

Radiothermoluminescence of Polyethylene and Disappearance of Free Radicals

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Polyethylene sheet was cooled down to 77°K and irradiated by 1.5 MeV electron beam. After receiving a dose of 5×10^7 r, the temperature was raised saw-toothwise and the intensity of thermoluminescence glow and the concentration of surviving free radicals were measured at respective stages. The correlation of the intensity of thermoluminescence glow with the disappearance of free radicals at the respective temperatures was examined. α and β peaks of thermoluminescence glow curve showed no correlation with the disappearance of free radicals but γ peak showed remarkable dependence upon the disappearance. Dose dependences of the thermoluminescence glow and that of the free radical concentration were studied from 10^5 r to 10^7 r and the former showed saturation at 10^6 r while the latter does not saturate over this dose range. It was found that thermoluminescence has no direct correlation with the radical disappearance. It is concluded that thermoluminescence is ascribed to the release of energy stored which is resulted from an intra- or intermolecular motion.

INTRODUCTION

Radiothermoluminescence of organic substances has been studied by several authors with the purpose to investigate intermediate species which can store the radiation energy and to analyze paths along which the quantum of absorbed energy reaches the final effects. However, there are few data which can make clear the mechanism of thermoluminescence in organic substances. Augenstine and his collaborators¹⁾ investigated radio-thermoluminescence of amino acids and several proteins but it can not be concluded whether trapping sites resulting in thermoluminescence are property of the molecular structure or of the crystalline structure. Recently they obtained²⁾ spectral distributions of thermoluminescence from several amino acids but the confusion about the interpretation of the mechanism became more serious because of the marked variation of the spectrum with temperature.

In the case of ionic crystals, thermoluminescence is resulted from recombination of holes and electrons which are trapped in vacancies of the crystal lattice. These colour centers can be called excited metastable states storing the radiation energy and these unpaired electrons can be detected by electron spin resonance technique. In organic solids, also thermoluminescence must be related to some excited electronic metastable states and therefore these electrons must have unpaired spin. They are presumably electrons in triplet states or

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those trapped at some imperfections of the crystal lattice or at some regions of charge concentration in the molecules. But one of the most plausible states is free radical.

In a variety of organic substances, Semenov³⁾ found that the peak temperature of the radiothermoluminescence glow coincides with the disappearance temperature of free radicals produced by irradiation. His results are not sufficient to conclude that thermoluminescence is resulted from the radical disappearance because the temperature of the glow peak depends on the rate of warming and the temperature of the disappearance is not so critical.

In this paper, some experimental results are shown to discuss the relationship between thermoluminescence and the disappearance of free radicals. Total intensity of radiothermoluminescence from polyethylene was measured as a function of the quantity of free radicals which have disappeared. The dose dependency of the radiothermoluminescence intensity and that of free radicals produced by irradiation were compared with each other and the mechanism of radiothermoluminescence in organic substances was discussed.

EXPERIMENTAL PROCEDURES AND RESULTS

A piece of polyethylene sheet, 1 mm×3 mm×20 mm Hizex 5000, was cooled down to 77°K and was irradiated in air by 1.5 MeV electron beam from a Van de Graaff accelerator. After being kept in the dark for a day the concentration of free radicals was measured at 77°K by 9400 MC electron spin resonance spectrometer. The ESR signal obtained, alkyl radicals, is shown in Fig. 1a. Thermoluminescence of the irradiated samples was recorded by the usual equipment⁴⁾ with the uniform warming rate of 12°K/min and the glow curves are shown in Fig. 1b.

After these preliminary experiments a new piece of the sample was irradiated to 5×10^7 r as before. The thermoluminescence glow emitted within some temperature ranges and the concentration of surviving radicals at those temperature were measured repeatedly by the following procedure.

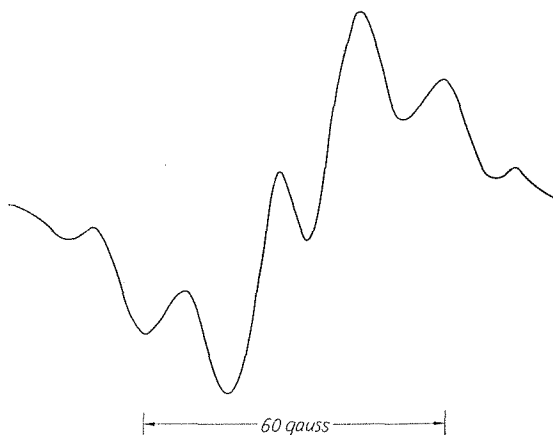


Fig. 1a. ESR spectrum of polyethylene Hizex 5000.

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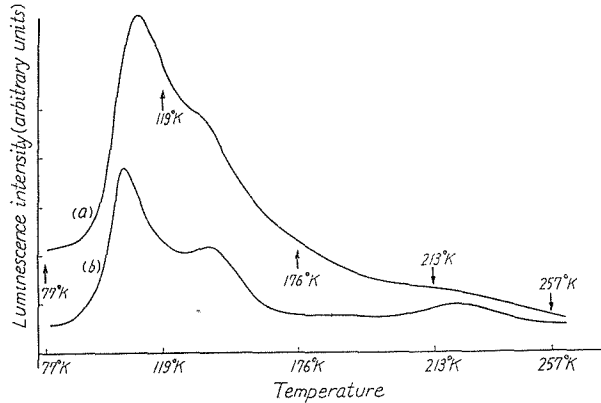


Fig. 1b. Thermoluminescence glow curve of polyethylene.
 (a) 1.5 MeV electron beam, 5×10^7 r.
 (b) Co^{60} γ -rays, 3.5×10^5 r.

At first, the radical concentration in the sample was measured by ESR at 77°K. The sample was transferred into the thermoluminescence apparatus and was warmed to 119°K, where the α peak of the polyethylene thermoluminescence glow curve was passed off, and the glow curve was recorded. Then the sample was cooled suddenly to 77°K and the concentration of surviving free radicals was measured as before. Next, the sample was transferred back into the thermoluminescence apparatus. The thermoluminescence glow curve was recorded on warming to 176°K. Again, it was cooled down to 77°K and the radical concentration was measured. Such saw-tooth warming was repeated for temperatures shown by arrows in Fig. 1b. The sample was always treated in the dark or under the very weak red light to avoid the optical bleaching of the traps.

The results are shown in Fig. 2 where the concentration of the surviving

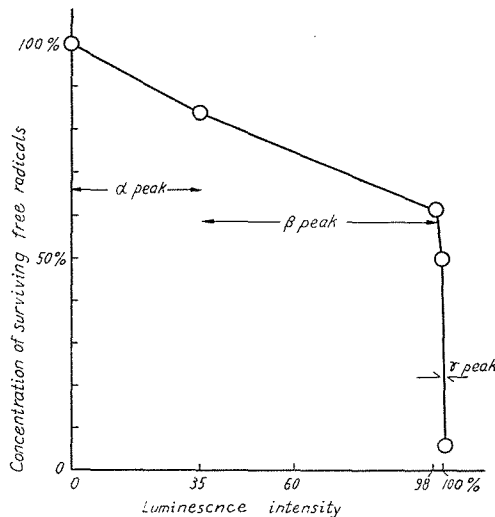


Fig. 2. The concentration of the surviving radicals as a function of total thermoluminescence intensity emitted below the temperature.

radicals is plotted as a function of total thermoluminescence intensity emitted below the temperature. The decrease of the radical concentration in α and β peaks was somewhat overestimated because the effect of the power saturation was not corrected. Within the temperature range where α and β peaks of the glow curve appear, the decrease of the free radical concentration is small although a large fraction of the luminescence glow is emitted. Therefore, in these regions thermoluminescence at α and β peaks and the disappearance of free radicals has no correlation with each other. Contrary to α and β peaks, radical disappearance is remarkable at γ peak and close correlation between the mechanism of thermoluminescence and the radical disappearance is suggested.

Dose dependency of the radical concentration was also studied. Pieces of polyethylene sheet were irradiated in the same condition as before. The absorbed doses were ranged from 10^7 r to 10^8 r. For microwave power ordinarily used, ESR signals of these samples showed remarkable power saturation especially in the case of low dose. Therefore, power saturation properties were carefully examined for each sample and the radical concentrations were obtained from these saturation curves (Fig. 3). Thus, the dose dependency of radical concentration was obtained as is shown in Fig. 4, where accuracy of each plot is $\pm 10\%$ and the absolute value of radical concentration is 8×10^{19} radicals/cc for the plot of 10^8 r with error of factor 2. The radical concentration continues to increase until 10^8 r. This gives some information on the mechanism of thermoluminescence is discussed below.

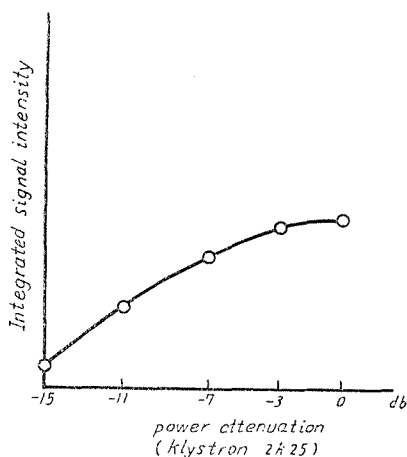


Fig. 3. Power saturation curve.

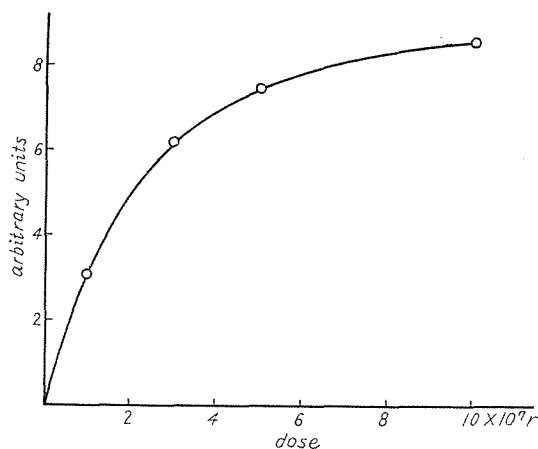


Fig. 4. Dose dependency of free radicals.
Sample : polyethylene Hizex 5000.

DISCUSSION

As is shown in Fig. 1b, γ peak of thermoluminescence glow became obscure for 5×10^7 r. Such broadening of the peak is widely observed for all peaks of various substances and is probably due to the broadening of the trap depth distributions. Therefore, an area of the glow curve from 213°K to 241°K is regarded as γ peak even if the peak is not distinct.

At the temperature range of γ peak, the radical disappearance is remarkable as is seen from Fig. 2. A close correlation must exist between the mechanism of thermoluminescence and that of the radical disappearance. However, it is not adequate to conclude that the former is induced from the latter. Both phenomena may possibly resulted from another phenomenon which arises at this temperature. In a variety of organic solids, there are many thermoluminescence glow peaks which do not coincide the radical disappearance³⁾. For the case of Diphenylpicrylhydrazyl (DPPH) and Kinnyon Banfield radical, which are stable at room temperature and are not produced by irradiation but by chemical reactions, did not show thermoluminescence at the temperature where those free radicals disappeared. Beside these experimental facts which suggest the independency between the mechanism of thermoluminescence and of the radical disappearance, the difference between the dose saturation properties of the radical concentration produced in polyethylene and of γ peak intensity of thermoluminescence glow curves denies the direct correlation between thermoluminescence and the radical disappearance. The γ peak intensity shows distinct saturation at 10^6 r⁵⁾ but the radical concentration continues to increase until 10^8 r (Fig. 4). Therefore we can conclude that the trapped state which contributes to thermoluminescence is not free radicals and that thermoluminescence is not the direct result of the recombination of free radicals. Although the dose dependency of radical concentration was not studied below 10^7 r and therefore it can not be concluded that there is no knick in the radical concentration curve at 10^6 r, it can be concluded that the most part of the radical recombination have no relationship with thermoluminescence.

At γ peak temperature, the segment motion of main chain of polyethylene become active and the glass transition of the lattice occurs. The collision probability of free radicals in the molecules as well as the rate of radical disappearance increases owing to this molecular motion as showed with polymethyl meta acrylate (PMMA)⁶⁾. At the same time, the stored energy which results in thermoluminescence is released and then the probability of the emission of photon increases. In other organic solids, also, radiation energy is stored at some lattice imperfection and the release of this stored state is induced by some intra- or intermolecular motion resulting in thermoluminescence. On the other hand, the disappearance of free radicals produced in the molecules of the solid is activated by another molecular motion. When both molecular motions are the same, thermoluminescence shows close correlation to the disappearance of free radicals. Semenov's results, where many examples which show the coincidence of the thermoluminescence glow peak temperature with the temperature of phase transition or of intramolecular motion are afforded, give powerful support to this consideration. There must be no "direct" correlation between thermoluminescence and the radical disappearance.

CONCLUSION

Temperature of γ peak in radiothermoluminescence glow curve of polyethylene

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coincides with the temperature of disappearance of free radicals, but the former is not resulted from the latter. Generally, radiothermoluminescence in organic solids will be resulted from the release of electrons trapped in crystal imperfection and some intra- and intermolecular motions will cause the release.

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