

RADICAL MIGRATION AS AN ELEMENTARY PROCESS IN DEGRADATION

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Abstract - There are several experimental evidences indicating that free radicals produced uniformly in polymers in the primary stage of γ -irradiation decayed preferentially in amorphous regions in the polymers, such as PE and PP. It was also shown that radical concentration was increased in amorphous surface regions of crystallites in polymers like PE after the γ -irradiation followed by the heat treatments. These facts require that free radicals in polymer matrices migrate from the original sites of productions by γ -irradiation to amorphous regions, where the radicals either decay by recombinations or are stabilized. A molecular mechanism for the radical migration was demonstrated by analysis of the changes in ESR spectrum of PE radicals. An unpaired electron migrates in a polymer matrix just like an elastic collision of molecules in a gas phase until its stabilization. This process losing no energy like an elastic collision is called the radical migration. The facts mentioned above were explained by this radical migration. Antioxidant molecules in polybutadiene (PB) rubber were preferentially converted into free radicals after mechanical fracture of PB. This fact suggest that an activity of the antioxidant is closely related with the radical migration.

INTRODUCTION

Free radical processes are involved in chemistry of polymer degradations, because decays of free radicals result in either cross-links or double bonds or other permanent changes in chemical structures of polymers, which cause variations in physical natures of polymers, mostly degradations of polymers. For example, photodegradation is a degradation of polymers caused by photo-illumination, which produces radicals in the polymers. Radiation damages of polymers are degradations caused by γ -irradiation, which also generates free radicals in polymers. Classification of degradations, such as photo, radiation, thermal, chemical and mechanical, is named after the difference in primary excitations from external origins, and a primary mechanism of free radical formation is different from one degradation to another. But the degradations are the results of radical decays. Therefore, a fate of free radicals, that is a process of radicals to the decay, plays an important role in any degradation. This decaying process is not directly influenced by primary excitations but determined by both chemical species of radicals and nature of polymer matrix trapping the radicals. From this view point a decaying process of radicals in a particular polymer, such as polyethylene (PE), should have some generality in chemistry of degradation irrespective of the primary excitations. γ irradiation of polymers at 77K is the most convenient method to produce free radicals in solid polymers and radicals are trapped in the irradiated polymer matrix. Both decays and conversions of free radicals in the system are able to be traced with ease by ESR after heat treatments. Information has been accumulated on the chemistry of free radicals in polymer matrices in such a way. In this paper the results obtained by γ -irradiation of polymers will be presented but the processes established in the experiments are applicable to other degradation as a decaying process of the same radical species in the same polymer matrix and approximately applicable to other polymers.

STEPWISE DECAY OF FREE RADICALS IN POLYMER MATRICES

PE was γ -irradiated at 77K and ESR spectrum was observed at 77K from this irradiated PE. Relative intensities of ESR spectra after the heat treatments at different temperatures were plotted against the temperatures and examples are plotted in Fig. 1 (Ref. 1) Since the ESR intensity is proportional to the radical concentration, the curves represent decays of the free radicals after the heat treatment. Thus, this curve is called the decay curve. As shown in Fig. 1 the radicals decays in stepwise. Such stepwise decays were observed for other polymers (Ref. 2, 3) and are a characteristic behavior of radicals decays in polymer

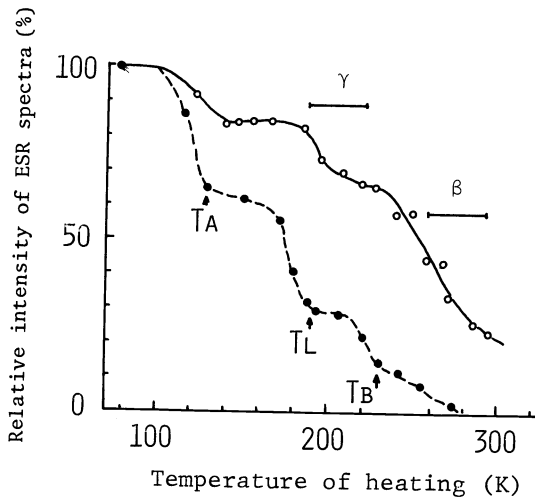


Fig. 1. Decay curves of PE free radicals produced by γ -irradiation.
 ● LDPE (crystallinity 51%) ○ HDPE (crystallinity 68%).

matrices. Reaction of radical decays in each step was analysed as a second order reaction, which indicates a recombination of two radicals as a decay mechanism. It was found that reaction rates of the decays were strongly correlated with the molecular motions liberated in amorphous region of PE at the particular temperatures, T_A , T_L , and T_B in Fig. 1. Decay behaviors are apparently different depending on the crystallinity of polymers trapping the radicals, as shown in Fig. 1. Decay in the first stage up to T_A is proportional to amorphous content, as shown in Fig. 2. All these experimental results convergently indicate that free radicals produced in PE decay preferentially in the amorphous regions, in spite of the fact that the radicals have been produced homogeneously all over the sample in the primary stage of formation. In other words the places of radical decays caused by the recombinations are different from the sites of radical formations. This requires migrations of radicals from the places of generations to the decay sites.

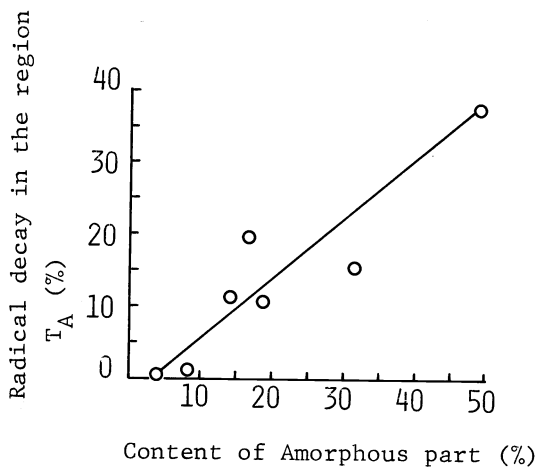


Fig. 2. Decrease of radicals in the temperature region below T_A against the amorphous fractions of PE having different crystallinity.

ACCUMULATION OF RADICALS IN SURFACE REGIONS OF CRYSTALLITES

Concentration of the free radicals generated by γ -irradiation of polymers was increased in the surface region of the crystallites by the mild heat treatments. (Ref. 4, 5) Primary distribution of free radicals before the heat treatment was rather homogeneous and fraction of the radicals trapped in crystalline parts was proportional to the crystallinity. No preferential presence of radicals in the amorphous surfaces of the crystallites were detected before the heat treatment. This result indicates that the radicals migrate from the

crystalline parts to the surface regions of crystallites by the mild heat treatment and the radicals are more stabilized in the surface region being more amorphous than in the regular crystalline sites.

CONVERSIONS OF THE CHAIN END RADICAL IN PE

It is well known that allylic radicals, $-C=C\dot{C}-$, were produced in PE after γ -irradiation of high dose. (Ref. 6) The allylic radical of PE shows a septet ESR spectrum. The sample, which had shown the allylic septet was photo-illuminated with the visible light and the observed spectrum was changed into an octet after this photo-irradiation. The octet was altered into a sextet by the slight heat treatment. The sextet returned back to the initial septet by the long heat treatment at the room temperature. The changes of ESR spectra are illustrated in Fig. 3 (Ref. 7). Based on the analysis of the spectra the changes of the spectra mean the conversions of radicals described in Fig. 4 (Ref. 7) The chain end radical of PE, which is produced by a β -scission followed by a hydrogen shift to an open chain end, is now converted into an alkyl radical by a hydrogen abstraction of the unpaired electron.

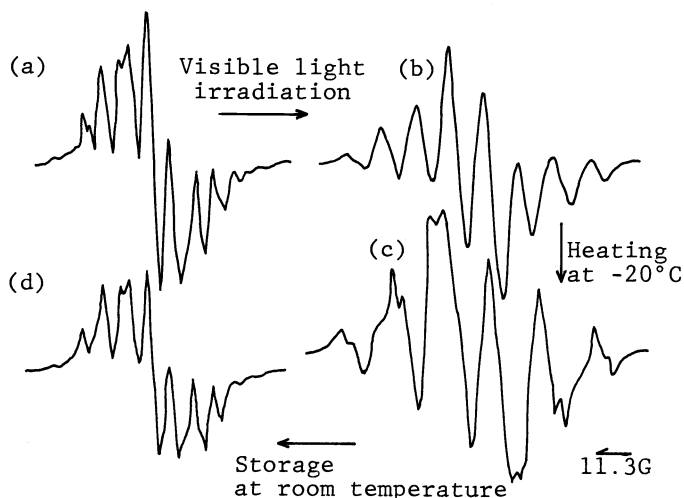


Fig. 3. Changes of ESR spectrum of PE allyl radical, which were caused by visible light illumination followed by the heat treatments.

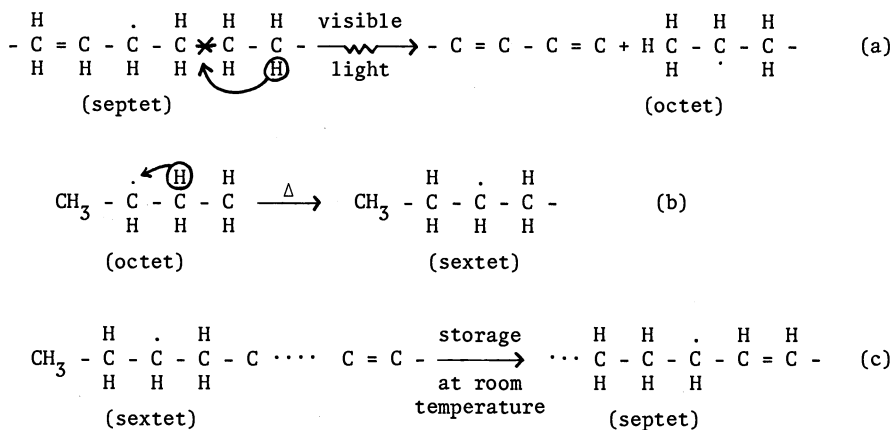


Fig. 4. The reaction of the allylic radical and the radical migration.
 a) a chain scission caused by photo-irradiation. b) one step migration.
 c) multi-step migration until a stabilization.

Successive hydrogen abstractions by the unpaired electron occur randomly until the unpaired electron is stabilized at the site adjacent to the double bond, that is a formation of an allylic radical. This process is a molecular mechanism of radical migration along the chain to a site which stabilizes the unpaired electron by a delocalization in this particular case. The rate constants of the radical conversions (b) and (c) in Fig. 4 were estimated and

the Arrhenius plots are shown in Fig. 5. The activation energies of these two rates are same, 18 Kcal/mol, within the experimental error but rates of the conversion to allylic radicals are much slower than the other. The process "b" is a migration of the unpaired electron just by a single bond but the process "c" is the successive long migration of the unpaired electron, in which the potential barrier overcome by the unpaired electron is identical to the single migration but the frequency factor is much higher because of the frequent random processes up to the stabilization site. This is quite compatible with the results shown in Fig. 4. The evidences so far accumulated indicate that the unpaired electron abstracts hydrogen successively either in an intrachain process as shown in Fig. 3 or in an interchain process and the hydrogen abstraction is a random process, through which the unpaired electron migrates randomly in a polymer matrix until its stabilization. It should be stressed that no energy is different before and after the single hydrogen abstraction along a chain because homogeneous molecular structure of PE. Therefore, this single hydrogen abstraction by the unpaired electron corresponds to an elastic collision of a molecule in a gas phase, by which the molecule loses no energy but changes a direction of its movement.

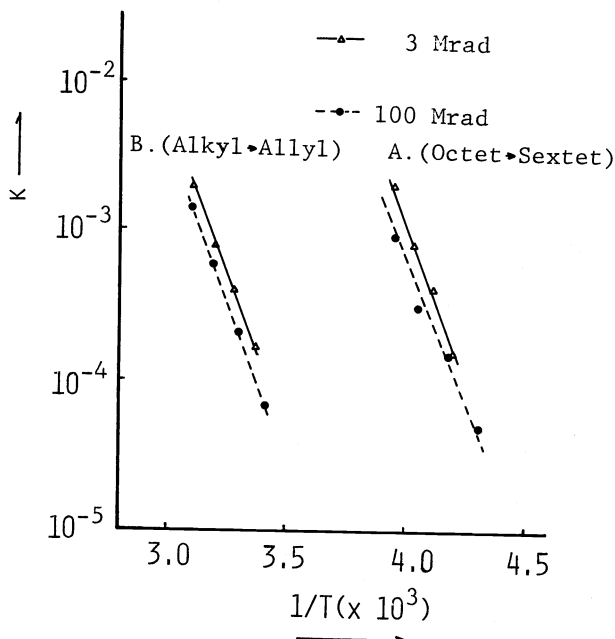


Fig. 5. Arrhenius plots of the radical conversions b and c in Fig. 4.

A MODEL FOR THE RADICAL MIGRATION

Suppose an alkyl radical, $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$, trapped in a crystalline region at a low temperature like 77K. The electronic configuration of the unpaired electron site is three sp^2 orbitals for planar bondings and a p_π orbital for the unpaired electron. The electronic and steric configuration of this site is different from the normal configuration of PE, that is a tetragonal configuration, and therefore the polymer chain is distorted at this site because of its difference in the electronic configuration. This distortion is not easily relaxed in a crystalline region at 77K and an elastic energy is stored at this site. Concerning the electronic energy of the unpaired electron no energy is changed before and after a hydrogen abstraction along a chain because of the homogeneous structure of PE. Then, the electronic energy seen by the unpaired electron is flat along the chain, and this flat level is taken as the zero level. The energy at the unpaired electron site is higher than the zero level by the stored elastic energy. If the unpaired electron situates at a site adjacent to a double bond, the energy becomes lower due to a delocalization of the unpaired electron. This means the stabilization of the unpaired electron by a formation of an allylic radical. If the unpaired electron meets other unpaired electron to form a double bond, the unpaired electron actually disappear by formation of the stable chemical bond. These situations are illustrated in Fig. 6 (Ref. 8). In this illustration the radical migration along a chain is assumed for a simplicity but the interchain migration is also possible and probable. For a polymer like polypropylene, which is less homogeneous than PE, the electronic energy of an unpaired electron could be different depending on the sites of either $-\dot{\text{C}}\text{H}-\text{CH}(\text{CH}_3)-$ or $-\text{CH}_2-\dot{\text{C}}\text{CH}_3-$. Then the energy of the unpaired is not expressed by a flat level. However,

if the unpaired electron moves by two bonds then the final energy is identical to the initial energy because of periodicity of the polymer. Thus, one may regard the flat level for the unpaired electron shown in Fig. 6 as a good approximation for any polymer. The unpaired electron, which has an excess energy over the activation energy, probably 18 Kcal/mol, moves back and forth in a random way along the chain until it reaches to the stabilizing sites, such as formations of either a double bond or an allylic radical or a cross-link. The excess energy required for the migration is provided by thermal energy of the heat treatment.

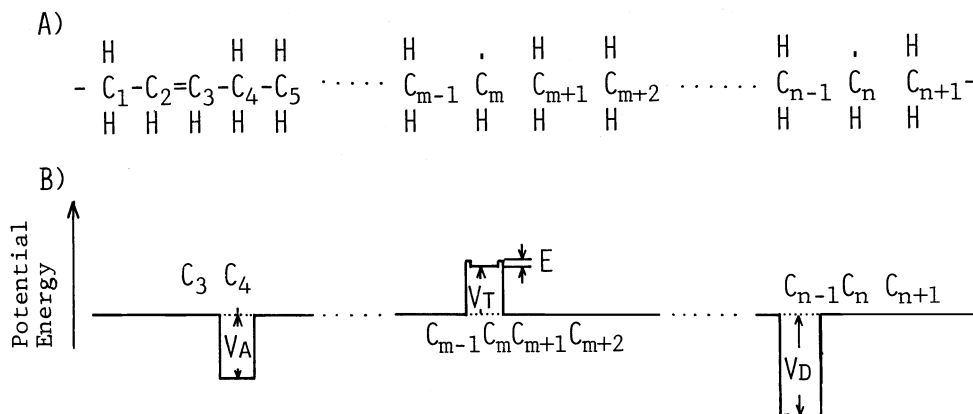


Fig. 6. A) Schematic model of polymer radical B) Schematic representation of energy seen by an unpaired electron on a polymer chain. V_A : trap for an allylic radical V_D : trap for a double bond. V_T : potential produced by the chain distortion at the site of unpaired electron. E : activation energy for the strain relaxation.

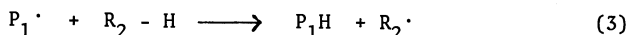
In an amorphous region conformations of polymer chains are more dispersed than in the crystalline region. Therefore distortion of the chain at the unpaired electron site is more easily relaxed in an amorphous region and the elastic energy V_T is reduced in the amorphous region because the distorted chain adjusts itself more easily in the amorphous region. Then, migration of such relaxed radicals back to the crystalline part becomes more difficult because of its lower energy state after the relaxation of the stored elastic energy. This is an explanation why the radical concentration is increased in the amorphous surface regions of the crystallites after the heat treatment. A higher concentration of radicals in the amorphous region as well as high mobilities of polymer chains in the amorphous region accelerate decay of the radicals. The explanation is compatible with the facts.

The consistency of the explanations derived from the model leads us to a conclusion that the radical migration as a random process plays a same role in a polymer matrix as an elastic collision of a molecule in a gas phase. Any rate of chemical reaction in a gas phase is governed by the frequency of elastic collisions of molecule. In similar way the rate of radical migration in a solid polymer may regulate reaction rate of radical decays. The rate of radical migration is influenced by temperature, morphology, molecular motions of polymers. The migration in a specified system, urea adducts of polymers, was studied in details by Japanese researchers (Ref. 9, 10), but details of the dependence on nature of the matrix are still open to question.

FUNCTION OF ANTIOXIDANT STUDIED BY ESR

Polybutadiene (PB) rubber sawed in liquid nitrogen and the saw dusts of PB were collected into an ESR sample tube, from which ESR spectrum was observed. Fig. 7 is an example of the spectrum observed from the mechano-radicals of PB containing no antioxidant. The asymmetric spectrum demonstrates presence of the peroxy radicals. This means that the mechano-radicals are primarily formed by chain scissions of PB molecules but the radicals are attacked by oxygen molecules dissolved in liquid nitrogen to form peroxy radicals of PB. The conversion to the peroxy radicals is so rapid that observed spectrum is that from the peroxy radicals. Similar experiment was carried out for PB containing an antioxidant, *t*-butyl-*p*-cresol. The observed spectrum is shown as "a" in Fig. 8. This spectrum is decomposed into two components, shown with thin and dotted lines. The component represented with dotted line is the asymmetric spectrum of peroxy radical and the other component shown with the thin line originates from the antioxidant radical. This analysis of the spectrum demonstrates that the primary mechano-radicals of PB are now converted into two species $\text{ROO}\cdot$ and the cresol radicals $\text{R}_2\cdot$.





$R_2\cdot$: cresol radical

The conversion reactions (2) and (3) are competitive each other. Both reactions (2) and (3) are diffusion controlled in solid PB at 77K. Oxygen molecules may diffuse in the matrix elastomer, but it is very unlikely that the bulky molecule, t-butyl-p-cresol, diffuse in the matrix at 77K. Almost same conversions into the $P_1OO\cdot$ and $R_2\cdot$ suggest that diffusion rate resulting in the formation of $R_2\cdot$ radical is nearly same to that of the oxygen. Remembering the radical migration described above it is considered that the diffusion responsible for the formation of $R_2\cdot$ is not a diffusion of the bulky molecule but the radical migration of PB radical in the matrix. The hydrogen abstraction by a PB radical from the cresol stabilizes

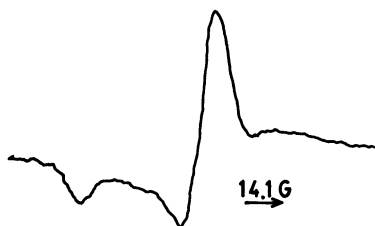


Fig. 7. ESR spectrum of cis PB without antioxidant after mechanical fracture at 77K.

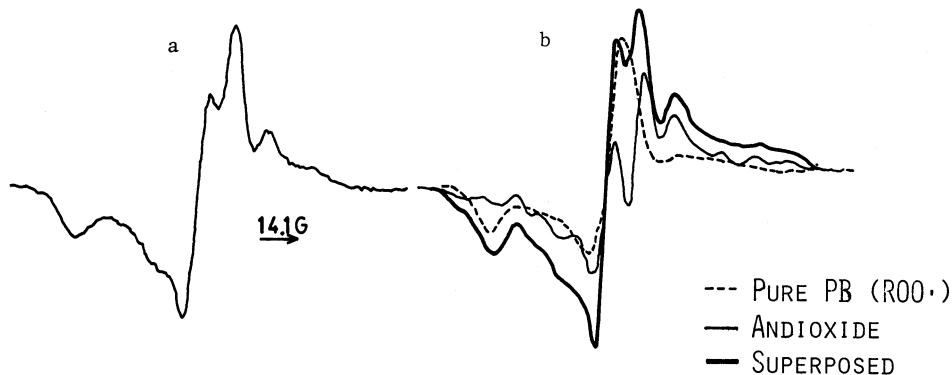
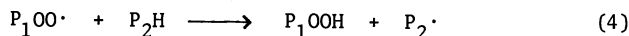


Fig. 8. a) ESR spectrum observed from mechano-radicals of PB containing an antioxidant, t-butyl-p-cresol. b) simulation of the spectrum
 ----: spectrum of the peroxy radical, —: spectrum of the pure antioxidant, —: superposition.

the unpaired electron, just as traps shown in Fig. 6. PB radicals lead to the changes in chemical structure of PB matrix by forming either cross-links or additional double bonds caused by the recombination of the radicals. The unpaired electrons stabilized as that in the cresol radical does not induce the changes in PB matrix. This is considered to be a mechanism of the antioxidant to prevent degradation of polymers. Decays of peroxyradicals as well as the cresol radicals were investigated and decay curves are shown in Fig. 9. The peroxy radicals decay monotonically but the cresol radicals are increased in the concentration in the temperature region between -150° and -90° . A peroxy radical decays by a hydrogen abstraction from a molecule nearby.



A newly formed polymer radical $P_2\cdot$ is converted into a peroxy radical in presence of oxygen and a cyclic reaction proceeds.



This process (5) must compete with the process (3) the conversion of the polymer radical to the cresol radical, in the system containing the antioxidant. This conversion interrupts the cyclic reactions, (4) and (5), and retards the degradation caused by the peroxy radicals. The observed increase in the concentration of the cresol radicals in the decay curve in Fig. 9 is taken as the experimental evidence for the conversion of polymer radicals $P_2\cdot$ into the cresol radicals $R_2\cdot$. This is the other function of the antioxidant, which scavenges the polymer radical in the secondary process.

Based on the ESR study the function of the antioxidant is divided into two processes; one is a trapping of a polymer radical in the primary state and the other is a scavenging of a polymer radical in the secondary stage. The former is a kind of competitive reaction between peroxidation and a conversion to the antioxidant radical immediately after the primary formation of polymer radicals. Both reactions are diffusion controlled in a solid polymer. Most of antioxidants are very bulky molecules, which are very unlikely to diffuse with a rate similar to that of oxygen molecule. The diffusion competitive with the oxygen molecule in such a system is not that of the antioxidant but the radical migration. For a system, in which the radical migration is rather slow, reaction with oxygen is more predominant in the primary stage and the scavenging of polymer radicals in the secondary stage becomes main mechanism of the antioxidation action. The conversions to the antioxidant radicals are one example to illustrate that the radical migration in a polymer matrix is very important elementary process in the chemistry of polymer degradation.

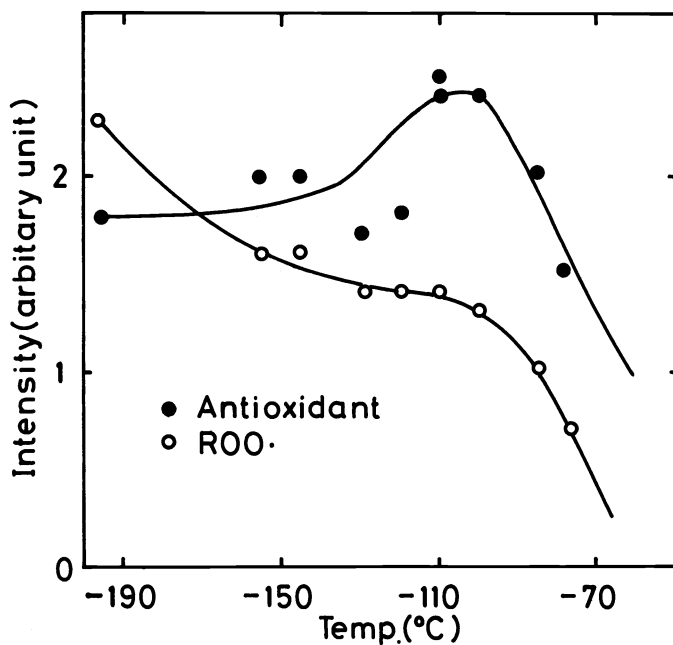


Fig. 9. Decay curves of antioxidant and peroxy radicals.

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