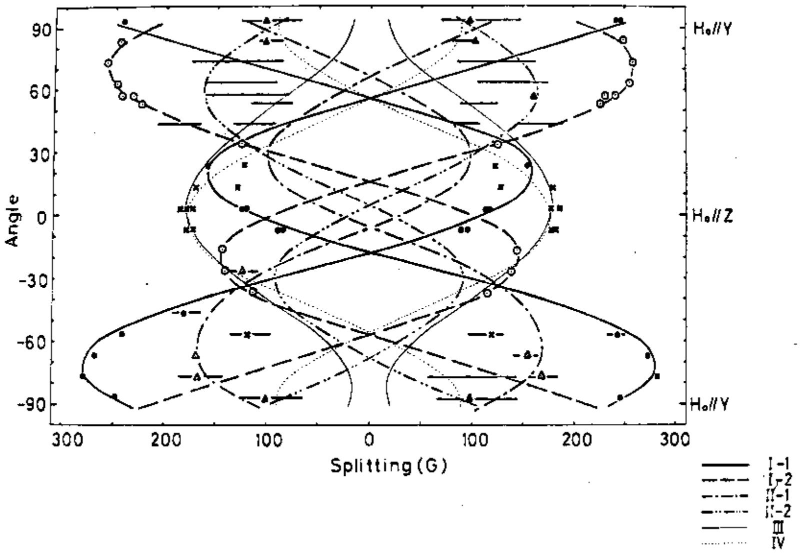


図 7　　XZ面内におけるラジカル対の微細分離の角度依存性

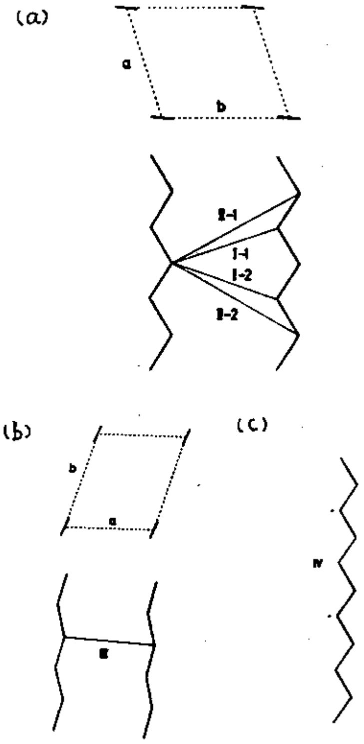


図 8　ラジカル対の構造
(a)　b 軸方向にならんだ分子鎖上に生成した分子間ラジカル対
(b)　a 軸方向にならんだ分子鎖上に生成した分子間ラジカル対
(c)　分子内ラジカル対

3. ポリエチレンにおけるラジカルの存在・反応領域

結晶性高分子であるポリエチレンのラジカル反応による照射効果を解明するには，ラジカルがポリエチレンのどの領域に存在するかを知る必要がある。その一例を次に挙げると，アリルラジカルは真空中室温で安定である。電線被覆としてしばしば使われるポリエチレンの肉厚のシートの内部において，酸素の拡散が抑えられるため，真空中の状態に近くなりアリルラジカルは長い間安定に存在するであろう。このようなことからアリルラジカルがどのような所に存在し，その遅い反応によって長時間経過した後で，材料にどのような影響を与えるかを調べる必要がある。

ポリエチレンの領域の別け方についてはいくつかの説があるが，ここでは次の別け方によった。

1. 非晶領域
2. 結晶の表面，結晶の欠陥

3. 結晶コア領域

非晶領域において，ポリエチレンの分子鎖は全くランダムになっている。これに対し結晶コア領域は，結晶部分の内部であって，分子鎖が規則正しく並んでいる領域である。結晶の表面は，結晶部分であるがその表面近くはfoldなどが存在するため，分子鎖が結晶コアよりも乱れている領域である。次に，結晶の欠陥とは結晶の内部であっても，高分子の結晶の場合は金属の結晶とは異なり，多くの欠陥を含んでおり，このような部分をさす。なお1.の非晶領域と2.の結晶の表面，結晶の欠陥はnon-crystalline regionとしてまとめて扱われることもある。

上記のように，ポリエチレンにはいくつかの領域があるが，ポリエチレンにおける重要な二種類のラジカル，アルキル，アリルがどのような領域に存在し，反応・消滅するかについては報告があまりない。このうちアルキルラジカルについては，いくつかの報告があるが，アリルラジカルについては，ほとんどないと言って良い。

本章では77°K照射によってポリエチレンに生成したアルキルラジカルが，ポリエチレンのどのような領域で反応し，消滅するかについて述べる。

次にポリエチレンの単結晶マットを試料として用い，77°Kで生成したアルキルラジカルと二重結合とが反応してアリルラジカルとなる反応が，どのような領域で起っているか，またその結果アリルラジカルがどのような領域に捕捉されるかについて述べた。また反応にあずかる二重結合の種類によってアリルラジカルの種類にも区別が生ずることも述べた。

3.1 照射したポリエチレンに生成するラジカルの減衰反応

実験に用いた試料およびその諸性質を表2に示す。77°Kで照射した各種ポリエチレン試料を各温度で5分間熱処理し，ふたたび77°Kで測定した際の熱処理温度に対するΔMs＝1 ESRスペクトル強度（全ラジカルの濃度に対応する）の変化を図9に示す。高密度ポリエチレンのスペクトル強度の変化において見られるように，熱処理によるアルキルラジカルの減衰には三つの領域がある。すなわち，第一減衰領域は120°K付近であり，第二減衰領域は200°K付近である。第三減衰領域は250°K以上である。

表　2

Characteristics of polyethylene

Sample	Rigid fraction[a]	Crystalline fraction[b]	Crystal size[b]	CH_3/1000C	M.W. $\times 10^{-4}$
High-density polyethylene (Sholex 6050)	93 %	83 %	207 Å	~0	4.8
Low-density polyethylene (Sumikathene G804)	—	54	—	28.6	1.7
Radiation-polymerized polyethylene* polymerized at					
30°C, p-24	90	76	130	2.5	8.2
95°C, p-2	76	67	160	90	2.2

* polymerized at 30°C and 95°C under a pressure of 400 kg/cm^2

a　measured with broad line NMR

b　measured with X-ray diffraction method

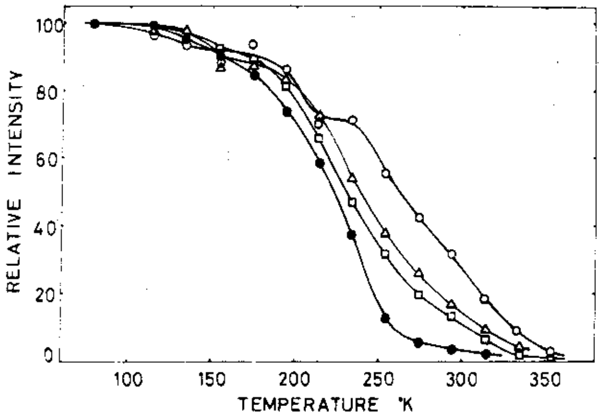


図9　77°Kで照射したポリエチレンにおける $\Delta Ms=1$ スペクトルの試料を熱処理することによる減衰曲線

○　高密度ポリエチレン
●　低密度ポリエチレン
△　放射線重合ポリエチレン（重合温度95℃）
□　放射線重合ポリエチレン（重合温度30℃）

第一減衰領域におけるラジカルの減衰にはラジカル相互間の距離を考える必要がある。図10に各種ポリエチレンに生成したラジカル対による $\Delta Ms=2$ のスペクトル強度の試料を熱処理することによる変化を示す。第一減衰領域（120°K付近）でかなり強度が減少しており，ラジカル対が減衰している。このことはラジカル対が第一減衰反応領域において重要な役割をはたしていること，すなわち二つのラジカル間の距離が重要な要因であることを示す。また77°Kにおける $\Delta Ms=1$ ESRスペクトルはブロードな成分とシャープな成分に分けられる。このブロードな成分は極めて近くにある二つのラジカルの相互作用によって生ずる。試料を熱処理するとブロードな成分のみが減衰する。すなわち互に極めて近くにあるラジカルのみが減衰している。このこともまた二つのラジカルの間の距離が第一減衰領域におけるラジカルの減衰に重要な要因となっていることを示す。

第二減衰領域についてはこの領域とnon-crystalline regionにおける分子運動と結びつけた従来の説が正しいと思われる。

第三減衰領域において実測されるESRスペクトルは完全な異方性を持っている。すなわち，この場合ラジカルは結晶領域に捕捉されていることがわかる。さらに，第三減衰領域内の二つの異なった温度におけるスペクトルを差し引いて得られたスペクトルが異方性を持つことから，この領域において，結晶領域にあるラジカルが減衰していることが明らかとなった。

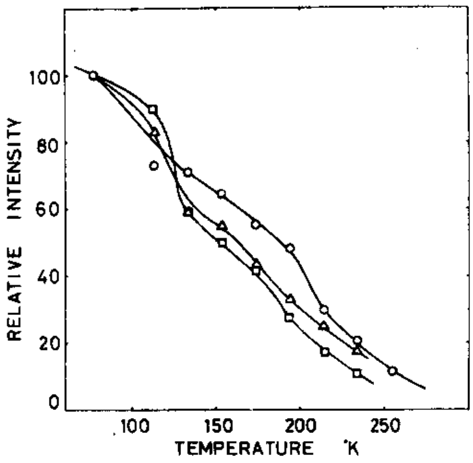


図１０　７７°Kで照射したポリエチレンにおける$\Delta Ms = 2$スペクトルの試料を熱処理することによる減衰曲線
○　高密度ポリエチレン
△　放射線重合ポリエチレン（重合温度９５℃）
□　放射線重合ポリエチレン（重合温度３０℃）

3.2　照射したポリエチレン単結晶マットにおけるアリルラジカルの存在領域

７７°Kで照射したポリエチレン単結晶マットを熱処理した際のアルキルラジカルからのアリルラジカルへの転換を図１１に示す。アリルラジカルは２２０°Kで現われ２６０°Kまでは増大するが，さらに熱処理すると減少する。この事実は７７°Kで照射した試料を室温で熱処理するならばアルキルラジカルからアリルラジカルへの転換が効果的に行われることを示している。

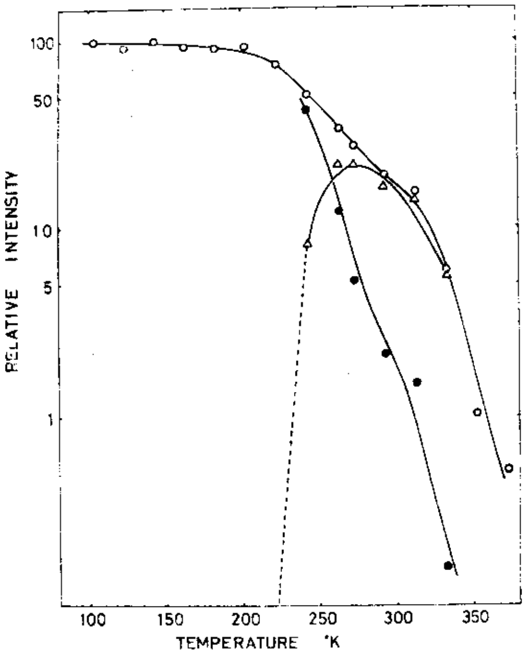


図１１　７７°Kで照射したポリエチレン単結晶マットを熱処理した際のアルキル→アリルへの転換
○　全ラジカル　　●　アリキルラジカル
△　アリルラジカル

図１２−１(a)(b)に上記のようにして得られたアリルラジカルのＥＳＲスペクトルを示す。単結晶マット試料を７７°Kで照射し，室温，真空中に３週間置いたものである。この試料を５分間３３３°Kで熱処理しても図１２−２に示すように，図１２−１に定義したスペクトルの分離度(R)はほとんど変化しなかった。（R＝0.20）図１２−３に図１２−１から図１２−２を差し引いたスペクトルを示す。図１２−１〜３まですべて異方性があり，この温度領域ではポリエチレン中に存在するアリルラジカルは結晶領域に存在し，かつ結晶領域において減衰していることがわかる。３３３°Kで５分間熱処理した試料を室温で４カ月真空中に放置して得られた試料のＥＳＲスペクトルを図１２−４に示す。スペクトルの分離度は図１２−２よりも良くなっている。（R＝0.40）このことは，アリルラジカルのうちより巾広いスペクトルを与える成分が室温で長時間放置したことにより減衰したことを示す。結晶領域には結晶コア領域と結晶の表面・結晶の欠陥がある。結晶の表面・欠陥に存在するアリルラジカルのＥＳＲスペクトルは，結晶コア領域に存在するアリルラジカルのそれよりもより巾広いはずである。上記のことからアリルラジカルは結晶のコア領域にも結晶の表面・欠陥にも存在することが明らかとなった。

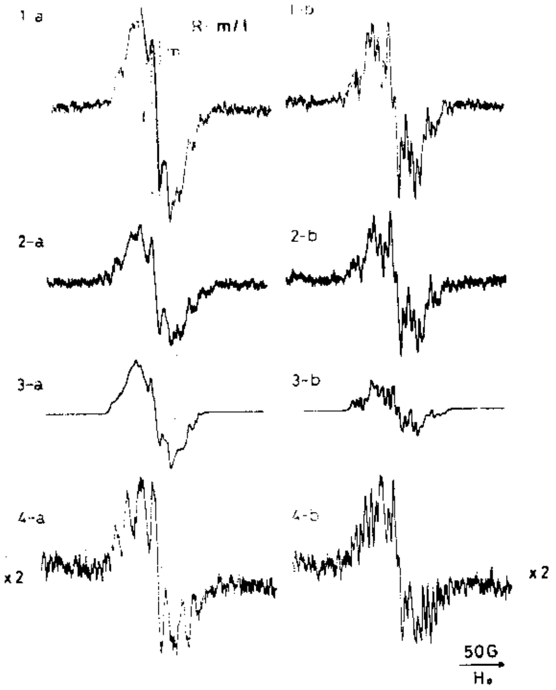


図１２　ポリエチレン単結晶マットに生成したアリルラジカルのＥＳＲスペクトル。観測は室温で行った。磁場はマット面に対して平行(a)，垂直(b)である

１−a，１−b；７７°K真空中で照射し，室温で３週間放置した試料
２−a，２−b；上記試料を５分間３３３°Kで熱処理した試料
４−a，４−b；２−a，２−b試料を４カ月室温で放置した試料
３−a，３−b；１−aおよび１−bから２−aおよび２−bを差し引いて得られたスペクトル

アリルラジカルはアルキルラジカルがポリエチレン中に存在する二重結合と反応して生成するとされている。二重結合のうちトランスービニレン型二重結合は照射により主として結晶コア領域に生成するとされている。したがって結晶コア領域に存在するアリルラジカルはトランスビニレン型アリルラジカルであると考えられる。一方未照射試料の，主として結晶表面に存在するビニルエンド型二重結合がアルキルラジカルと反応して，ビニルエンド型アリルラジカルを生成すると考えられる。

4. 結　論

本研究の結果，放射線を照射したポリエチレンには分子内および分子間ラジカル対が存在することを示し，それぞれ二重結合・架橋の先駆体であることを示唆した。また，ポリエチレンに数種の異なった構造を持ったラジカル対が存在することは，照射したポリエチレンに生成するラジカルの分布が不均一であることを明確に示すものである。

次に，放射線を照射したポリエチレンに生成するアルキルラジカルの低温における減衰には，ラジカルーラジカル間の距離が重要な要因となることを示した。さらにアルキルラジカルが二重結合と反応してできるアリルラジカルは，結晶コア領域および結晶の表面の両領域に存在することなどを示した。

2. Electron Spin Resonance Study of Radicals in Irradiated Polyethylene

Contents

2.1 Introduction

The reason for the great interest in studying the chemistry and radiation chemistry of polyethylene is found to be due to the simplicity in its chemical structure as a fundamental material for the research of polymeric system. One of the significant characteristics of physical state of polyethylene is that there are two regions, crystalline and non-crystalline.

The studies of radiation effect on polyethylene have appeared at the end of the 1940's,[1] which was primarily aimed to elucidate the radiation-induced reaction in polyethylene including the formation of gaseous products and cross-link, the reduction of existing unsaturation and the production of new unsaturation.

A few years after the early studies, electron spin resonance (ESR) studies was started to detect and identify the free radicals produced in irradiated polyethylene. Three types of radicals have been found and the structure of these free radicals was made clear as following; alkyl $(\text{-CH}_2\text{-}\dot{\text{C}}\text{H-CH}_2\text{-})$,[3] allyl $(\text{-CH=CH-}\dot{\text{C}}\text{H-CH}_2\text{-})$[4] and polyenyl radicals $(\text{-CH}_2\text{-}\dot{\text{C}}\text{H}\ (\text{CH=CH})_n\text{-CH}_2\text{-})$.[5,6] Many studies have also been carried out about the behavior of these radicals.[7,8]

When two radicals are frozen very closely with each other, the set of these two radicals are called radical pairs. In the organic single crystals of low-molecular-weight compounds, the pairwise trapping of radicals has been studied by several workers and the structures of radical pairs have been made clear.[9,10] In the polymeric system, although the presence of radical pairs have been clarified,[11] their structure have not been determind. Radical pairs produced in polymers are important as the precursors in the reaction leading to the crosslink and double bond formation.

At the first part of the present work, we report the determination of the structure of radical pairs produced in oriented polyethylene. This is the first which determines the structure of radical pairs in the polymeric system. In the single crystal of the irradiated n-eicosane which can be regarded as a model compound of polyethylene, the structures of radical pairs were also determined.

As mentioned previously, there are crystalline and non-crystalline regions in polyethylene. It is important to know in what region these radicals are trapped in order to elucidate the mechanism of radiation effects resulting from these radicals.

Although rather small number of studies[12-15] concerned with the region of radical trapping have been appeared, these are fragmentary and concern with only one kind of radical. Moreover, several respects which are insisted in these studies are contradictory to each other. The second part of this work aimes to investigate in detail the regions where the trapping, converting, reacting and disappearing of alkyl and allyl radicals take place.

The present work clarified in the first part the distribution of radicals produced in irradiated polyethylene by determing the structure of radical pairs. In the following part of this work the regions where radicals behave was also made clear. These results and conclusions will contribute to the elucidation of the mechanism of radiation effects.

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2.2 Electron Spin Resonance Study on the Structure of Radical Pairs in Irradiated Polyethylene and Single Crystal of Model Compound

2.2.1 Introduction

When solid absorbs radiation energy, chemical bonds are ruptured and the resulting two fragments, which are radicals or ions, appear. These species behave in some different ways depending on the kinetic energy of the fragments and the "hardness" of matrices in which the fragments are produced. Firstly, the geminate recombination to form parent molecules takes place (cage effect). Secondly, the fragments diffuse in the solid and are then trapped in the matrix when the fragments lose their kinetic energy (isolated radicals). Thirdly, the fragments formed are frozen very closely with each other within a distance of several times of the length of chemical bonds (radical pairs). The pairwise stabilizing of fragments must play an important role in the reaction which occurs in irradiated solids. As shown following, radical pairs are also formed by the other mechanism different from the one indicated above. When a molecule decomposes, a light atom is usually released from the molecule which reacts with neighboring molecule to give the second radical. This is the case that the present work describe.

The theoretical background for the ESR spectra due to radical pairs have been given by Kurita.[1] It has been shown that ESR spectra are split in doublet due to dipolar interaction between two unpaired electrons of radicals. Under some condition, this splitting is larger than the whole hyperfine splitting of isolated radicals. Therefore, we can take clear spectra due to radical pairs in both sides of the spectrum resulting from isolated radicals. If the sample used is anisotropic, these doublet-splittings vary widely when the orientation of sample to the direction of the magnetic field is changed. This variation of splittings due to the change of the orientation of the sample makes it possible to determine the distance between two radicals and the orientation of vector connecting two radicals to the axis of anisotropic samples. Knowledge on the structure of radical pairs indicates the location of radicals in the lattice of crystal. This method opens a new potentiality for the study of elementary reaction in radiation chemistry.

Since Kurita[1,2] found the radical pairs in the single crystal of dimethylglyoxime and determined the structure of the pairs, many studies have been carried out about the single crystals of low-molecular-weight organic compounds.[3-14] Radical pairs were also found in polymeric system, such as polyethylene and polypropylene by Iwasaki[15] and his co-workers. However, the structure of radical pairs has not been determined.

In the present work, we have shown the evidence of radical pairs of intrachain type formed in oriented polyethylene irradiated at 77°K and also determined the structure. The structure determined in the present work suggests that the radical pairs of intrachain type are the precursor of double bond formation.

With regard to the radical pairs of interchain type, the experimental evidence strongly suggests that they are present in irradiated polyethylene. It was difficult, however, to determine their structure. These situations forced us to take up the single crystal of n-eicosane which can be regarded as a model compound of polyethylene. The structure of interchain radical pairs produced in this crystal were clearly determined. This is the first report concerning the determination of the structure of radical pairs in n-hydrocarbons by means of the complete ESR analysis.[16-18] The presence of interchain radical pairs in n-eicosane strongly suggests that the radical pairs of this type also present in irradiated polyethylene.

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2.2.2 Electron Spin Resonance Study on the Structure of Radical Pairs in Irradiated Oriented Polyethylene

(1) Synopsis

A well-resolved $\Delta Ms=1$ ESR spectrum due to radical pairs was observed in oriented polyethylene irradiated at 77°K; this spectrum is ascribed to the pair of alkyl radicals. The change of the fine splitting with the angle between the magnetic field and the draw direction reveals that the radical pairs produced are intrachain type rather than interchain type. When the magnetic field is parallel to the chain axis, the maximum fine splitting, 371 G, is obtained. This splitting is due to interactions between members of the radical pair; interspin distance is calculated to be 5.31 Å. The concentration of the paired radicals giving the observed $\Delta Ms=1$ spectrum is about 0.3% of that of the total radicals. On warming the sample above 77°K, the intensity of the $\Delta Ms=1$ spectrum due to the radical pair decreases faster than that of the $\Delta Ms=2$ spectrum. Some evidence was also found for the existence of other types of radical pairs in irradiated polyethylene.

(2) Introduction

The pairwise trapping of radicals has been reported in many organic substances irradiated at low temperatures by detecting the ESR signals due to the ΔMs=1 transition,[1,2] and interest has greatly increased in the study of their structure and correlation with radiation chemical reactions.[2]

The pairwise trapping of radicals in irradiated polymers has been found by detecting the ESR signals of ΔMs=2.[3,4] Iwasaki, Ichikawa and Ohmori[4] obtained the ΔMs=2 spectra due to radical pairs in irradiated polyethylene and other polymers and found the existence of radical pairs in the polymers irradiated at 77°K. The ΔMs=1 spectrum of radical pairs in polymers has not been clearly obtained. The failure to observe the ΔMs=1 spectrum has been attributed to the presumption that the paired radicals have not a specific distance in the case of polymers because of the complicated structure of polymers.[4] It is difficult, however, to obtain reliable information about the structure and behavior of radical pairs from the ΔMs=2 spectrum only.

We considered that the ΔMs=1 spectrum of radical pairs should be clearly observed in the polymeric system, if some regularity is given in the system. On the basis of this idea, we have previously obtained the ΔMs=1 spectrum with hyperfine structure due to radical pairs trapped in a single-crystal mat of polyethylene irradiated at 77°K.[5] Here, using an oriented polyethylene, we will report about the well-resolved ΔMs=1 spectrum due to radical pairs.[6] The details of the structure and of the thermal decay of radical pairs in irradiated oriented polyethylene will be reported.

(3) Experimental

Samples used are high-density polyethylene, Sholex 6050, purified with boiling xylene. A sheet of thickness 0.5 mm was formed by compression molding at 180°, quenched in ice water, and then cut into strips 3 cm wide. The strips were drawn at 60°, until an elongation of about 1000% was obtained. Good orientation of the c axis in this sample was obtained; the width at half-maximum of the angular distribution as measured from the [002] X-ray reflection is within 7°.

Irradiations were performed in vacuo at 77°K with a Cockcroft-Walton type of electron beam which provides a dosage of 15 Mrads. The energy of the electrons was 2 MeV and the current 500 μA; the dose rate was about 0.16 Mrads/sec. Some experiments were carried out with ^{60}Co γ rays to a dosage of 15 Mrad; the dose rate was 0.7 Mrad/hr. The spurious ESR signal from the irradiated quartz ampoule was eliminated by heating the ampoule while the sample was cooled in liquid nitrogen at the opposite end of the ampoule. ESR measurements were made at 77°K with Varian V-4502 X-band spectrometer. Some measurements were made with Varian E-4 spectrometer.

(4) Results

The $\Delta Ms=1$ spectrum obtained with drawn polyethylene irradiated in vacuo at 77°K with electrons is shown in Figure 1, when the magnetic field is parallel to the draw direction or the chain axis of polyethylene. Well-resolved multiplets are obviously observed on both sides of the main sextet spectrum; the sextet comes from the isolated alkyl radicals $-CH_2-\dot{C}H-CH_2-$. The outer multiplets consist of eleven lines as estimated later. The separation between the two eleven lines is 371 G and the hyperfine splitting of the eleven lines is 17 G, which is half of the value, 33.5 G, of the main sextet. When the sample was irradiated with γ rays, the spectrum of the same shape and intensity was observed.

The spectrum changes with the angle γ between the magnetic field and the draw direction as shown in Figure 2. A remarkable change of the outer spectrum is observed even at the small change of angle γ. When the magnetic field is perpendicular to the draw direction, the outer spectrum is hardly observed (see Figure 2d). The change of the main sextet spectrum is well explained by the change of α-H coupling of the alkyl radicals as already reported.[7]

The observed angular dependence of the fine splitting is indicated by open circles in Figure 3. When the angle γ is changed from zero, the fine splitting decreases. At about 20° it becomes difficult to determine the spectral position, since the spectrum is smeared out and its height decreases rapidly.

The $\Delta Ms=2$ spectra are also obtained at $g \approx 4$ with the same sample as shown in Figure 4. When the magnetic field is parallel to the draw direction, the spectrum was estimated to consist of eleven lines with hyperfine splitting of 17 G which is the same as that of the $\Delta Ms=1$ outer spectrum. When the magnetic field is perpendicular to the draw direction, a well-resolved spectrum was not obtained. These results reveal that the outer parts of the $\Delta Ms=1$ spectra undoubtedly come from radical pairs. The intensity ratio of the outer spectrum due to radical pairs to the main sextet due to isolated radicals is 3×10^{-3}. The anisotropy of the $\Delta Ms=2$ spectrum can be explained by the anisotropy of hyperfine splitting in the isolated alkyl radical.

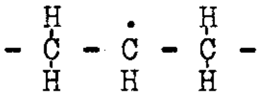
The radical pairs are less stable than the isolated radicals at 77°K. On warming of the sample, the radical pairs decay rapidly as shown in Figure 5, where the intensities of the $\Delta Ms=2$ and $\Delta Ms=1$ spectra due to the paired radicals are plotted against the temperature of heat treatment. Heat treatment of the sample was carried out by warming the sample irradiated at 77°K to the given temperature for 5 min and then cooling it back to 77°K for the measurement. It can be seen that both $\Delta Ms=1$ and $\Delta Ms=2$ spectra begin to decay at about 130°K. However, the decay amount of the $\Delta Ms=2$ spectrum is smaller than that of the $\Delta Ms=1$ spectrum. Around 200°K the $\Delta Ms=1$ spectrum decays faster than the $\Delta Ms=2$ spectrum. It is observed that the $\Delta Ms=2$ spectrum still remains at the temperature where the $\Delta Ms=1$ spectrum has almost decayed. The $\Delta Ms=1$ spectrum due to the isolated radical does not decay even at 150°K. The decay curve of the $\Delta Ms=1$ spectrum due to isolated radicals as well as that of the $\Delta Ms=2$ spectrum due to radical pairs in powder sample will be shown elsewhere.

(5) Discussion

5-1 Type of radicals composing a radical pair

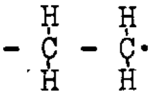
The following three types of radicals can be presumed for radical pairs in the irradiated polyethylene.

main chain type



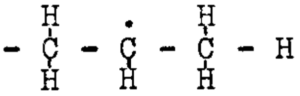
$-\overset{H}{\underset{H}{C}}-\overset{\bullet}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$

chain scission type



$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}\cdot$

chain end type



$-\overset{H}{\underset{H}{C}}-\overset{\bullet}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$

In the $\Delta Ms=2$ spectrum, when the magnetic field is parallel to the draw axis, the observed intensity ratio of the central seven lines is 1 : 2.3 : 4.3 : 5.3 : 4.4 : 2.4 : 1. In the $\Delta Ms=1$ spectrum (Figure 1) due to radical pairs, the intensity ratio of the central seven lines of the lower field spectrum is 1 : 2.5 : 4.4 : 5.2 : 4.4 : 2.8 : 1.8 and that of the higher field spectrum is 1.4 : 2.6 : 4.3 : 5.1 : 4.4 : 2.5 : 1. These results are in good agreement with 1 : 2.67 : 4.67 : 5.60 : 4.67 : 2.67 : 1, which is the theoretical intensity ratio of the central seven lines in eleven lines. Since an eleven-line spectrum comes from ten equally coupled protons, the radical pairs giving the $\Delta Ms=1$ and $\Delta Ms=2$ spectra are presumed to consist of the main chain type. The spectral intensity ratios calculated for the radical pairs of chain-scission and chain-end types do not agree with that of the observed spectra.

5-2 Structure of radical pairs for the observed spectrum

In the $\Delta Ms=1$ spectrum a fine splitting, d, due to radical pair can be expressed as follows, if the point dipole approximation is valid[1]

$$d = 3\mathbf{g}\beta\,(1 - 3\cos^2\Theta)/2\mathbf{r}^3 \qquad (1)$$

where **g** is the **g** tensor, β is the Bohr magneton, and Θ is the angle between the magnetic field Ho and the vector **r** connecting two radicals of a radical pair.

In order to calculate the theoretical angular dependence of the fine splitting in the oriented sample, a coordinate system is fixed in the sample as shown in Figure 6. The Z axis of this coordinate frame is taken to be along the draw axis, and the magnetic field defines the YZ plane. The vector **r** is defined by angles θ and ϕ in this frame, and γ is the angle between Ho and the draw axis. In this frame, angle Θ is expressed by

$$\cos\Theta = \sin\theta\sin\phi\sin\gamma - \cos\theta\cos\gamma \qquad (2)$$

Various types of radical pairs can be postulated for the main-chain alkyl radicals by use of the crystallographic data of polyethylene. Since the crystal lattice constants of drawn polyethylene at 77°K are not known, they were estimated by multiplying the lattice constants of powdered polyethylene at 77°K[8] by the ratio of the lattice constants of the 10 times drawn polyethylene to those of an undrawn one at room temperature.[9] The estimated constants are a=7.184 Å, b=4.909 Å, and c=2.547 Å. Figure 7 shows the crystal structure of drawn polyethylene with the estimated lattice constants at 77°K. The values of $\mathbf{r}$ and θ can be calculated for various sets of radical pairs by using this constant. When the values of $\mathbf{r}$ and θ are substituted in eq 1 and 2, the corresponding d values are calculated. Four d values near the observed value, 371 G, are selected as shown in Table I. It is found that the radical pairs of the interchain type C_0-$C_{7,0}$, which is the radical pair produced between C_0 and $C_{7,0}$ carbon atoms (see Figure 7), and C_0-$C_{8,-1}$ and the intrachain type C_0-C_4 have values relatively close to those observed. However, these intercarbon distances are not so different that the structure of the radical pair cannot be decided only from this comparison.

In order to decide the structure of radical pairs, the angular dependence of the fine splitting should be considered. By using eq 1 and 2, the calculated angular dependences of fine splittings are obtained as shown in Figure 3 for three types of radical pairs selected above. The calculated curve obtained with the radical pairs C_0- C_4 of the intrachain-type agrees relatively well with the observed result. However, the curves with interchain radical pairs C_0-$C_{7,0}$ and C_0-$C_{8,-1}$ differ with the observed result. The calculated curves of other radical pairs were also examined; they are far from agreement with the observed result.

These results suggest that the observed spectrum of the radical pairs is attributed to the intrachain radical pair C_0-C_4(0° intrachain type) where the vector connecting two radicals is parallel to the chain axis. The difference between the observed d value, 371 G, and the calculated d value, 419 G, may be explained by the following consideration. Since the spin densities at the α carbons of two alkyl radicals which compose a radical pair are smaller than 1, the interaction between two radicals is expected to be reduced[10] and the observed d value may be smaller than the calculated value.

5-3 Other types of radical pairs

It was presumed that the observed spectrum of radical pairs in irradiated drawn polyethylene is attributed to the 0° intrachain type. However, there are some evidences suggesting the existence of other types of radical pairs. When the sample irradiated at 77°K is heated, the $\Delta Ms=1$ spectrum due to radical pairs decays faster than the $\Delta Ms=2$

spectrum as shown in Figure 5. The intensity of the $\Delta Ms=2$ spectrum reflects all radical pairs present in the sample, while the intensity of the $\Delta Ms=1$ spectrum reflects the radical pair which is presumed to be the 0° intrachain type. This fact suggests the existence of different types of radical pairs from the observed type.

The presence of other types of radical pairs is also suggested by the following results. Figure 8 shows the intensity of $\Delta Ms=2$ spectrum vs. the angle between Ho and the chain axis. It is noticed that the intensity is almost independent of the angle. The ratio of transition probability for $\Delta Ms=2$ to that for $\Delta Ms=1$ is given by [11]

$$I_2/I_1=1/8\ (d_{/\!/} \sin 2\theta\ /Ho)^2 \qquad (3)$$

Here, $d_{/\!/}$ is the value of d when θ is zero in eq 1. If the radical pairs produced in the drawn polyethylene are composed of 0° intrachain type only, the $\Delta Ms=2$ spectrum should not be observed when γ is zero, since in this case θ becomes 0° and I_2/I_1 equals zero. Actually, however, the spectrum is observed. This result suggests the existence of the other types of radical pairs, where the vector connecting two radicals is neither 0° nor 90° to the chain axis.

Although the existence of interchain radical pairs is suggested, the problem is that they do not give distinct $\Delta Ms=1$ spectra. In the drawn polyethylene used here, the chain axes are well oriented, but there is disorder in the interchain directions because of the presence of the amorphous or the defective crystalline regions. This situation presumably causes a rather broad distribution of the d values, which smears out the $\Delta Ms=1$ spectra of interchain paired radicals. In the case of intrachain radical pairs, however, the distance between paired radicals is fixed through the covalent bond, and thus a distinct spectrum is obtained if the sample has a good orientation of chains.

In our recent investigation with the single crystal of n-eicosane, several interchain radical pairs have been observed, while the radical pairs of the intrachain type such as C_0-C_4 in the drawn polyethylene have not been clearly observed.[12] This observation may support the existence of the interchain radical pairs presumed in polyethylene.

(6) References

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Table

Intercarbon and interspin distances and d values for the radical pairs selected

Type of selected radical pairs	Intercarbon distance A	cos	d_{calcd}, G	$d_{obsd}{}^{a}$- d_{calcd}, G	Interspin distance A
C_0-$C_{5,0}$	4.70	0	265	106	4.21
C_0-$C_{7,0}$	4.03	0	421	-50	4.21
C_0-$C_{8,-1}$	4.06	0.313	290	81	3.75
C_0-C_4	5.10	1	419	-48	5.31

[a] Observed d-value is 371 G.

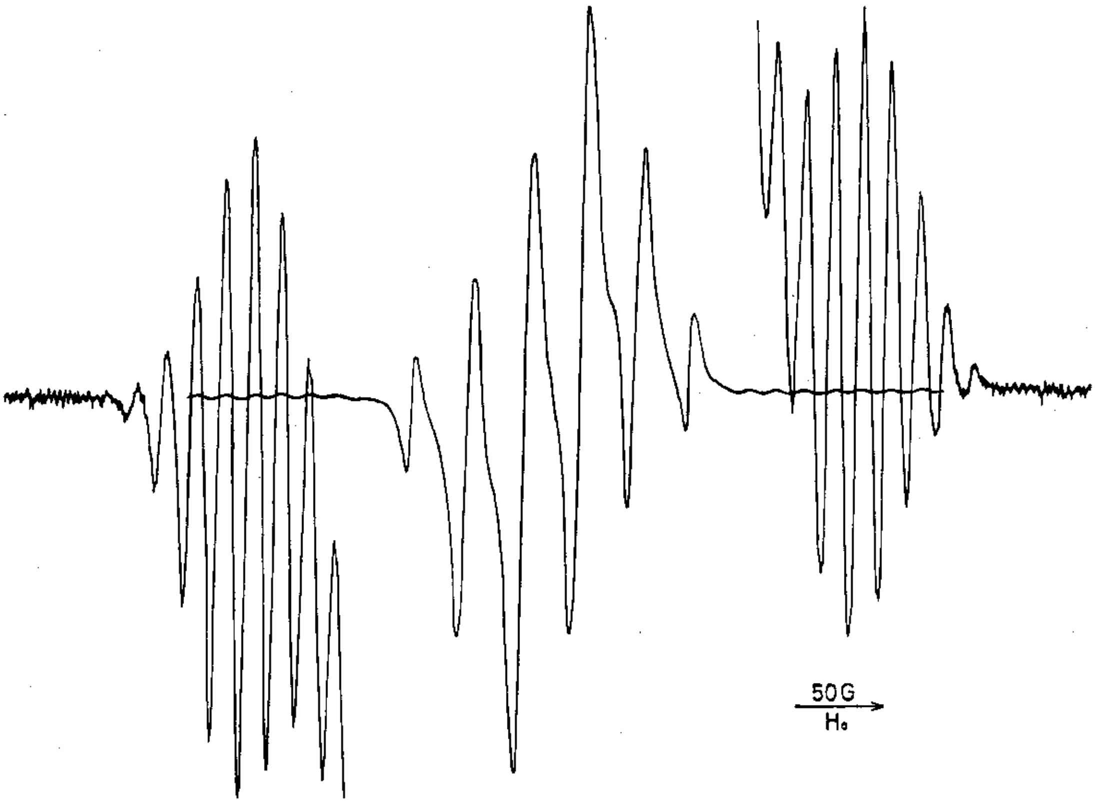

Fig. 1 The $\Delta M_s=1$ spectrum in drawn polyethylene irradiated at 77°K. Magnetic field is parallel to the draw direction or chain axis of polyethylene. Outer parts of the spectrum are recorded at increased gain (200 x).

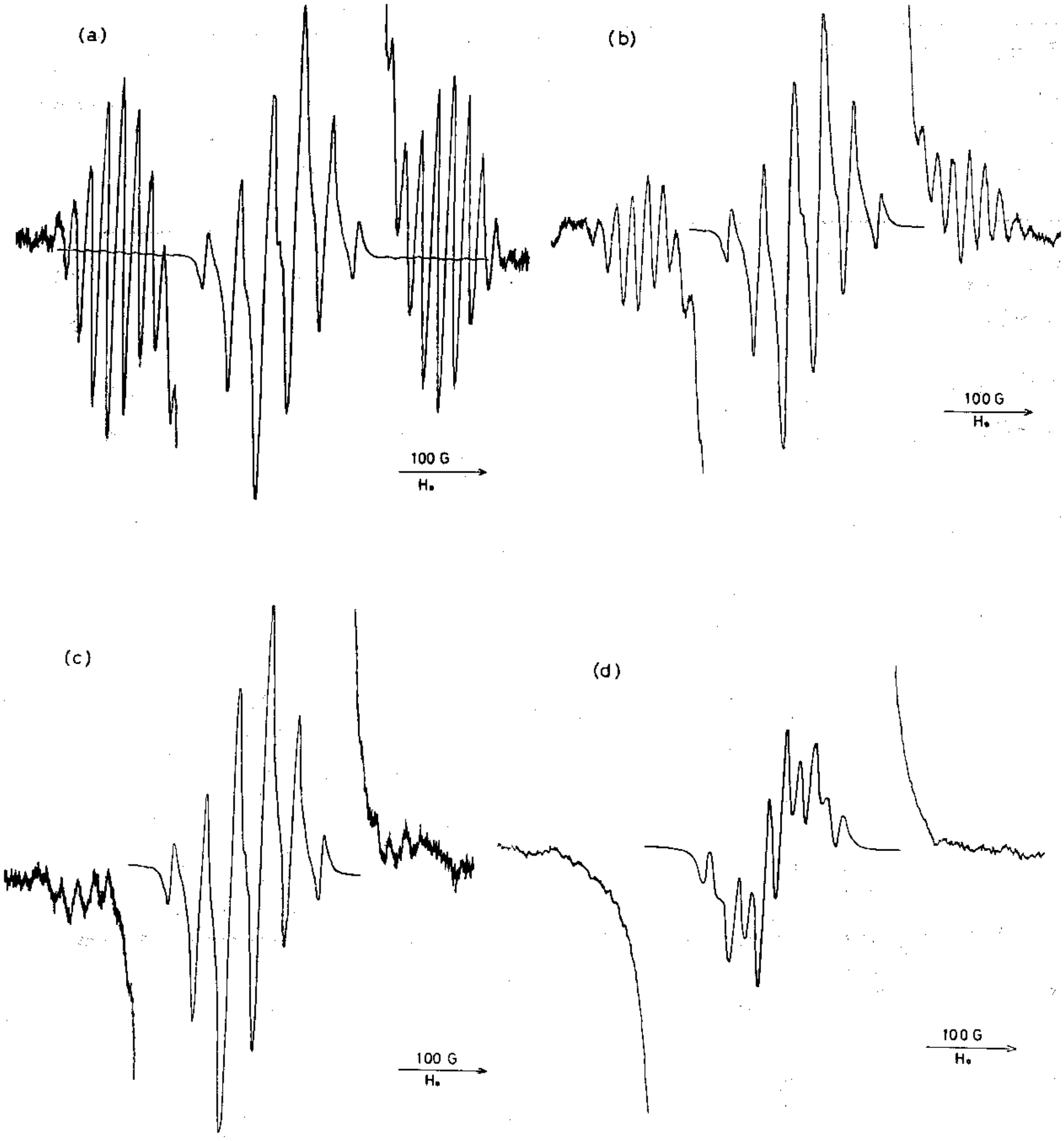

Fig. 2 Angular dependence of the $\Delta Ms=1$ spectra in drawn polyethylene irradiated at 77°K. The angle γ between magnetic field H and draw direction is (a) 0°, (b) 10°, (c) 15°, and (d) 90°.

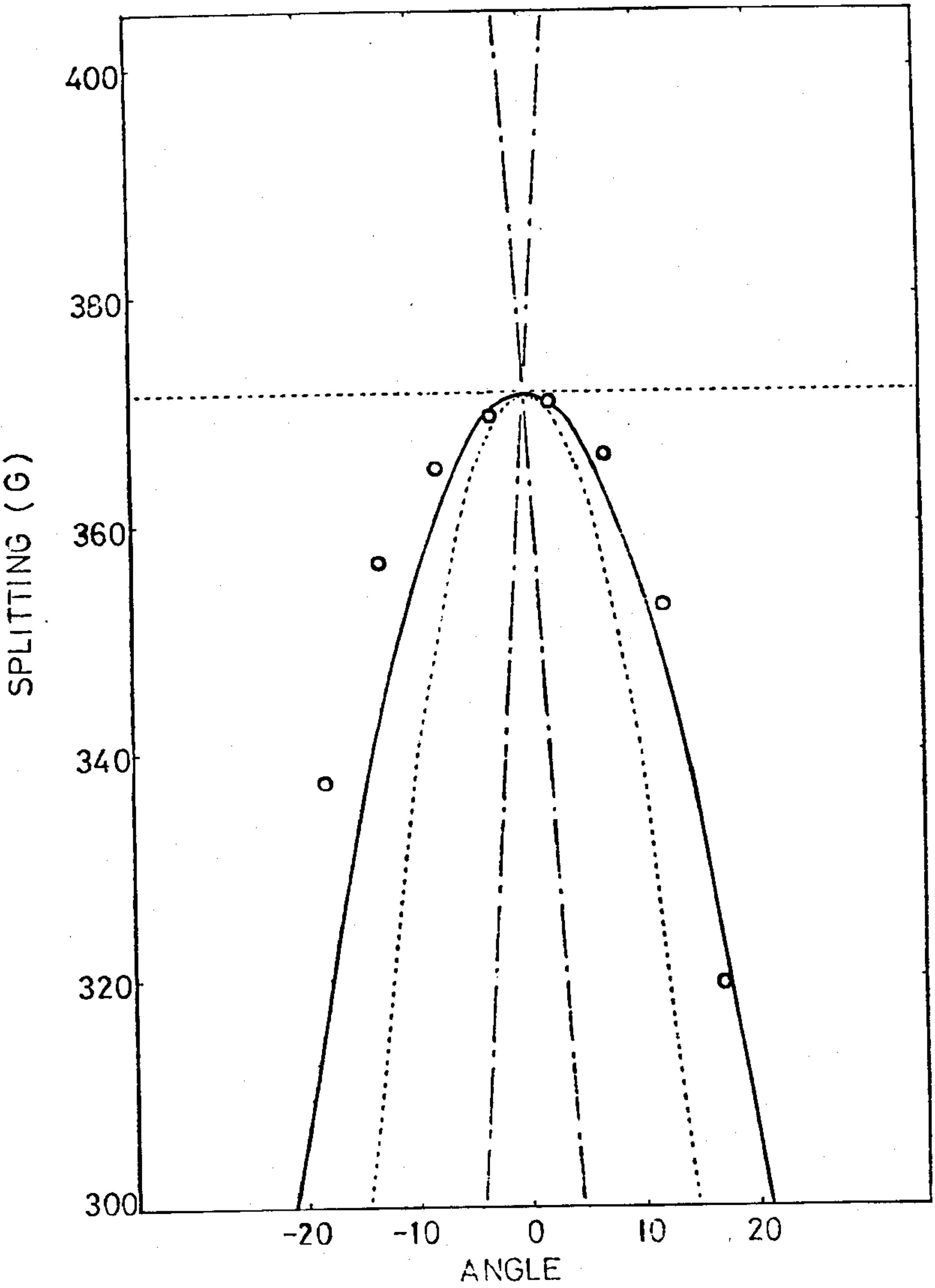

Fig. 3 Angular dependence of the observed and calculated d values of ΔMs=1 spectra due to radical pairs in drawn polyethylene irradiated at 77°K. Circles indicate observed values. Calculated values: ——, C_0-C_4; - - - -, C_0-C_7, 0; — - —, C_0-C_8, -1. (see Figure 7) The calculated d values at γ =0° are fitted to the observed values.

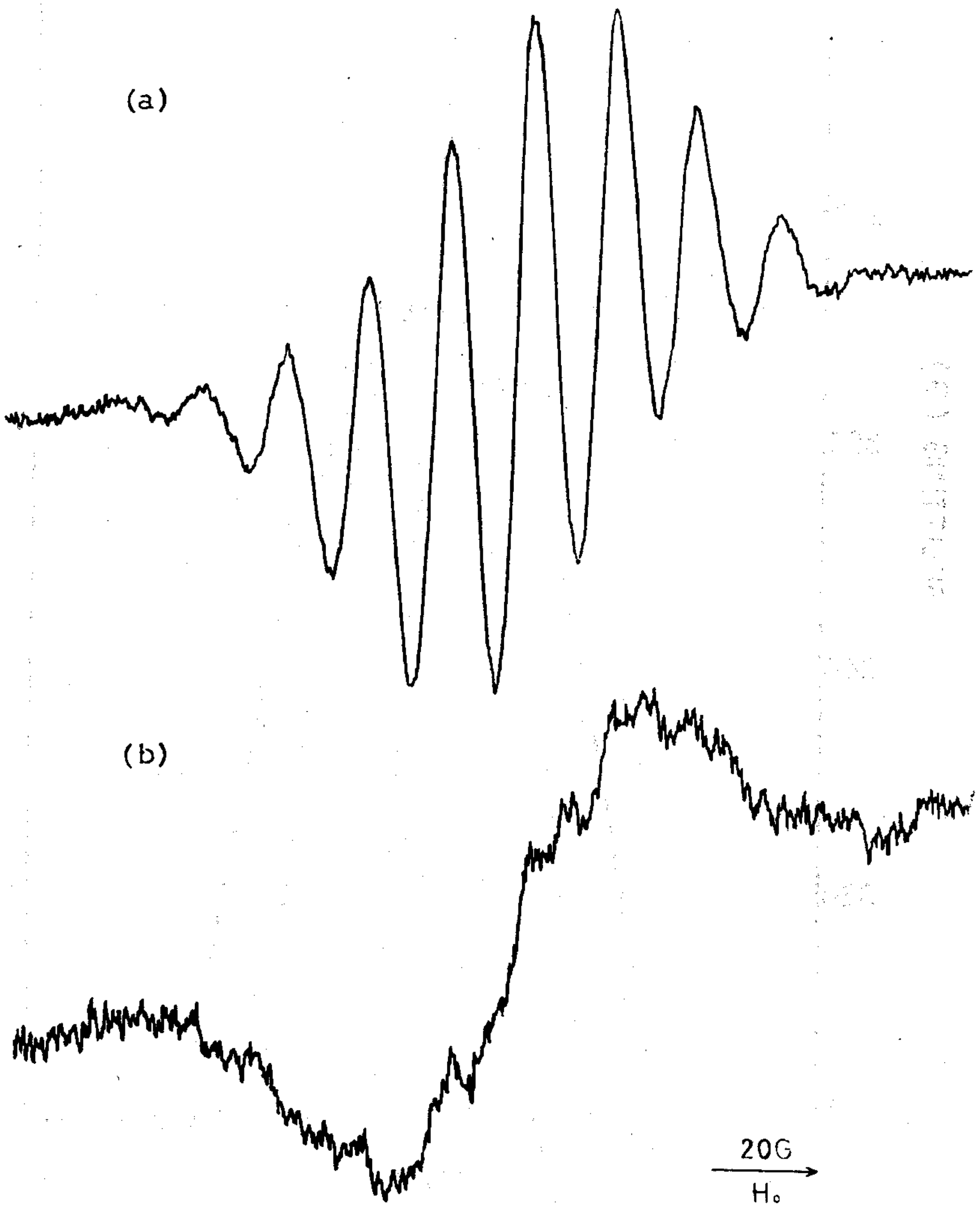

Fig. 4 The $\Delta M_S=2$ spectra in drawn polyethylene irradiated at 77°K. The angle γ between magnetic field H and draw direction is (a) 0° and (b) 90°.

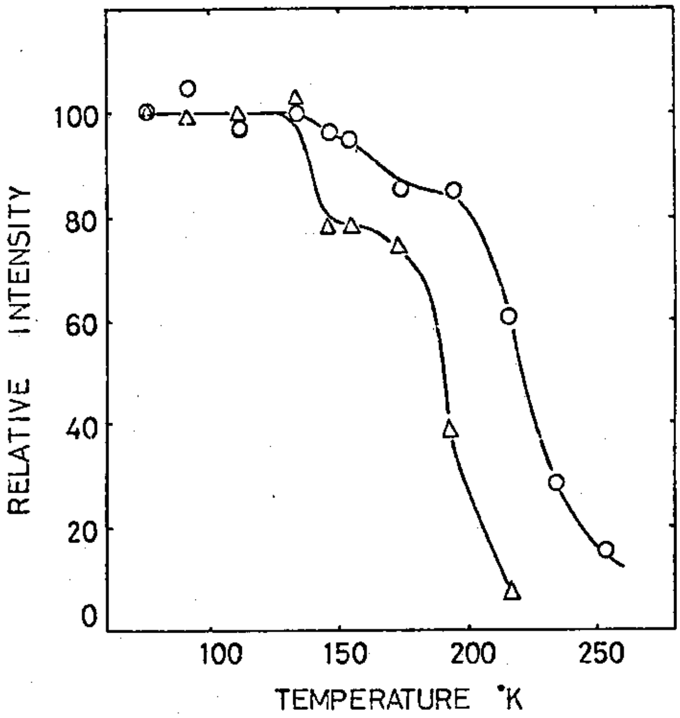

Fig. 5 Decay curves of the spectra due to radical pairs: ○, ⊿ Ms=2; △, ⊿ Ms=1.

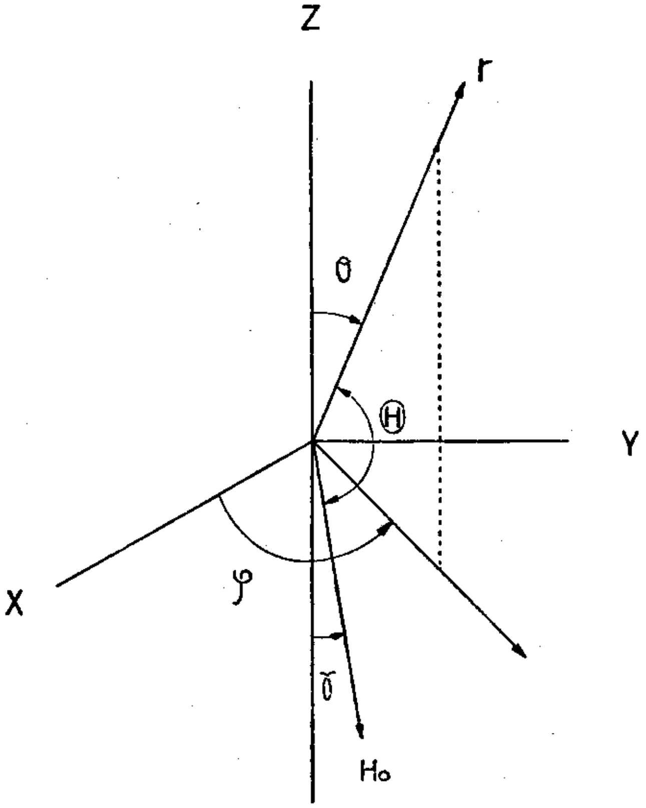

Fig. 6 Coordinates relating draw and field axes. The magnetic field defines the YZ plane.

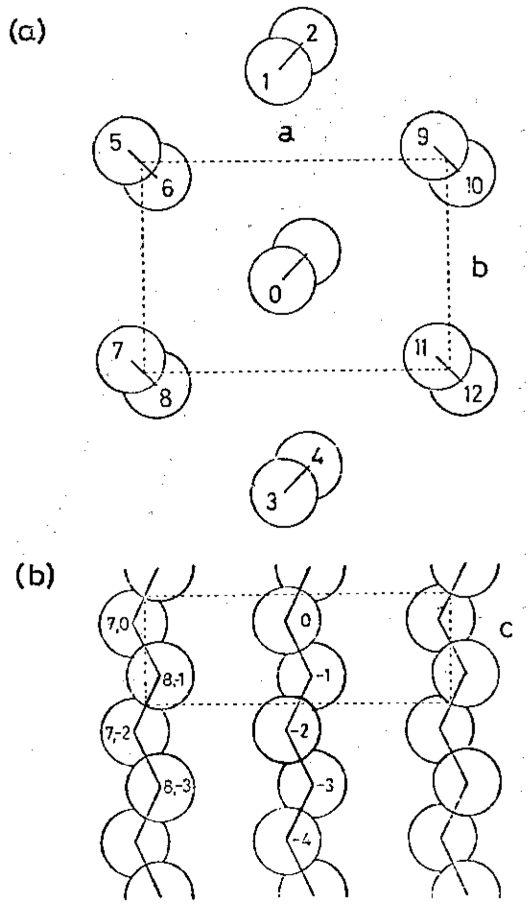

Fig. 7 Crystal structure of polyethylene at 77°K: (a) projection on (001); (b) projection on (010).

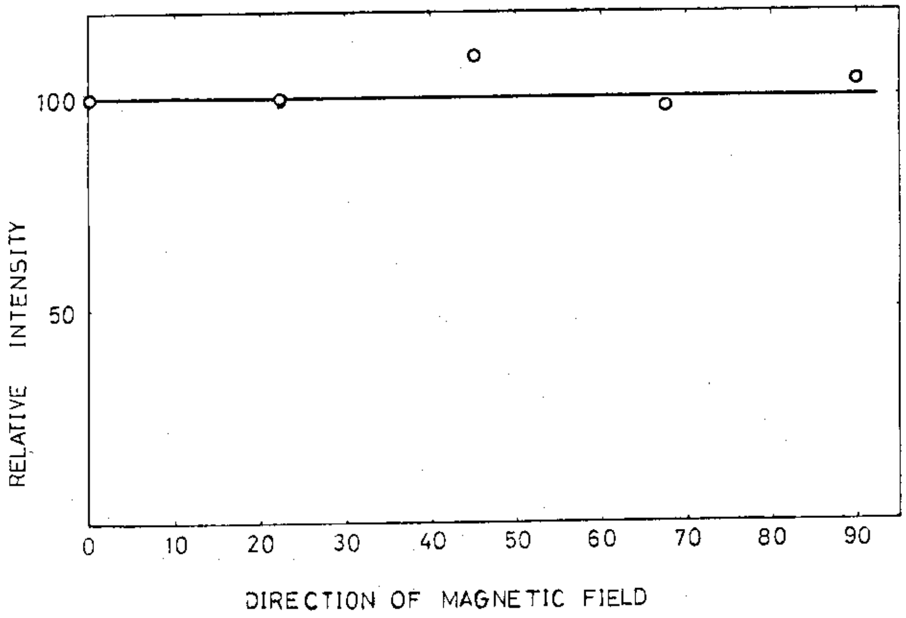

Fig. 8 Intensity of the $\Delta M_s=2$ spectrum vs. the angle γ between magnetic field and Z axis.

2.2.3 The Structure of Radical Pairs in Irradiated Single Crystal of n-Eicosane as Studied by Electron Spin Resonance

(1) Synopsis

The ESR spectra of a single crystal of n-eicosane have been analyzed. The angular dependence of the fine splitting in $\Delta Ms=1$ spectra reveals that several different radical pairs are produced in the single crystal of n-eicosane irradiated at 77°K. Five different pairs are clearly identified; they are interchain type. Among these five radical pairs four species are produced in the adjacent chains aligned along the **b** axis; their interspin distances are 4.42, 4.54, 5.22, and 5.33 Å. One other is produced in the chains along the **a** axis and has the interspin distance of 4.25 Å. The presence of the intrachain radical pairs (biradical) is also suggested. The structure of radical pair found in n-eicosane was compared with that found in oriedted polyethylene.

(2) Introduction

Radical pairs have been identified in a number of organic solids irradiated with ionizing radiation by the method of ESR.[1-7] Knowledge on the structure of radical pairs is important in the understanding of radiation chemical reactions in the solid phase.

In chapter I, we have obtained the well-resolved spectra of ESR at ΔMs=1 transition due to radical pairs in oriented polyethylene.[6,7] Analyzing the angular dependence of the fine splitting, we have determined that the observed spectrum is due to the radical pairs of the intrachain type (biradical). On the other hand, the spectrum due to the radical pairs of the interchain type was not observed, although other experimental results revealed the existence of the interchain radical pairs. The failure of the observation was presumably attributed to the disorder in the interchain directions of oriented polyethylene owing to the presence of the amorphous or the defective crystalline regions. This situation causes a rather broad distribution of fine splittings, and smears out the ΔMs=1 spectra of interchain paired radicals. To obtain more evident information concerning the structure of radical pairs, it is useful to take up the single crystal of n-alkane.

Gillbro and Lund[8] have found six different radical pairs in the single crystal of n-decane-d_{22}. They determined the upper limits of the true distances between two radicals constituting the pairs. However, the directions of the vectors connecting two radical pairs were not obtained. Hamanoue et al.[9] have studied the single crystal of n-eicosane and attempted to deduce the structure of radical pairs by compairing the intercarbon distances calculated from the crystallographic data and the interspin distances calculated from the fine splittings observed with radical pairs. In most cases, however, the intercarbon distance differs from the interspin distance.[7,10] Therefore, the structure of radical pairs proposed by these authors has not been established.

We have recently taken up the single crystal of n-eicosane and suggested the presence of at least five different radical pairs.[11] Here, we will report the angular dependence of fine splitting in the $\Delta Ms=1$ spectrum observed with radical pairs in the single crystal of n-eicosane. Several different radical pairs were found and the structure of these pairs was clearly determined.

(3) Experimental

Sample

The sample plate was cut from a large ingot of a n-eicosane($C_{20}H_{42}$) single crystal along the (001) face, because it was easily cleaved in this direction. This single crystal has a visible growth axis which is aligned along the crystal [210] axis.

The crystal structure of an n-eicosane single crystal at room temperature has been studied by Crissman et al.[12] The crystals are triclinic with space group $P\bar{1}(C_i^1)$ and have the following lattice constants:

a=4.281 Å, b=4.820 Å, c=25.52 Å,

α=91.18°, β=93.53°, γ=107.35°.

The lattice constants at 77°K were obtained by observing the temperature dependence of interplanar spacings below room temperature with a wide angle X-ray diffraction method. The lattice constants obtained are a=4.18 Å and b=4.70 Å, assuming other lattice constants, c, α, β, and γ, are the same as those at room temperature.[13]

Irradiation

Irradiation were performed in vacuo at 77°K with a Cockcroft-Walton type of electron beam which provides a dosage of 15 Mrad. The energy of the electrons was 2 MeV and the current 500 μA; the dose rate was about 0.16 Mrad/sec. The spurious ESR signal from the irradiated quartz ampoule was eliminated by heating the ampoule, while the sample was cooled in liquid nitrogen at the opposite end of the ampoule.

ESR measurements

ESR measurements were made at 77°K with Varian V-4502 X-band spectrometer. Conventional X, Y, and Z axes were chosen in such a way that the Z axis is parallel to the c axis, the X axis perpendicular to the Z axis in the (210) plane and the Y axis perpendicular to both the X and Z axes as shown in Figure 1. The rotation of the single crystal in the magnetic field was made by using three sample plates, which were used for the rotation in the YZ, ZX, and XY planes.

(4) Results and Discussion

4-1 ESR spectra

The $\Delta Ms=1$ spectrum obtained with n-eicosane single crystal irradiated in vacuo at 77°K with electrons is shown in Figure 2a, where the magnetic field is 10° from the Z axis in the YZ plane. The whole spectrum is composed of a central spectrum due to isolated radicals, and the weaker spectra due to radical pairs in both sides of the central one. The central spectrum is mainly composed of six lines which are attributed to the alkyl radicals of the main chain type $-CH_2-\dot{C}H-CH_2-$. The hyperfine splitting of the spectrum due to radical pairs is 17 G, which is half of the value, 34 G, of the main sextet. Other peaks observed in the central spectrum are attributed to alkyl radicals of the chain end type $-CH_2-\dot{C}H-CH_3$. The relative concentration of alkyl radicals of the chain end type is small, which agrees with the results obtained by Kimura et al.[14]

4-2 The packing of the molecular chains in the crystal

The packing of the molecular chains in the crystal of n-eicosane has not been determined. The packing for n-octadecane, which has the similar crystal structure as n-eicosane, has been reported.[15] However, some ambiguity is present in this result according to Crissman et al.[12] Therefore, we determined the packing from the angular dependence of the ESR spectrum due to the isolated alkyl radicals $-CH_2-\dot{C}H-CH_2-$. The angular variation of the α splitting when the magnetic field defines the XY plane is shown in Figure 3. Since the minimum principal value of the α splitting is along the direction connecting the radical carbon atom and the α proton, and the α proton lies in C-C zigzag plane, angle φ in Figure 1 is determined from the minimum value of α splitting in Figure 3. Thus, the angle φ was obtained to be 6°.

4-3 Angular dependence of the spectrum

The angular dependence of the observed ESR spectra when the magnetic field defines the YZ plane is shown in Figures 2 and 4. In Figure 4, the spectra due to two different radical pairs can be clearly seen as indicated by the bars A and B. The inner spectrum in Figure 4 is shifted to the position marked with arrow A in Figure 2b. Another spectrum C can be seen at the completely separated position in Figure 2b, which is different from the spectrum B in Figure 4. The observed positions of the spectra due to radical pairs, when the magnetic field defines the YZ plane, are plotted in Figure 5. It is expected that several different radical pairs are present in the sample.

In Figures 2b and 2c, the resolution of the radical pair spectra at the higher field is better than that at the lower field. Such phenomena may be attributed to the hyperfine anomaly which was interpreted by Iwasaki et al.[16,17] in terms of the forbidden transition arising from the mixing of the nuclear spin states by the anisotropic hyperfine interaction.

4-4 The structure of the radical pair

It is well-known that angular dependence of fine splitting can be expressed by[1]

$$d = 3\mathbf{g}\beta(1 - 3\cos^2\theta)/2\mathbf{r}^3 \qquad (1)$$

where **g** is the **g** tensor, β is the Bohr magneton, and θ is the angle between the magnetic field Ho and the vector **r** connecting two radicals of the radical pair.

Comparison of the observed data for the radical pairs in the single crystal of n-eicosane with the theoretical curve was carried out by the following procedure. At first the calculated curves for fine splittings due to radical pairs conceivable in the crystal of n-eicosane were made by using Eq. (1) and the crystallographic data at 77°K. Then some calculated curves were selected among them in such a way that the angles at the maximum separation of the calculated curves coincide with that of the observed plot. The selected curves were further examined to see whether the maximum d values are near the observed value or not; the curves where the d values are far from the observed value are omitted. Then the corrected calculated curve was constructed as shown in Figure 5 by fitting the maximum d values of the selected curves to that of the observed plot.

Consequently, four different radical pairs were selected by the above procedure. It is found that these four pairs are produced between the molecular chains aligned along the b axis as shown in Figure 6. The four radical pairs are divided into two groups (I, II); radical pairs in each group are produced in nearly symmetric positions with respect to the b axis. In Table I the interspin and intercarbon distance are compared. The interspin distance, which is the distances between two spins, was calculated from the observed d value. The intercarbon distances between two carbon atoms, where unpaired electrons are present, was calculated from the crystallographic data at 77°K. The concentration of radical pair (I-1) was about 0.3% of that of total radicals.

4-5 Other types of radical pairs

In Figure 5 the observed points marked by crosses near Ho//Z cannot be explained by the above mentioned radical pairs. The detailed inspection of the spectrum near Ho//Z suggests that the d value has a maximum when Ho is parallel to the Z axis, i.e., the long axis of the n-eicosane molecule. In order to obtain information about other types of radical pairs, the experiments, when the magnetic field defines the XZ or XY planes, were carried out. However, the resolution of the spectra due to radical pairs in the XZ plane was not as clear as those in the YZ plane, because of the dense overlap of the spectra due to different radical pairs. In the XY plane we were unsuccessful in obtaining the angular dependence of fine splitting, because of a poorly resolved ESR spectrum of the radical pairs.

The results in the XZ plane are shown in Figure 7. In this figure, the theoretical curves for the radical pairs (I-1, I-2, II-1, and II-2) were drawn by using the structure of radical pairs determined from the experiments in the YZ plane. These four curves do not fit the observed points near Ho//Z and Ho//X. It is evident that other types of radical pairs must exist in the sample.

The possible radical pairs which give these unassigned signals were examined. The calculated curve for the selected radical pair thus obtained is shown by thin solid lines in Figures 5 and 7. The selected radical pair is the interchain type (Ⅲ), where two radicals of the pair are produced in the molecular chains aligned along the a axis as shown in Figure 8(a). The interspin and intercarbon distances are shown in Table I.

The intrachain radical pair(IV) as shown in Figure 8(b) was also selected, since it gives similar variation of d values near Ho∥Z. The calculated curve is given by thin broken lines in Figures 5 and 7. In this case, however, no definite signal can be found at other angles because of the dense overlap of the spectra. Therefore, it is not clear whether the intrachain radical pairs are definitely present or not. It is noticed that the radical pairs of the same intrachain type was found in oriented polyethylene.[6,7] Although the d value has a maximum along the long axis of the n-eicosane molecule in the present study, this maximum was not found in the decane crystal.[8]

The radical pair of the interchain type found by Hamanoue et al.[9] was not clearly found in the present study. However, some observed points which do not fit the calculated curves drawn in Figures 5 and 7 suggest the presence of other types of radical pairs than those mentioned above.

It is noted that among five different radical pairs which were clearly identified, four pairs are found in the adjacent chains aligned along the b axis, while only one is found along the a axis. However, it cannot be concluded that radical pairs are selectively produced along the b axis, since the appearance of radical pairs in the spectrum greatly depends on the experimental condition. In the experiment when the magnetic field defines the YZ plane, the fine splitting due to the radical pairs along the b axis shows a large angular dependence. This situation makes it rather easy to pick up the spectrum of one type of radical pair from the others. On the other hand, the fine splitting due to the radical pairs produced along the a axis shows rather small angular dependence in this condition. Therefore, the spectra tend to overlap with those due to other types of radical pairs and isolated radicals. Consequently, it is rather difficult to pick up the spectrum.

In the experiment, when the magnetic field defines the XZ plane, the spectra of the radical pairs along the b axis show rather small angular dependence. This discloses one of the spectra due to radical pairs produced along a axis. The spectrum due to the radical pairs along the a axis may be more clearly observed when the magnetic field defines the XY plane, since the fine splittings should show a larger angular dependence in this condition. Unfortunately, no reliable spectrum due to radical pairs was obtained in this case.

The intrachain radical pairs were not clearly identified in the single crystal of n-eicosane, since the spectrum of the intrachain radical pairs tends to overlap with those of the interchain radical pairs which have sometimes large d values. This result is in contrast to the case of oriented polyethylene,[6,7] where the only spectrum observed is attributed to the intrachain radical pair. The appearance of the spectrum of the intrachain radical pairs in oriented polyethylene is attributed to the phenomena that the spectra of the interchain radical pairs are smeared out.

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Table I

Interspin and intercarbon distances and direction cosines for the radical pairs produced between the molecular chains aligned along the b (I,II) and a (Ⅲ) axes.

Radical pairs	Intercarbon distance Å	Direction cosines with respect to X	Y	Z	Interspin distance Å
I-1	4.00	0.356	0.860	0.366	4.42
I-2	4.05	0.345	0.833	0.432	4.54
II-1	5.28	0.233	0.857	0.460	5.22
II-2	5.38	0.229	0.843	0.487	5.33
Ⅲ	4.18	0.829	0.556	0.068	4.25

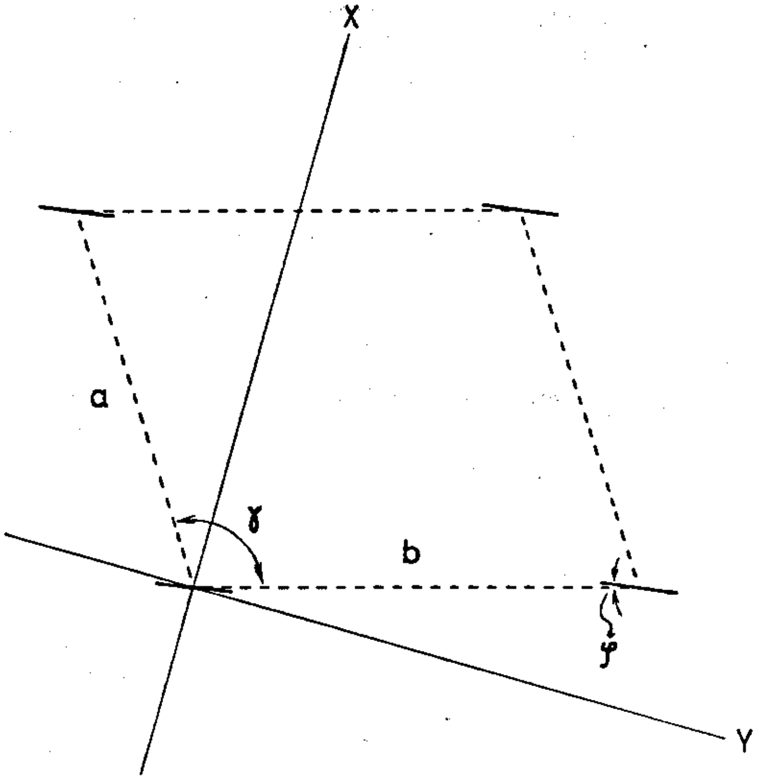

Fig. 1 Crystal structure of n-eicosane. Projection on (001). φ is the angle between the C-C zigzag plane and the projection of the b axis on the XY plane. See test.

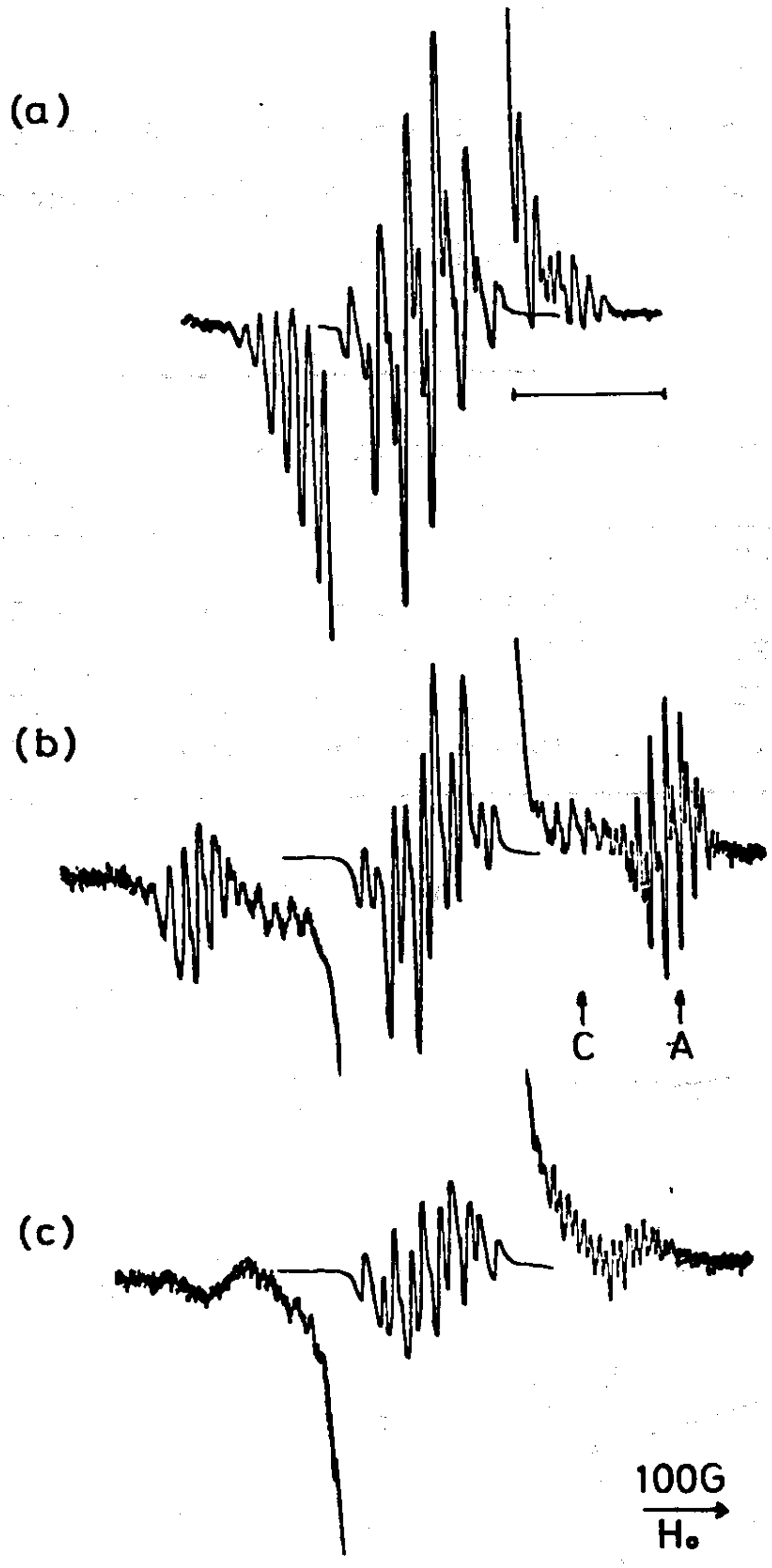

Fig. 2 ESR spectra of a n-eicosane single crystal irradiated and observed at 77°K. Measurements are made in the YZ plane at (a) -10°, (b) -80°, and (c) 54° from the Z axis. Outer parts of the spectra are recorded at increased gain (180 x). The horizontal line in (a) indicates the region of the expanded spectrum given in Fig. 4.

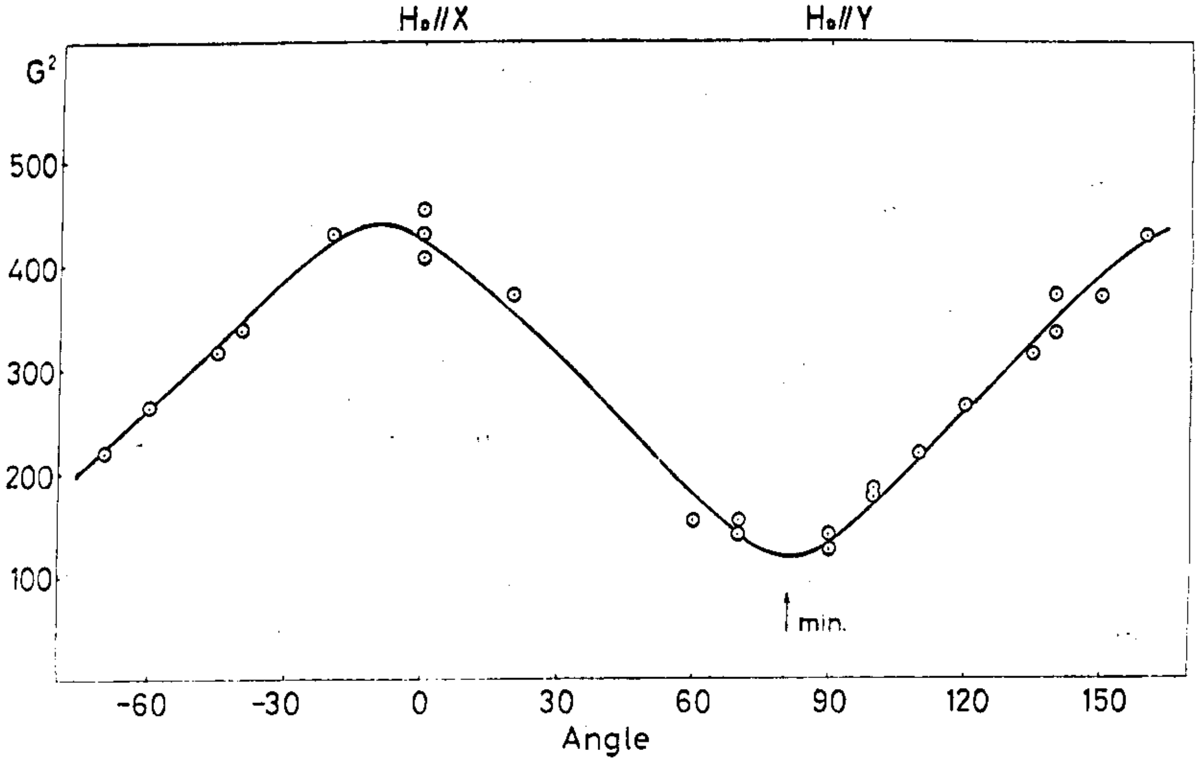

Fig. 3 Angular dependence of α splitting of the alkyl radical, $-CH_2-\dot{C}H-CH_2-$ produced in a n-eicosane single crystal. Measured in the XY plane.

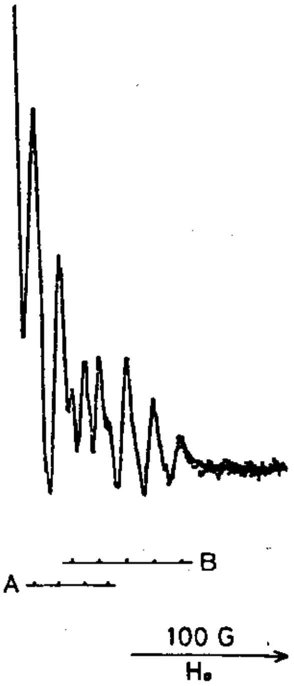

Fig. 4 The expanded spectrum of Fig. 2(a).

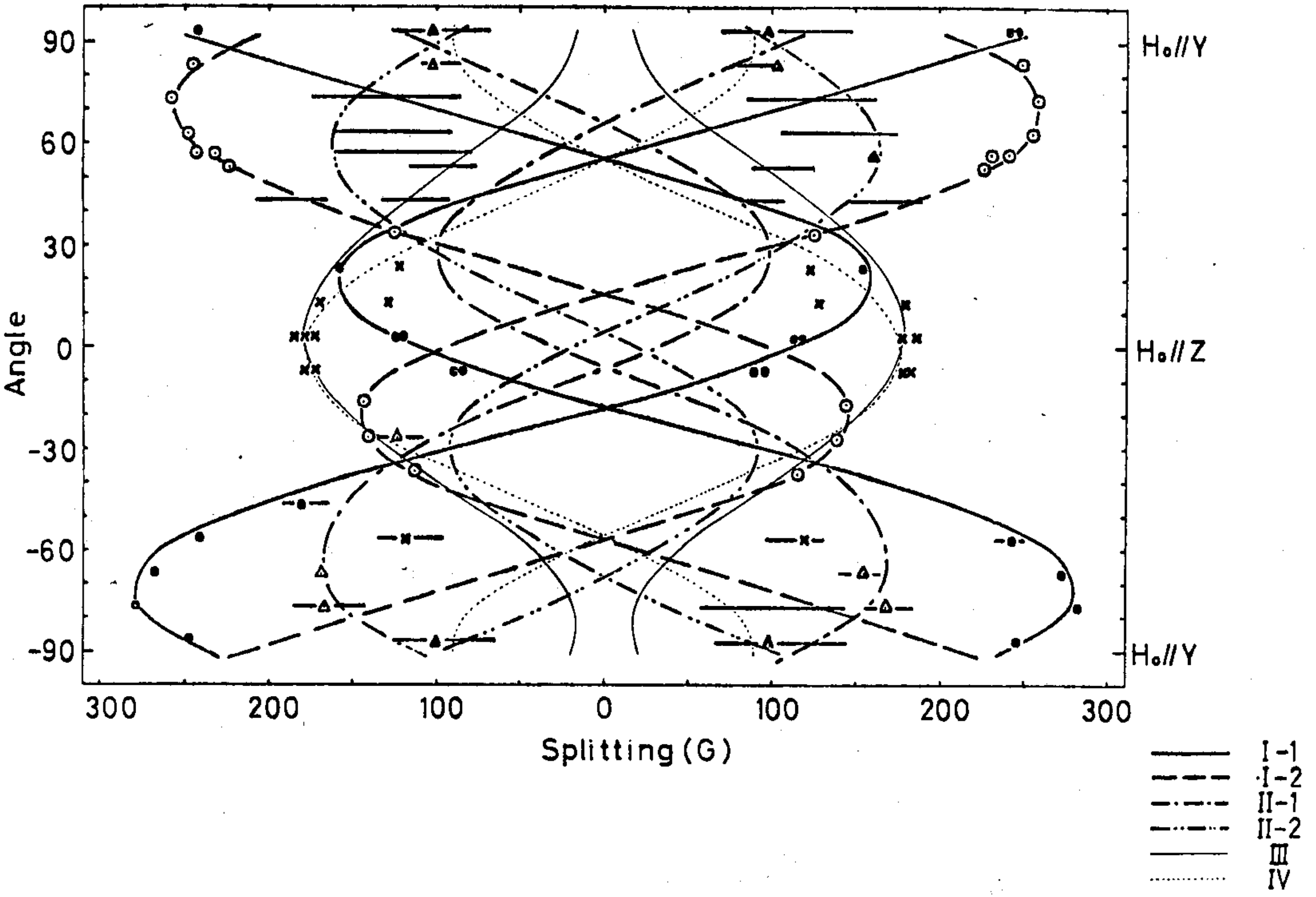

Fig. 5 Angular variation of the fine splitting of radical pairs measured in the YZ plane.

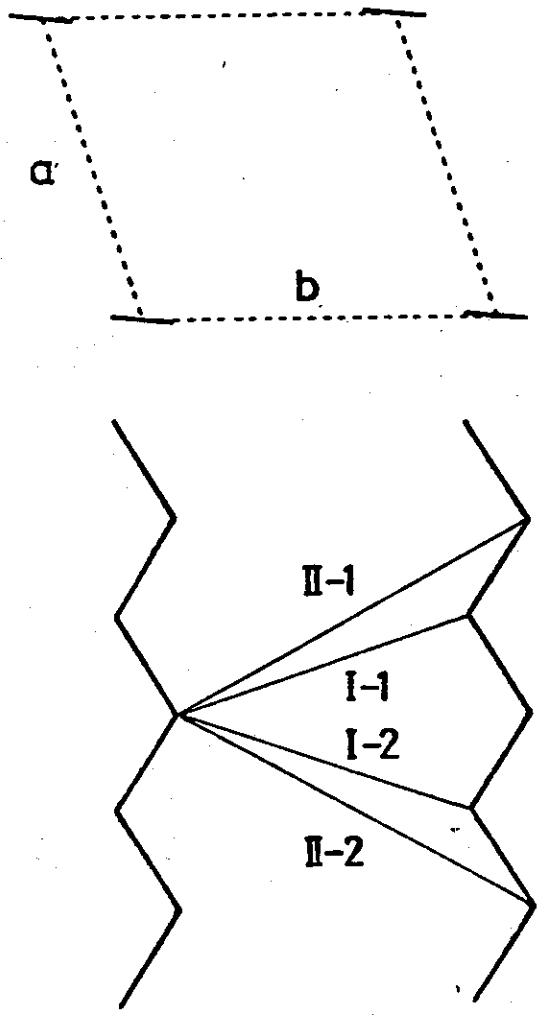

Fig. 6 The sites of the paired radicals produced on the molecular chains aligned along the b axis.

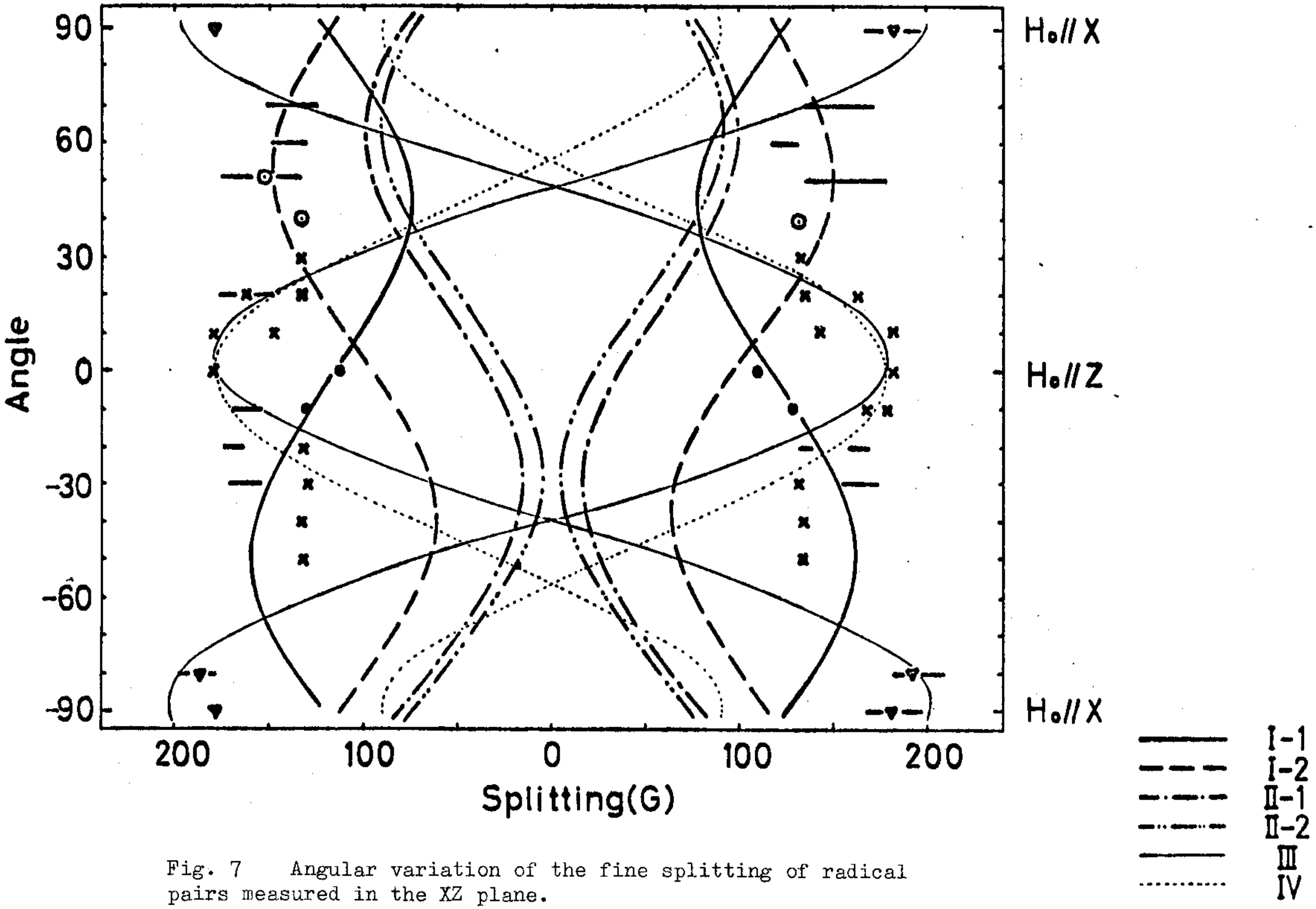

Fig. 7 Angular variation of the fine splitting of radical pairs measured in the XZ plane.

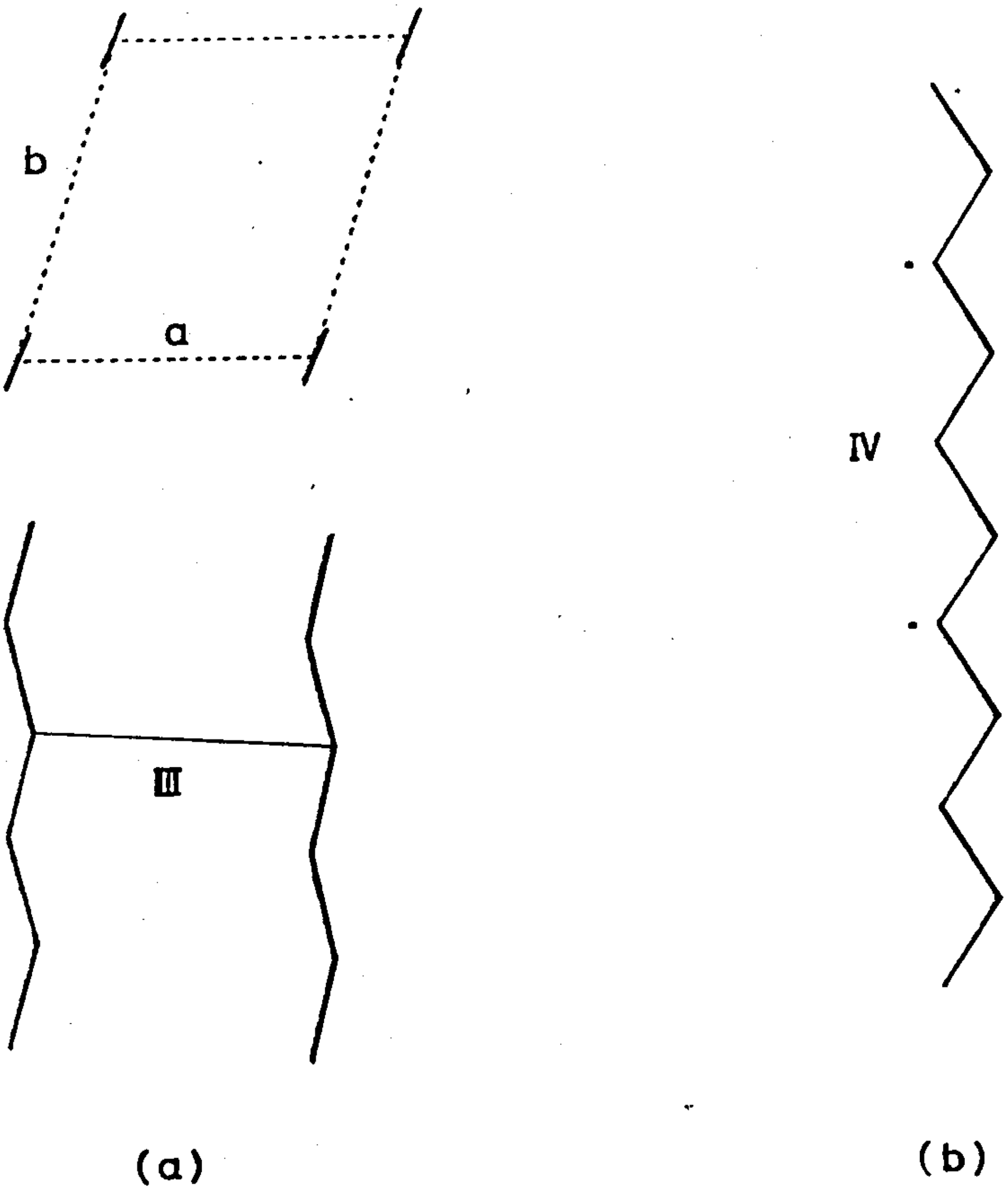

Fig. 8 (a) The site of the paired radicals produced on the molecular chains aligned along the a axis. (b) The site of the intrachain paired radicals.

2.3 Trapping Regions for Alkyl and Allyl Radicals and Conversion of Alkyl to Allyl Radicals in Irradiated Polyethylene

2.3.1 Introduction

There are two regions, crystalline and non-crystalline in polyethylene. Therefore, in order to clarify radiation effects resulting from the reaction of radicals, it is necessary to know in which regions the radicals are trapped. Although there have been several theory how to define the region in polyethylene, following is adopted here.

1. Amorphous region
2. Crystal surfaces, Defects in the crystal
3. Crystal core

In amorphous region, the molecular chains of polyethylene are distributed at random. On the contrary, the chains are arranged regularly in the crystal core which is inside the crystal. On the crystal surfaces, the molecular chains are more disordered than that in the interion of the crystal since there are folds on the crystal surfaces. The crystals of polymers differ from the crystals of metals in the content of defects . In some cases, amorphous region, crystal surfaces and crystal defects are integrated as non-crystalline region.

As shown above, there are some regions in polyethylene. However, there have been few reports[1-4] describing the regions where the two important radicals, alkyl and allyl radicals, are trapped, react and disappear. A few workers[1-4] have reported the regions for alkyl radicals, while the location for allyl radicals have been scarcely studied.

The present work will show in the chapter I the locations of trapping of alkyl radicals which are produced in polyethylene by the irradiation at 77°K. The chapter I will also show the regions where alkyl radicals react and decay when the sample is annealed up to room temperature. In the chapter II we will show the regions where alkyl radicals, which are produced by the irradiation at 77°K, react with double bonds and are converted to allyl radicals. The chapter II will also show the locations where the allyl radicals are trapped. It will be shown that the different types of double bonds react with alkyl radicals to produce allyl radicals of different types.

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2.3.2 Electron Spin Resonance Study on the Thermal Decay of Radicals in Irradiation Polyethylene

(1) Synopsis

The role of radical pairs in the decay of radicals in irradiated polyethylene and the correlation of the decay of radicals with the trapping region of alkyl radicals produced in irradiated polyethylene have been investigated by using various types of polyethylene. When the sample irradiated at 77°K is warmed above this temperature, the decay curve of radicals against temperature shows three-step decay. The first decay region is ascribed to the decay of radical pairs. The second decay region is connected with the radicals trapped in the non-crystalline regions. The third decay region is correlated to the radicals trapped in the crystalline region.

(2) Introduction

When polyethylene is irradiated at 77°K with high-energy radiation, main active species detected by ESR are alkyl radicals as is well known.[1] The alkyl radicals decay when warming the samples above 77°K and the decay curve against temperature shows three-step decay of alkyl radicals.[2] Correlation of the three-step decay with the molecular motion characteristic of polyethylene has been studied.[2-4] However, it seems no definite conclusion has been made on the cause of the three-decay regions.

Recently, it has been found that some of the alkyl radicals detected at 77°K are trapped very closely each other, that is in the form of radical pairs.[5-7] The detailed studies on the structure of radical pairs produced in polyethylene[6,7] and related compounds[8,9] have disclosed the presence of paired alkyl radicals with different directions and distances in polyethylene irradiated at 77°K.

The aim of the present work is to clarify the role of paired radicals in the decay of radicals in irradiated polyethylene and the correlation of the three-step decay of radicals with the trapping region of alkyl radicals produced in irradiated polyethylene. It will be shown that the first-decay region is ascribed to the decay of paired radicals, the second region is correlated to the decay of radicals trapped on the non-crystalline region, the third region is connected with the decay of radicals trapped in the crystal.

(3) Experimental

Samples used are various types of polyethylene: high-density polyethylene (Sholex 6050), low-density polyethylene (Sumikathene G 804) and two types of radiation polymerized polyethylene(Takathene). High-density polyethylene was used in the form of powder and also the oriented mat of single crystal which was prepared from 0.1% xylene solution at 70°C. Low-density polyethylene is in the form of melt-crystallized rod. Takathene was used in powder form as polymerized in gas phase of 400 kg/cm^2; sample p-24 was polymerized at 30°C, and sample p-2 was polymerized at 95°C. The characteristics of the samples are listed in Table I.

Irradiations were performed in vacuo at 77°K with a Cockcroft-Walton type of electron beam which provides a dosage of 15 Mrad. The energy of the electrons was 2 MeV and the current 500 A; the dose rate was about 0.16 Mrad/sec. Some experiments were carried out with ^{60}Co γ-rays to a dosage of 15 Mrad; the dose rate was 0.7 Mrad/hr. The spurious ESR signal from the irradiated quartz ampoule was eliminated by heating the ampoule, while the sample was cooled in liquid nitrogen at the opposite end of the ampoule. ESR measurements were made at 77°K with Varian V-4502 X-band spectrometer with 100 kHz field modulation. Heat treatment of the sample was carried out by warming samples irradiated at 77°K to the given temperature for 5 min and then cooling it back to 77°K for measurement.

(4) Results and Discussion

4-1 Radical species giving the ESR spectra observed at 77°K

The ΔMs=1 spectrum obtained with high-density polyethylene in the form of powder irradiated at 77°K and observed without warming is shown in Figure 1(a). The sextet spectrum, the average hyperfine splitting of which is 32 G, is assigned to isolated alkyl radicals as is well known. The ΔMs=2 spectrum which is due to radical pairs[10] consists of eleven lines, the hyperfine splittings of which are 16 G as shown in Figure 1(b).

The ΔMs=1 spectrum obtained with the single crystal mat of high-density polyethylene is shown in Figure 2. When the mat is mounted so that the magnetic field is perpendicular to the mat plane, the ΔMs=1 spectrum is a well-resolved sextet. When the outermost parts of the spectrum are taken at increased gain (500 x), the hyperfine structure appeares on the tail of the main spectrum as shown in Figure 2. This hyperfine structure is similar to the structure observed in the irradiated drawn polyethylene.[6,7] In the drawn polyethylene, intrachain type of radical pairs, that is the vector connecting two radicals is parallel to the chain axis, was found. The spectrum of radical pairs produced in single crystal mat of polyethylene in the present work must be attributed to these radical pairs of intrachain type found in the drawn polyethylene. Besides radical pairs of intrachain type, other type of radical pairs are produced in irradiated polyethylene; for several radical pairs of interchain type which are composed of two radicals in the adjacent macromolecules were found in the single crystal of n-eicosane ($C_{20}H_{42}$)[8] and n-decane,[9,11] which can be regarded as the model compounds of polyethylene.

These facts show that the ESR spectra obtained with the polyethylene irradiated at 77°K are attributed to isolated alkyl radicals, radical pairs of intrachain type and interchain type. In the powder sample of polyethylene, radical pairs give the ΔMs=1 spectrum of broad background without any structures.

4-2 Temperature dependence of radical decay

When the sample irradiated at 77°K was heated and cooled back to 77°K for measuring, the ΔMs=1 spectrum was observed to vary both in shape and in intensity. The variations of relative intensity and degree of spectral resolution, denoted S, with heating temperature are shown in Figures 3 and 4 for four types of polyethylene; three decay regions are observed. In the case of high-density polyethylene, the first-and second-decay region is around 120°K and 200°K respectively and the third-decay region comes above 250°K. Nara et al.[3] reported that the decay amount of first-decay region is proportional to the fraction of amorphous region in the polyethylene. However, the present experiment shows that no remarkable difference is observed in the amount of decay in the first-decay region among four types of polyethylene with various densities and crystal sizes as shown in Figure 3.

The spectral resolution, S, of alkyl radicals increases at the temperature of the first- and the second-decay regions, where the decrease of intensity occurs. Evidently, diffuse components of the spectrum decay, leaving the stable sharp sextet. However, around 300°K the spectral resolution starts to decrease. This decrease is due to the conversion of the sextet to the septet components, since the tail of the septet spectrum affects the resolution of the sextet spectrum. The septet spectrum is attributed to allyl radicals. Figure 5 illustrates the conversion of alkyl radicals to allyl radicals for high-density polyethylene in the form of powder. The amount of allyl radicals are calculated by subtracting the intensity of the alkyl radicals from that of total radicals.

When the sample irradiated at 77°K was heated and cooled back to 77°K for measuring, the $\Delta Ms=2$ spectrum was also observed to vary both in shape and in intensity. The first-and second-decay region is around 120°K and 190°K. Above 250°K the $\Delta Ms=2$ spectrum was not observed. The variation of relative intensity and degree of spectral resolution, denoted Q, with heating temperature are shown in Figures 6 and 7. The spectral shape become sharper with heating temperature.

The anisotropy of $\Delta Ms=2$ spectra due to radical pairs[10] for the single crystal mat of polyethylene is shown in Figure 8. When the mat is mounted so that the magnetic field is perpendicular to the mat plane, a well-resolved spectrum (a) is obtained and when the field is parallel to the mat plane, a diffuse spectrum (b) is obtained. These $\Delta Ms=2$ spectra of the single crystal mat of polyethylene decrease in intensity with elevating temperature and disappear at the temperature range of the second-decay region.

Thus far the three-step decay of radicals trapped in irradiated polyethylene has been discussed only from the viewpoint of molecular motion of polyethylene.[2,3] However the three-step decay of radicals should be also discussed from the viewpoint of the distribution of alkyl radicals. As shown in the preceding section, the interchain and intrachain type of radical pairs have been found in irradiated polyethylene. This fact shows clearly that the distribution of radicals is not homogeneous but heterogeneous in irradiated polyethylene. This heterogeneous distribution of radicals play some role in the decay of radicals.

In the following section, the effect of radical pairs as well as the trapping region of radicals in the polyethylene on the radical decay will be shown.

4-3 The first-decay region

Now consideration should be given about the origin of decay reaction in the first-decay region. A composition of Figure 3 and Figure 6 suggests that the ΔMs=2 spectral intensity decreases in the first-decay region of Figure 3. This results suggests that the radical pair play some role in the first decay region.

The shape of ΔMs=1 spectrum become sharper with elevating temperature of heat-treatment as shown in Figure 4. The ΔMs=1 spectrum obtained with polyethylene at 77°K can be divided into two components, a sharp sextet and a diffise component which spreads over the whole spectrum. This diffuse component is presumably attributed to the spin-spin interaction of two radicals which constitute a radical pair. The relative intensity of the sharp sextet, which is represented by the peak to peak height "h" as shown in Figure 9, since the diffuse component has little effect on the height "h". The sharp component of the sextet spectrum does not change its intensity in the first- and second-decay regions, while the intensity of the whole spectrum decreases. Obviously the diffuse component, which is due to radical pairs, decay in this region and makes the $\Delta Ms=1$ spectrum sharper as shown in Figure 4.

The amount of the radicals which decay in the first-decay region is about 9 % of total radicals and is almost independent of the type of polyethylene or the physical state of polymer as shown in Figure 3. We have previously reported that the concentration of the paired radical of intrachain type giving the $\Delta Ms=1$ spectrum in irradiated drawn polyethylene is about 0.3 % of that of total radicals.[7] We have also reported that more than six different radical pairs of interchain type are produced in irradiated single crystal of n-eicosane, and the concentration of one of them is 0.3 % of that of the total radicals.[8] Such interchain type radical pairs must exist in irradiated polyethylene also. These result indicate that the concentration of paired radicals in polyethylene irradiated at 77°K is, say, 2 % in all of that of total radicals. This result, however, cannot explain 9 % decrease of radicals for the first decay region. This discrepancy may be explained as follows.

When polyethylene is irradiated up to a dosage of 15 Mrad at 77°K, the average distance between two radicals can be calculated as 29 Å when the G-value of alkyl radicals at 77°K is 4.6. Interspin distance of intrachain radical pair observed in irradiated drawn polyethylene was 5.3 Å. Innumerable kinds of radical pairs, the interspin distances of which are between 29 Å and 5.3 Å, are produced in irradiated polyethylene.[9]

In these innumerable kinds of radical pairs, only a few types of radical pairs which have short radical-radical distance near 5.3 Å can be observed with ESR at the outer parts of the spectrum due to isolated radicals in irradiated polyethylene or n-eicosane. The radical pairs which have long radical-radical distance near and shorter than 29 Å may observed by ESR as isolated radicals because these pairs have very weak spin-spin interactions. The spectrum of the radical pairs which have intermediate radical-radical distance, for example 10 Å, are hindered by the spectrum of isolated radicals, for the d-splittings of these pairs are smaller than the overall hyperfine splittings of isolated radicals.

These innumerable kinds of radical pairs decay faster than the radicals which have average radical-radical distance, which is 29 Å. The radicals decaying in the first-decay region is the radical pairs which have shorter interspin distance than the average. These consideration can explain the discrepancy about the amount of radicals.

4-4 The second-decay region

The temperature of the second-decay region is independent of the type of polyetylene as shown in Figure 3. The broad line NMR experiments[12] of the same samples as the present work discloses that the narrowing temperature of the absorption curve at low temperature due to γ-process is almost independent of the type of polyethylene. Nara et al.[3] investigated that the isothermal decay in the second-decay region and obtained the activation energy of the decay reaction as 9.4 kcal/mol which agrees with the activation energy of γ-process 9.5 kcal/mol.

These results suggest that the second-decay region of the radicals is caused by the molecular motion of γ-process. Since γ-process is connected with molecular motion in the non-crystalline regions, the radicals which disappear in the second-decay region are presumably trapped in such regions as the amorphous region or the defects or surface of crystal.

4-5 The third-decay region

In the third-decay region, the spectra obtained with the oriented mat of single crystal in this region are shown in Figure 10. Clear anisotropy of spectra shows that alkyl radicals which decay last must be trapped in the crystalline region.

Nara et al.[3] proposed that the third-decay region is connected with the molecular motion associated with the β-dispersion, which is primary dispersion due to the segmental motion of molecules in the non-crystalline region. Their grounds were the consistents of the temperature range of radical decay and the activation energy. However, if this decay region is connected to β-dispersion, anisotropy should not be observed with an oriented sample.

Among four types of polyethylene, the third-decay region begins at the lowest temperature in the low-density polyethylene. This decay region begins at the second lowest temperature in p-24 polymerized at 30°C, at the third in p-2 polymerized at 95°C and high-density polyethylene at the highest temperature. This order is coinside with the order of temperature for the beginning of NMR α-process, but is not correlated to that of β-process.

These results discloses that the third-decay region can be connected with α-process, that is the molecular motion in the crystalline region. The temperature of the third-decay region observed here is lower than that of the NMR α-process. This result can be explained by the following two facts. First, the presence of hydrogen molecules, which are produced by irradiation and reside in the sample, can accelerate the radical migration[13] and lower the temperature of decay region. Secondly, the presence of radicals forms a kind of defects in the crystalline region, where molecules become more mobile than that in the regular crystalline region. Therefore, the radicals at the defects decay prior to the molecular motion in the crystal.

The radicals trapped in p-24 polymerized at 30°C decay at lower temperature than the radicals in high-density polyethylene. The results is attributed to the fact[12] that p-24 polymerized at 30°C has defective crystalline regions which favor the rapid migration of radicals.

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Table I; Characteristics of polyethylene

Sample	Rigid fraction[a]	Crystalline fraction[b]	Crystal size[b]	CH_3/1000C	M.W. x10^{-4}
High-density polyethylene (Sholex 6050)	93 %	83 %	207 Å	~0	4.8
Low-density polyethylene (Sumikathene G804)	—	54	—	28.6	1.7
Radiation-polymerized polyethylene* polymerized at					
30°C, p-24	90	76	130	2.5	8.2
95°C, p-2	76	67	160	90	2.2

* polymerized at 30°C and 95°C under a pressure of 400 kg/cm^2

a measured with broad line NMR

b measured with X-ray diffraction method

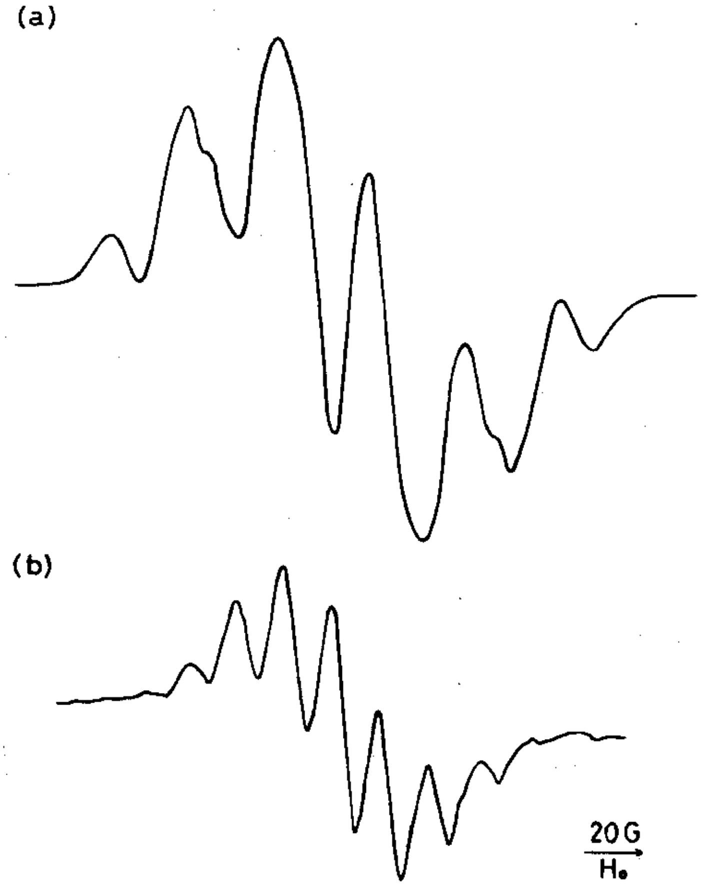


Fig. 1 ESR spectra of the ⊿Ms=1 (a) and ⊿Ms=2 (b) transition in high-density polyethylene in the form of powder irradiated at 77°K.

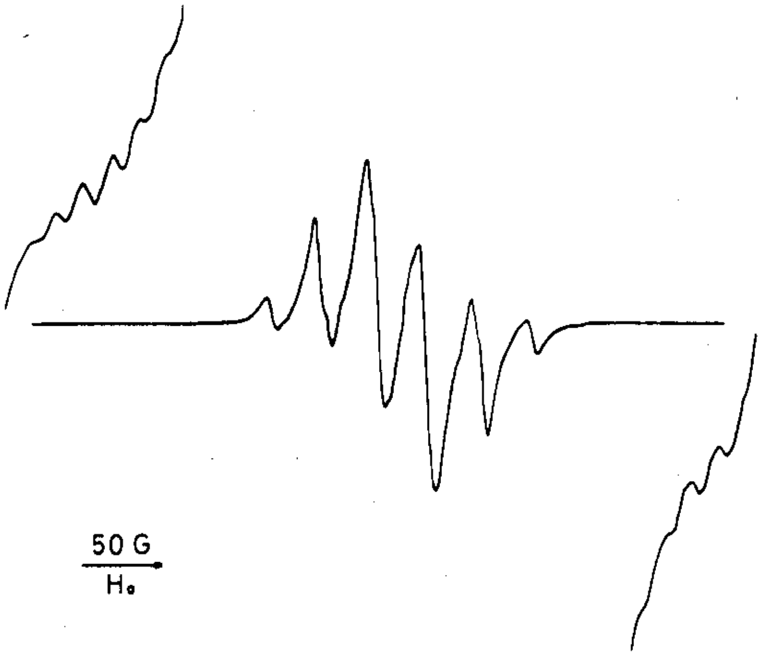


Fig. 2 ESR spectra of the ⊿Ms=1 transition in the single crystal of high-density polyethylene. Magnetic field is perpendicular to the mat plane. Outer parts of the spectrum is recorded at increased gain (500 x).

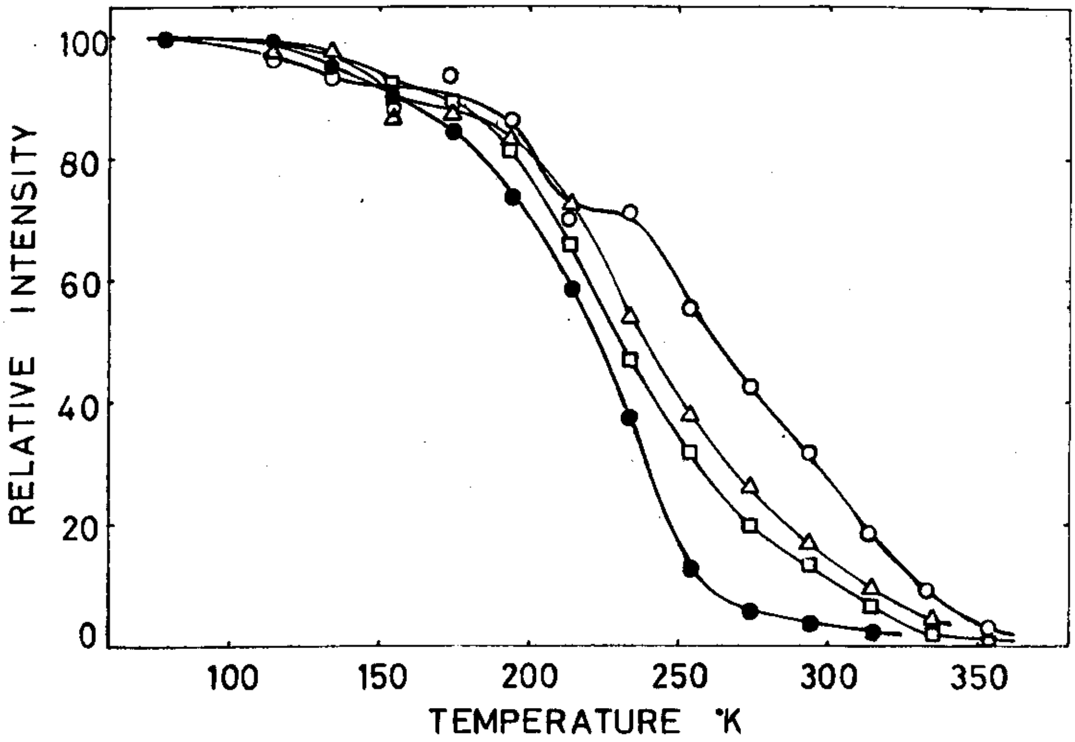


Fig. 3 Decay curves of the ΔMs=1 spectrum of polyethylene irradiated at 77°K. ○, high-density polyethylene; ●, low-density polyethylene; △, p-2 polymerized at 95°C ; □, p-24 polymerized at 30°C.

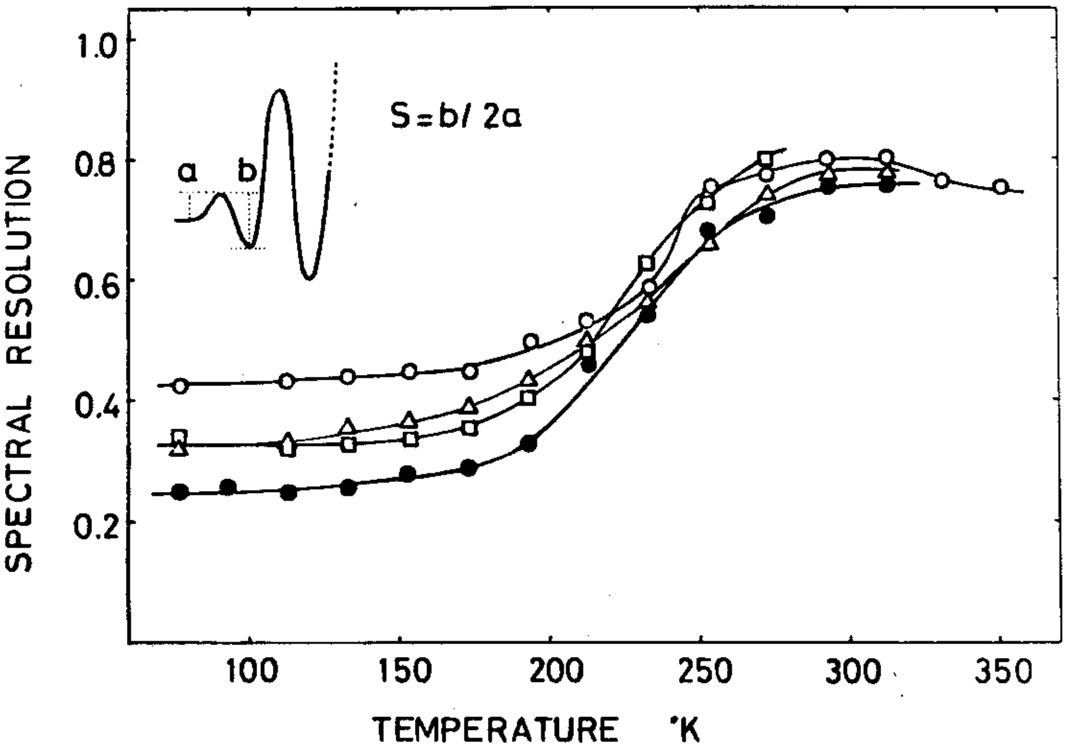


Fig. 4 Change of spectral resolution of alkyl radical with temperature of heat treatment. ○, high-density polyethylene; ●, low-density polyethylene; △, p-2 polymerized at 95°C; □, p-24 polymerized at 30°C.

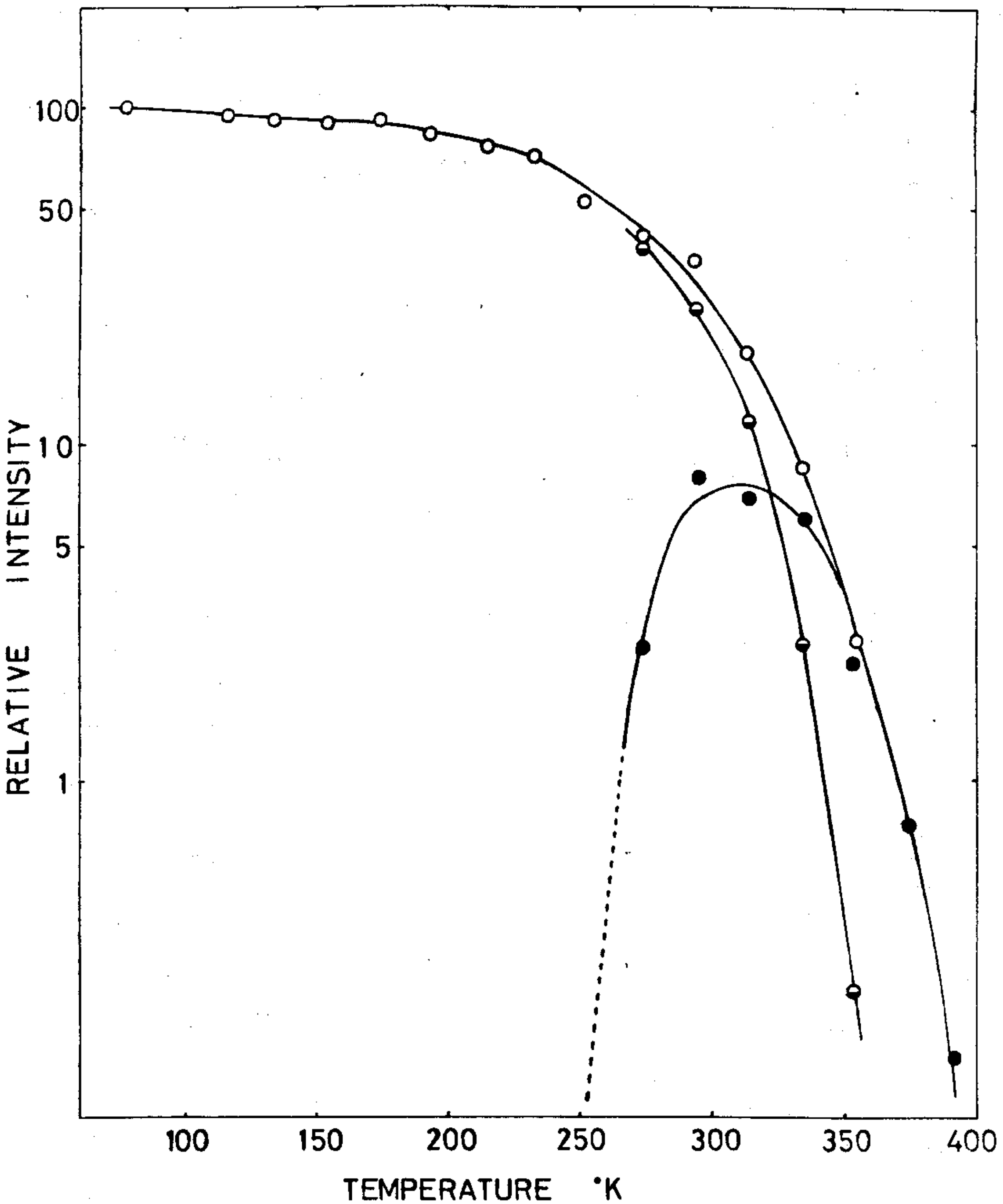


Fig. 5 Decay of alkyl radicals and conversion to allyl radicals in high-density polyethylene.

o total radical ◒ alkyl radical ● allyl radical

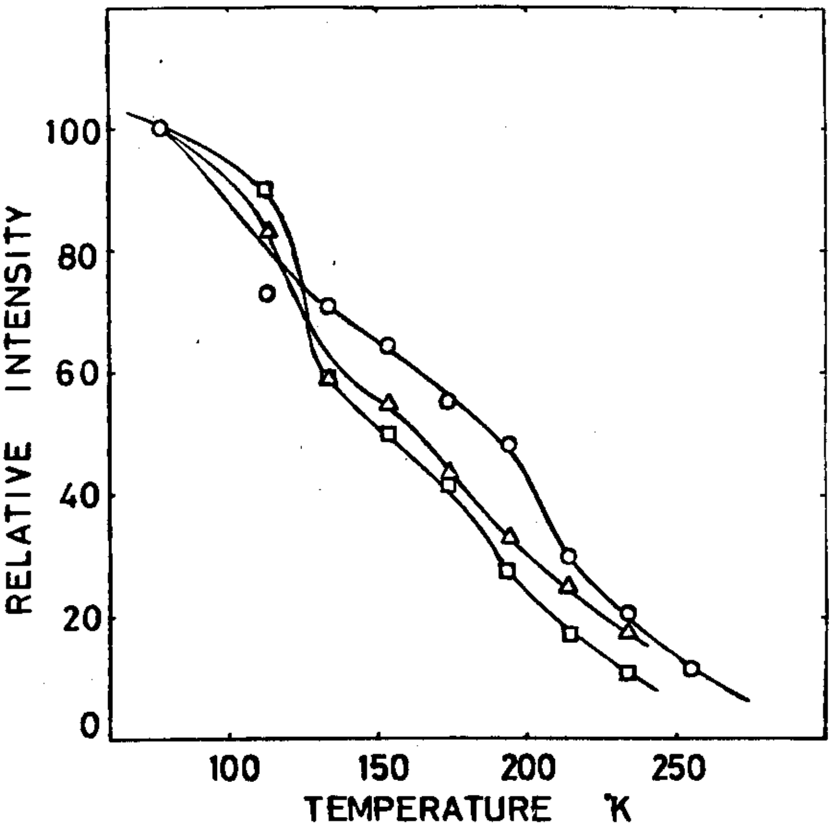


Fig. 6 Decay curve of the ⊿Ms=2 spectrum of polyethylene irradiated at 77°K. ○, high-density polyethylene; △, p-2 polymerized at 95°C; □, p-24 polymerized at 30°C.

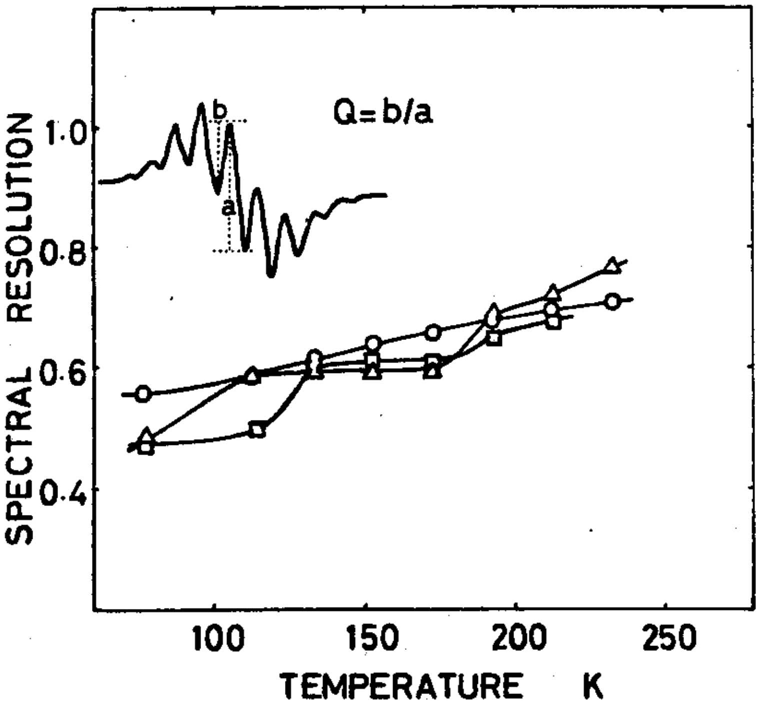


Fig. 7 Change of spectral resolution in the ⊿Ms=2 spectrum of polyethylene irradiated at 77°K.
○, high-density polyethylene; △, p-2 polymerized at 95°C;
□, p-24 polymerized at 30°C.

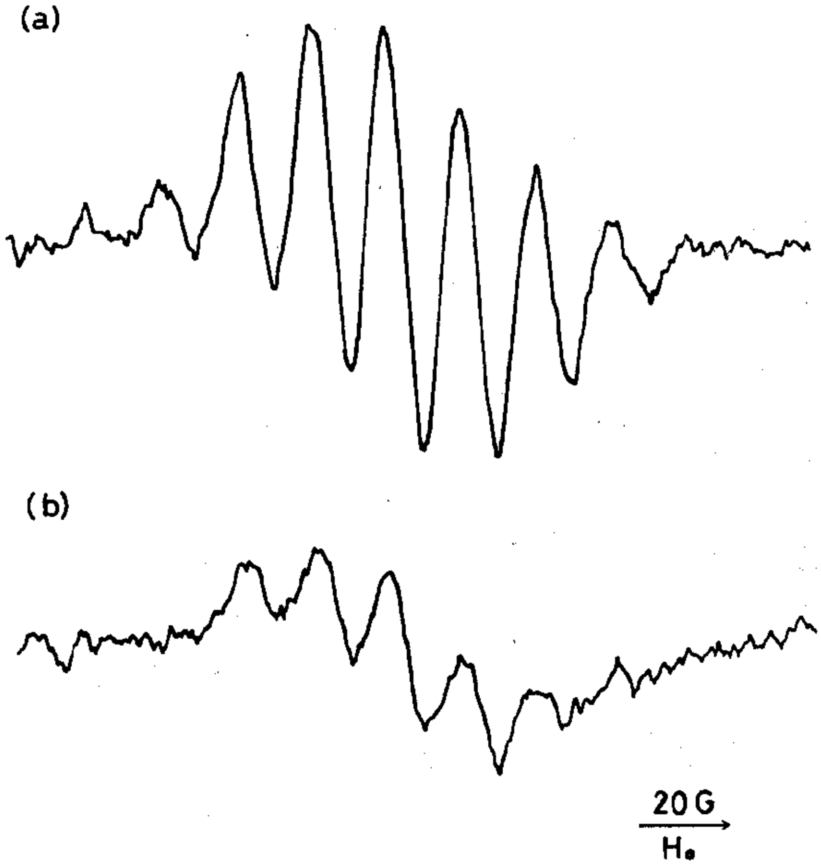


Fig. 8 ESR spectra of the ⊿Ms=2 transition in the single crystal of high-density polyethylene. (a) Magnetic field is perpendicular to the mat plane; (b) magnetic field is parallel to the mat plane.

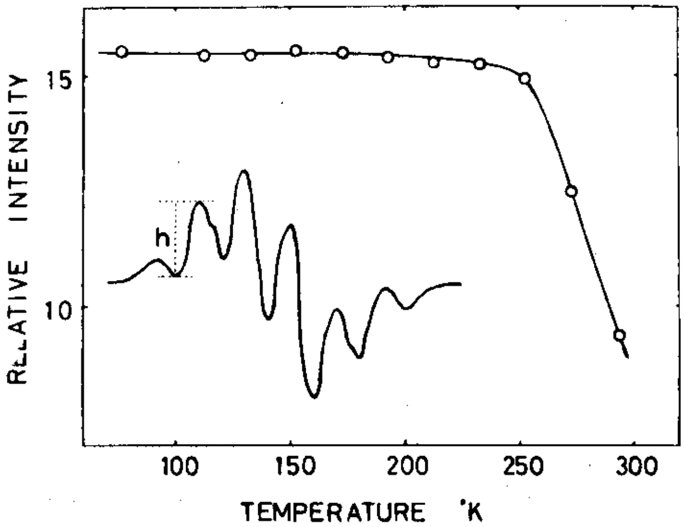


Fig. 9 Intensity changes of sharp component of alkyl radical with temperature in high-density polyethylene.

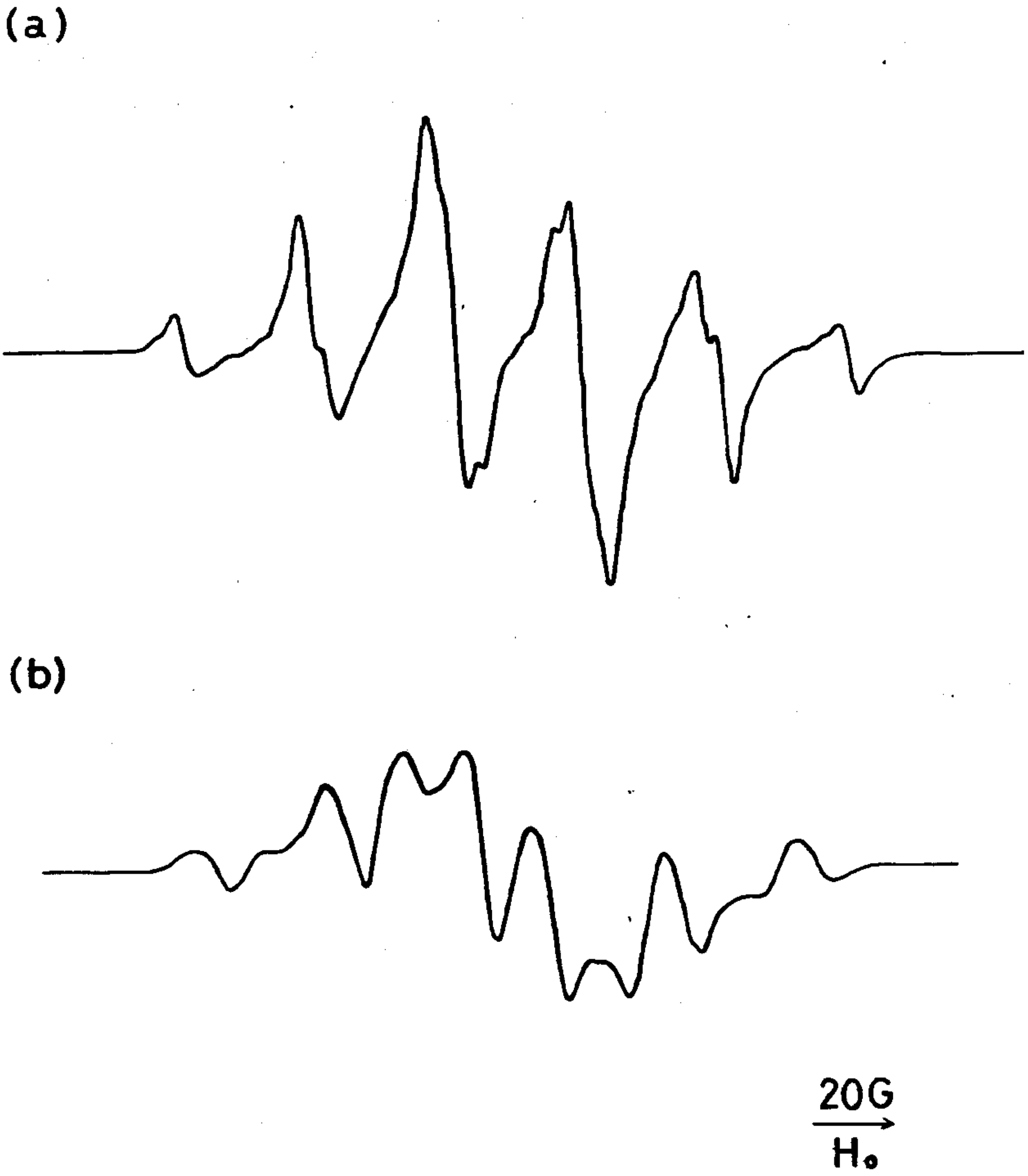


Fig. 10 ESR spectra of the ΔMs=1 transition in the single crystal of high-density polyethylene irradiated at 77°K and annealed at 293°K. (a) Magnetic field is perpendicular to the mat plane; (b) magnetic field is parallel to the mat plane.

2.3.3 Conversion of Alkyl Radicals to Allyl Radicals and Location of Allyl Radicals in Irradiated Single Crystal Mats of Polyethylene

(1) Synopsis

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 ESR. 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; in the crystal surface, alkyl radicals react with vinyl end group 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.

(2) Introduction

Chapter I mainly took up alkyl radicals produced in polyethylene in the form of powder irradiated at 77°K. Three decay regions were found in the decay curve of alkyl radicals when the sample was heated up to room temperature. Among three decay regions, first-decay region was ascribed to the decay of radical pairs. The second- and the third-decay regions were correlated with the radicals trapped in the non-crystalline region and crystalline region respectively.

Another important radical species, allyl radicals, can not be found in polyethylene irradiated and observed at 77°K. It has been clarified that alkyl radicals react with double bonds and are converted to allyl radicals[1] when the sample irradiated at 77°K are heated up to room temperature. However, the relation has been scarcely known between the decay regions of alkyl radicals and the trapping regions of allyl radicals.

This chapter will describe the decay region of alkyl radicals,[2] the sites of conversion of alkyl radicals to allyl radicals and the location where allyl radicals are trapped.

(3) 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 70°C. The samples in vacuo at 77°K were γ-irradiated from a ^{60}Co source with up to 12.7 Mrad at a dose rate of 0.7 Mrad/hr.

ESR measurement were made at room temperature or 103°K 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 77°K were heated to fixed temperatures for 5 min and cooled to 103°K in order to take measurements.

(4) Results

4-1 The decay of alkyl radicals and conversion to allyl radicals

ESR spectra of single crystal mats irradiated in vacuo at 77°K and observed at 103°K are shown in Figure 1-1. The magnetic field was parallel(a) and perpendicular(b) to the plane of the crystal mat. When the sample was heated to 263°K and 293°K, the spectrum altered both in intensity and shape represented by the spectral resolution, as shown in Figure 1-2 and 1-3 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.[2] The difference spectra obtained by subtracting spectra of Figure 1-3 from spectra of Figure 1-2 are shown in Figure 1-4. 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 200°K, the second region is from 200°K to 260°K and the third region is above 260°K.

The spectral resolution, at the outer part of spectrum, S=b/2a, as indicated in Figure 1-2 and the spectral resolution at the central part of spectrum, A=x/y as indicated in Figure 1-1 are shown in Figure 3. Around 280°K, 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 300°K, 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 radicals. Allyl radicals appear around 220°K and increase in number to 260°K 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 irradiated at 77°K and annealed at room temperature alkyl radicals are effectively converted to allyl radicals.

4-2 Location of allyl radicals

ESR spectra obtained with single crystal mat of polyethylene irradiated in vacuo at 77°K and stored at room temperature for three weeks are shown in Figure 5-1. Only allyl radicals are observed in this sample. The magnetic field was parallel(a) and perpendicular(b) to the plane of the mat. Anisotropy is clearly observed as reported in the literature.[3,4] The single-crystal mat treated as above was further annealed at 333°K for 5 min; spectra recorded at room temperature are shown in Figure 5-2. Anisotropy is also evident in this case and suggests that allyl radicals are present in the crystalline regions. The degree of spectral resolution, denoted by R=m/l (as indicated in Fig. 5-1) is scarcely different between the spectra in Figure 5-1 and that in Figure 5-2. For instance, in Figure 5-1(a), R is 0.16, and in Figure 5-2(a), it is 0.20. The spectral intensities are lower in Figure 5-2 than in Figure 5-1.

Difference spectra obtained by subtracting spectra of Figure 5-2 from spectra in Figure 5-1 are shown in Figure 5-3. In this case, the anisotropy of the spectrum also indicates that the radicals which decay by annealing are present in the crystalline region of polyethylene.

The sample annealed at 333°K for 5 min, was then stored at room temperature for four months. The spectra are shown in Figure 5-4. The spectral resolution is better than in Figure 5-2 with R=0.40. This result shows that the population of allyl radicals, which give the broader spectrum, decays during storage at room temperature leaving allyl radicals which give the sharper spectrum. Anisotropy is also maintained in these spectra.

(5) Discussion

5-1 Decay of alkyl radicals and conversion to allyl radicals

Three decay regions of alkyl radicals are observed in Figure 2. The first-decay region below 200°K is correlated with the decay of radical pairs. Radical pairs are observed in single crystal mats of polyethylene.[5] For polyethylene in powder form, the first-decay region has been correlated with the decay of radical pairs.[6] The intrachain type of radical pair is observed in drawn polyethylene irradiated at 77°K.[7,8] This intrachain type of radical pair should be produced in single crystal mats of polyethylene irradiated at 77°K and should be converted to the trans-vinylene double bonds when the sample is heated to room temperature.

The second-decay region, from 200°K to 260°K, 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($A\fallingdotseq x/y$) increase in the second-decay region as shown in Figure 3. This increase indicates that the diffuse component of the spectrum decay, 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. In this decay region some alkyl radicals are converted to allyl radicals by the reaction with double bonds, which are mostly vinyl end group, as shown in the next section, and other alkyl radicals disappear to form double bond or crosslinkings.

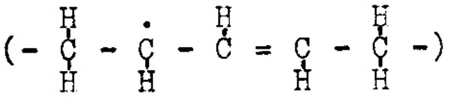
The third-decay region is correlated with the decay of alkyl radicals trapped in the crystal core. The sharp component of the spectrum remains when the diffuse component decays in the second region. This sharp component of the spectrum is correlated with alkyl radicals in the crystal core where molecular 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 by the reaction with double bonds, which are mostly trans-vinylene double bonds as shown in the next section, and other alkyl radicals disappear to form double bonds or crosslinkings.

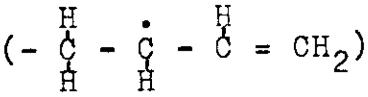
5-2 Location of allyl radicals

As shown in the above section, alkyl radicals are converted to allyl radicals both in the crystal core and crystal surface. This demonstration is supported by the results shown below. In a mat irradiated at 77°K followed by annealing at room temperature, allyl radicals are formed both in the crystal core and the crystal surfaces. The molecular chains of polyethylene are aligned more regularly in the crystal core than in the crystal surfaces. Therefore, it is expected that the spectrum caused by allyl radicals in the crystal core would be sharper than that from the crystal surfaces. When the sample is further annealed at 333°K, molecular motion occurs both in the crystal core and the surfaces. This molecular motion causes the decay of allyl radicals in both regions. Therefore, the line shape remains unchanged during annealing at 333°K. On the other hand, when the sample is stored in vacuo for four months at room temperature, molecular motion occurs in the crystal surfaces only. Therefore, allyl radicals trapped at the crystal surfaces decay. Consequently, only allyl radicals in the crystal core survive and the spectrum becomes sharper. The assumption that allyl radicals are formed only at the crystal surfaces or in the crystal core does not agree with the above experimental results.

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 and double bonds cannot migrate in the polymer. On the location of double bonds, the following evidence have been reported.

Keller and Priest[9] reported the location of unirradiated single crystals of polyethylene. They found that about 90% of the vinyl end groups are excluded from the crystal lattice and should lie on the crystal surfaces. In irradiated polyethylene, Pater[10] found on the basis of IR measurements that crystal core is preferential site for formation of the trans-vinylene double bonds.

Therefore, in the crystal core, trans-vinylene double bonds produced by the irradiation react with alkyl radicals to form trans-vinylene allyl radicals.  $(-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\bullet}{C}}-\overset{H}{C}=\underset{H}{C}-\underset{H}{\overset{H}{C}}-)$

On the otherhand, on the crystal surface, vinyl end group which are already present before irradiation mainly react with alkyl radicals to form allyl radicals of vinyl end type.  $(-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\bullet}{C}}-\overset{H}{C}=CH_2)$

The trans-vinylene double bond are produced by the recombination of two alkyl radicals. Recently it has been found that some of alkyl radicals are trapped very closely each other, that is pairwise in irradiated polyethylene[7,8] at 77°K. An intrachain type of radical pairs, that is, the vector connecting two radicals is parallel to the chain axis was found and their structure was clearly determined.[8] These pairs of two alkyl radicals react together to form trans-vinylene double bonds. As a whole three alkyl radicals form one trans-vinylene allyl radical.

(6) Conclusion of Chapter II in Part II

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 is correlated with the decay of radicals 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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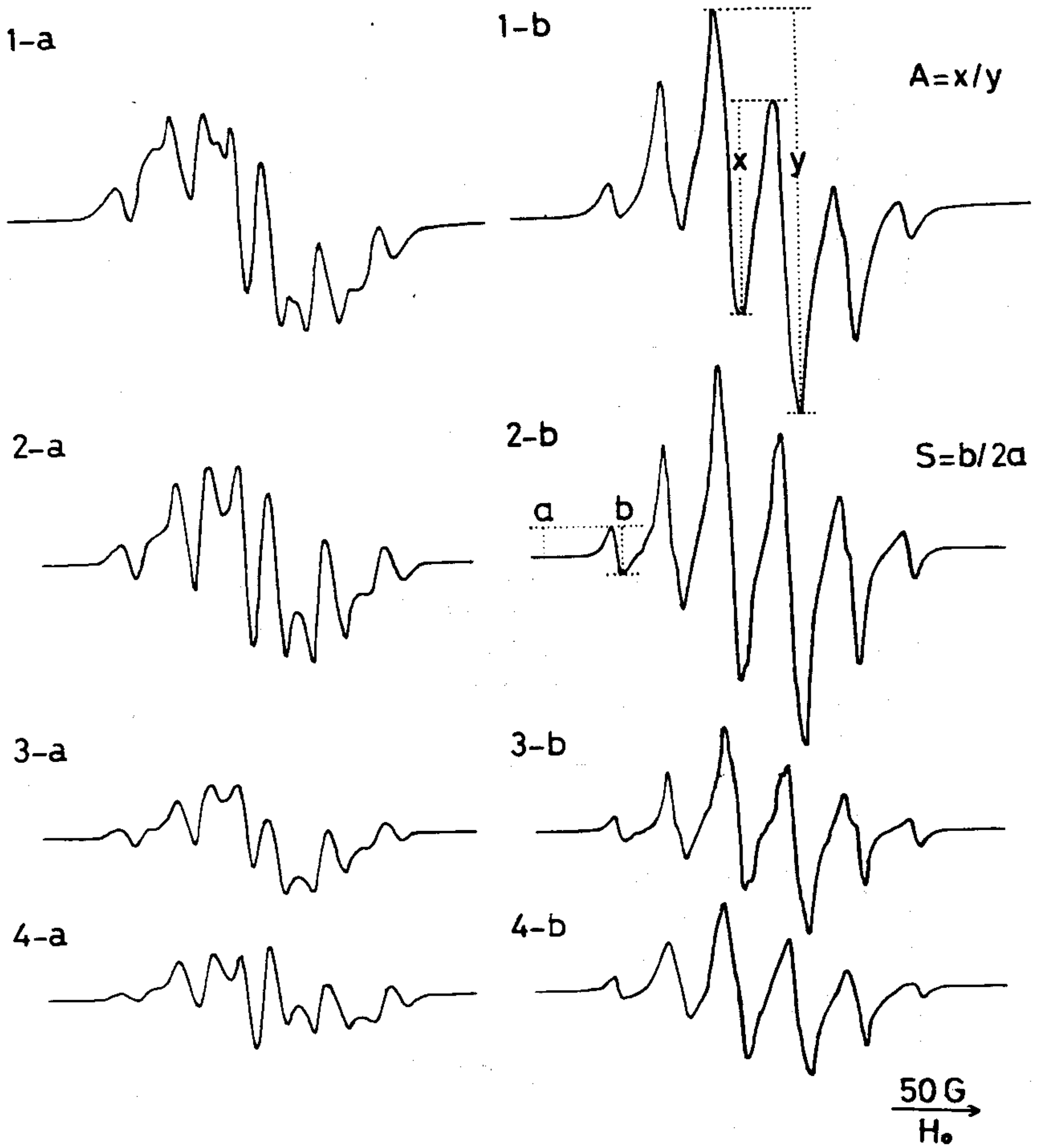

Fig. 1 ESR spectra of alkyl radicals produced in a single crystal mat of polyethylene. Observation were carried out at 103°K. The magnetic field was parallel (a) or perpendicular (b) to the mat plane of the mat. 1-a; 1-b, The sample was irradiated in vacuo at 77°K. 2-a; 2-b, The same sample was annealed at 263°K for 5 min and cooled to 103°K for measurement. 3-a; 3-b, Sample further annealed at 293°K for 5 min and cooled to 103°K for measurement. 4-a; 4-b, The difference spectra obtained by substracting spectra of 3-a and 3-b from spectra of 2-a and 2-b.

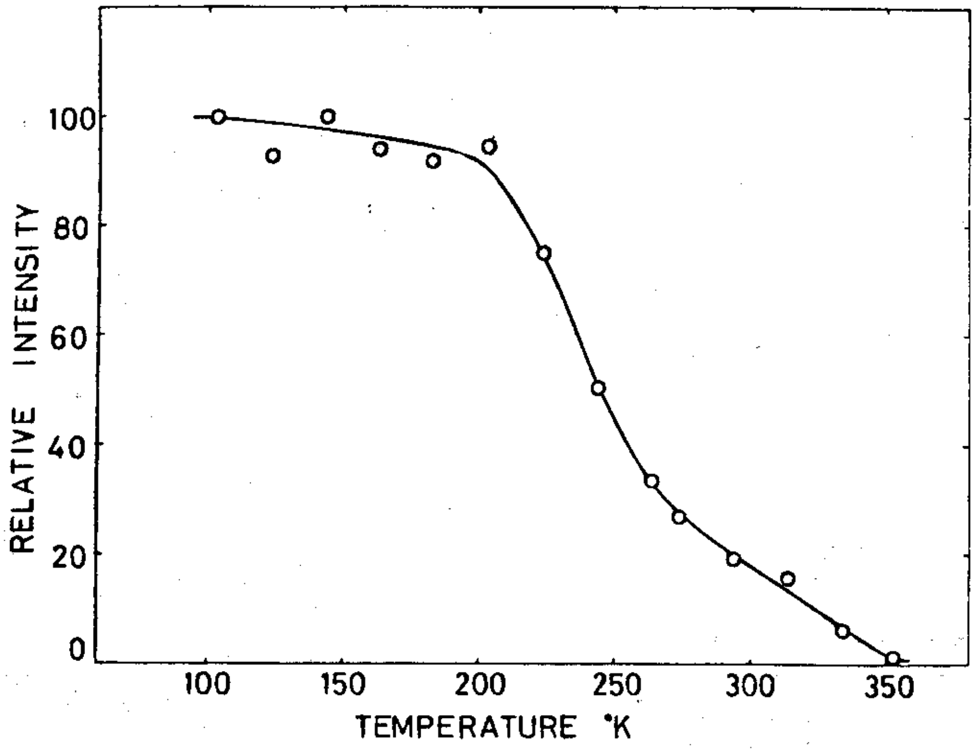

Fig. 2 Variation of relative intensity of the spectrum for the single crystal mat of polyethylene irradiated at 77°K and versus temperature of annealing. Observations were carried out at 103°K.

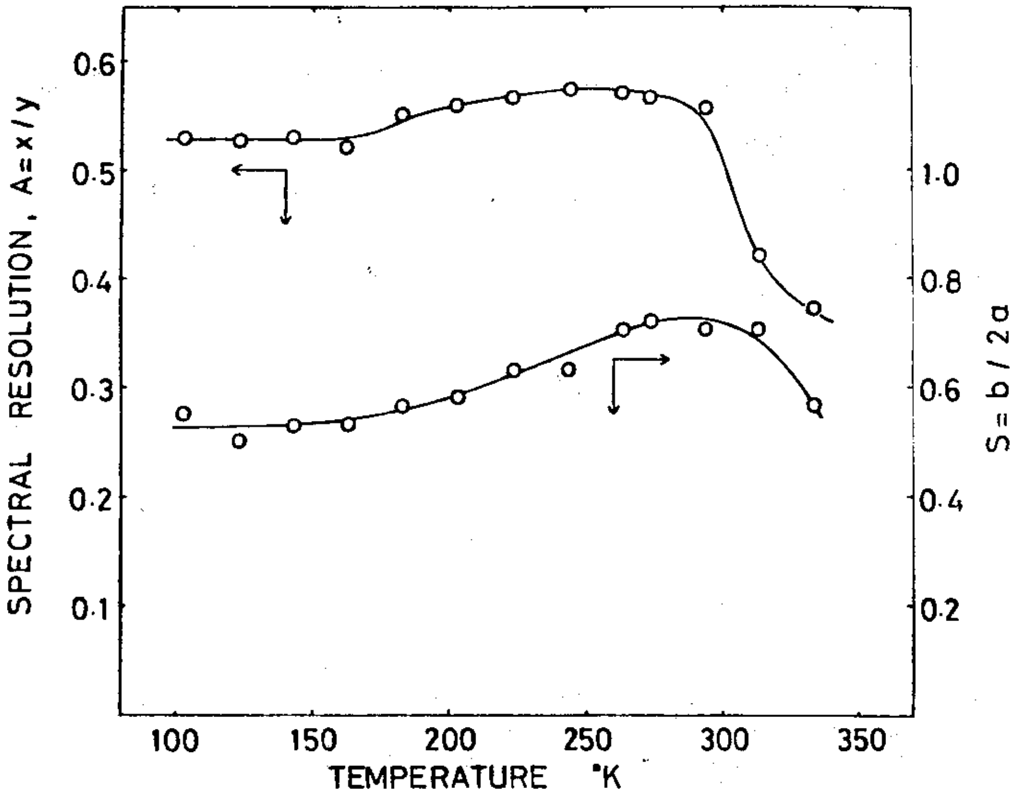

Fig. 3 Change of spectral resolution of alkyl radicals produced in the single crystal mat of polyethylene irradiated at 77°K versus temperature of annealing. A=x/y represents the resolution of the central part; S=b/2a represents the resolution of the outer part. (see Figure 1)

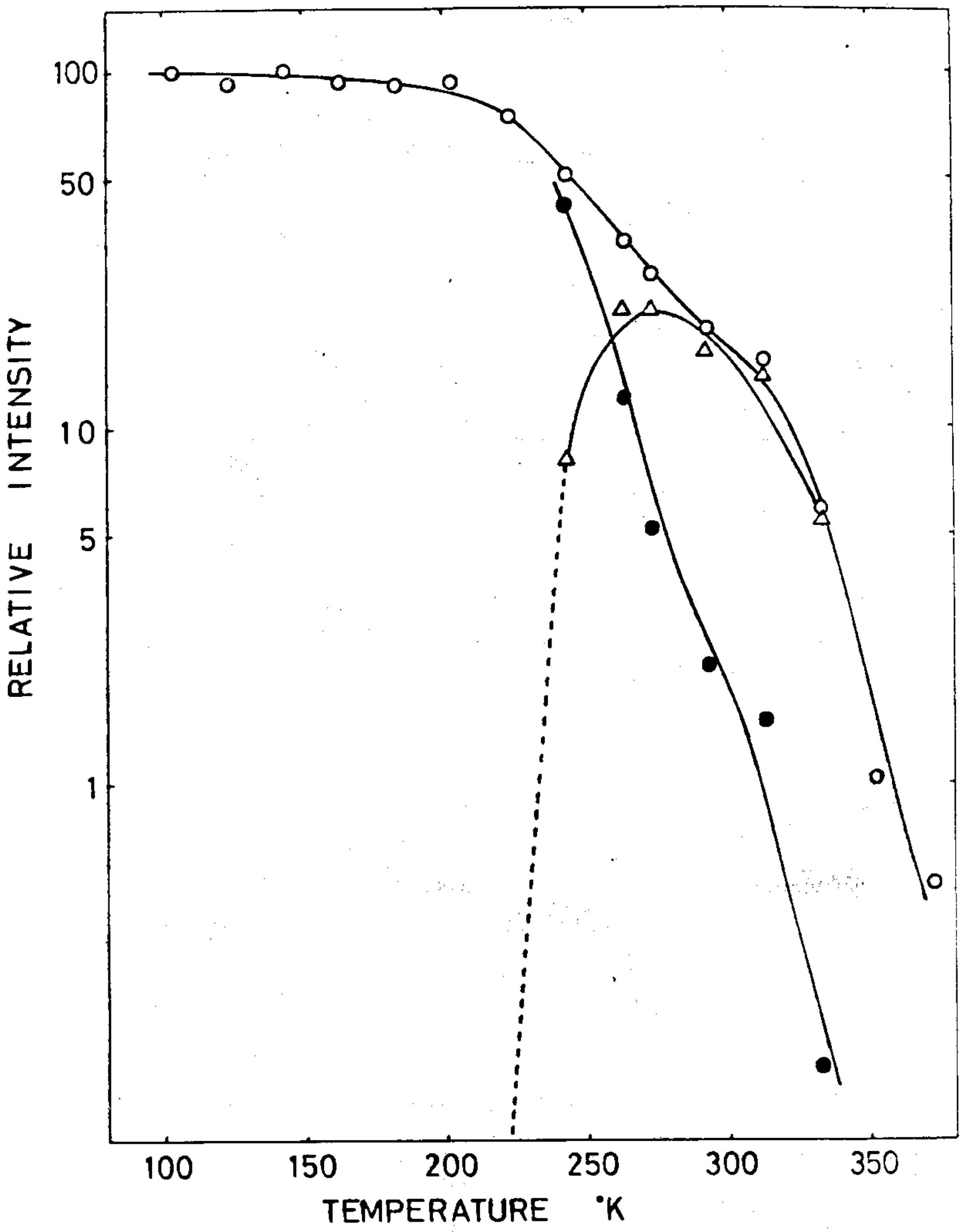

Fig. 4 The conversion of alkyl radicals to allyl radicals in the mat irradiated at 77°K versus temperature of annealing.
○, Total radical ●, alkyl radical △, allyl radical

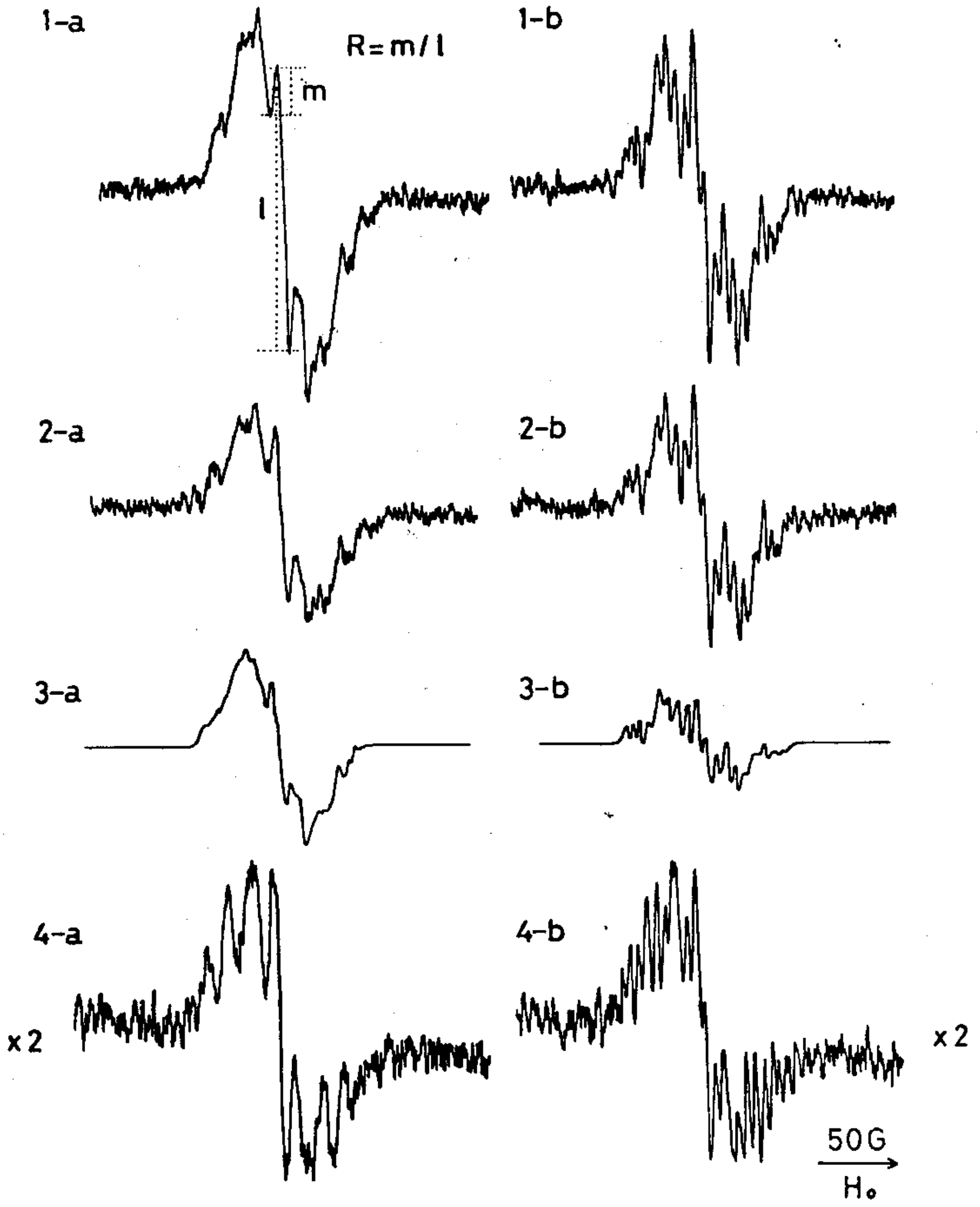

Fig. 5 ESR spectra of allyl radicals produced in a single crystal mat of polyethylene. Observation were carried out at room temperature. The magnetic field was parallel(a) or perpendicular(b) to the plane of the mat. 1-a; 1-b, The sample was irradiated in vacuo at 77°K and then annealed at room temperature for three weeks. 2-a; 2-b, The sample treated above was further annealed at 333°K for 5 min 4-a; 4-b, The sample annealed at 333°K for 5 min was then stored at room temperature for four months. 3-a; 3-b, The difference spectra obtained by substracting spectra of 2-a and 2-b from spectra of 1-a and 1-b.

[4] Acknowledgment

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