Electron trapping model of u.v. induced thermoluminescence in polyethylene

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(*Received* 27 *July* 1981)

An electron trapping model is proposed to explain the previously observed thermoluminescence output from polyethylene exposed to ultraviolet radiation. Ionization of luminescent molecules by a double excitation mechanism is assumed to be followed by competition for the ejected electrons between shallow traps and radiation-produced alkyl radicals, with electrons in shallow traps also being untrapped by the incident radiation. It is shown that this model not only explains all the available data on thermoluminescence induced by ultraviolet radiation but also correlates well with the very different data on thermoluminescence and alkyl radical production induced by true ionizing radiation.

Keywords Electron trapping; thermoluminescence; polyethylene; ultraviolet radiation; ionization

INTRODUCTION

The thermoluminescence emission produced by irradiation of polyethylene with ultraviolet (u.v.) radiation at low temperatures followed by warming was studied some years ago by Charlesby and Partridge[1]. The thermoluminescence output was found to be proportional to both dose and dose rate at low irradiation doses, but inversely proportional to dose and independent of dose rate at high doses, as shown in *Figure 1*. The dose rate dependence at low doses was ascribed to the molecules responsible for the actual emission being ionized by a double excitation process. In this process each molecule was assumed to be raised to the triplet state, via intersystem crossing from the lowest excited singlet state, by a first photon and then to have an appreciable probability of absorbing a second photon while still in the triplet state (due to its long lifetime, often several seconds) which would supply enough extra energy to cause complete ionization. There seems no reason to doubt the general correctness of this mechanism, especially as similar photon ionizations have since been observed in other organic systems[2], but the reason for the thermoluminescence dose curves rising to a maximum and then declining was less clear. Charlesby and Partridge suggested that this was due to destruction of the luminescent molecules (i.e. their conversion to non-luminescent forms) and this was certainly demonstrated for the case of a series of u.v. irradiations each followed by warming of the polyethylene to room temperature before cooling again for the next irradiation. The amount of destruction in this case, as measured by the diminution in thermoluminescence output as a function of total accumulated dose, was found to be proportional to both dose and dose rate. However, to fit the observed output curve for single irradiations it was found necessary to assume that the destruction occurring at low temperature was proportional only to dose while being independent of dose rate, and no clear mechanism for this destruction was apparent.

Subsequently Wintle[3] suggested an alternative explanation for the medium and high dose regions of the output curve. This assumed that two destructive processes were simultaneously operative during a low temperature irradiation, one being due to a bimolecular reaction between triplet state molecules and the other involving only molecules that were already ionized. With the destruction rate of the former process being proportional to the square of the triplet state concentration and the rate of the latter process being assumed to be proportional to both dose rate and concentration of ionized luminescent molecules, Wintle showed that by a suitable choice of parameters a good fit could be obtained to the original experimental dose curves.

The main problem with the Wintle model lies in the assumed bimolecular destruction reaction between triplet state molecules because, since these will have a very low concentration, an appreciable amount of diffusional motion must be assumed in order for them to come together to react. Wintle estimated that a diffusion coefficient of $\sim 10^{-13}$ m^2 s^{-1} was necessary and noted that this was of the order found for small molecules in polyethylene. However, diffusion of this magnitude is only found above the glass transition temperature of polyethylene. At 77 K even oxygen molecules are completely 'frozen in'[4] and they do not start to react with radiation-produced alkyl radicals around them until the temperature is raised to ~140 K. Thus diffusion at 77 K by the appreciably more bulky luminescent molecules, many of which are aromatic species[4], is most unlikely. The suggested destructive reaction of excited luminescent ions is possible, but there seems to be no evidence for it. Finally it should be noted that the model provides no correlation with the data on thermoluminescence induced by ionizing radiation, which might reasonably have been expected.

ELECTRON TRAPPING MODEL

In view of the problems with the two models discussed above a new model of u.v. induced thermoluminescence in

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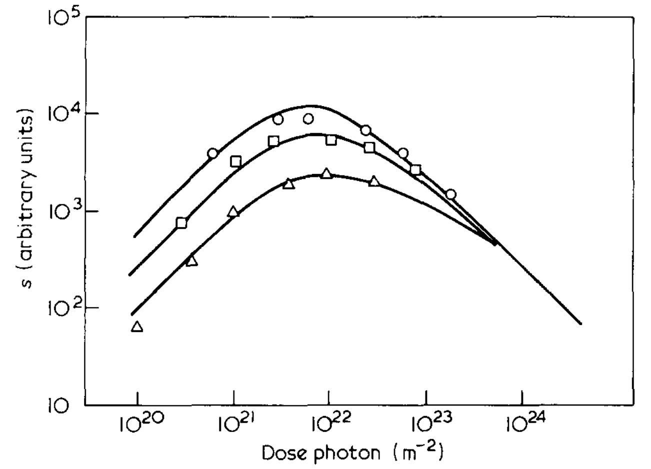

Figure 1 Thermoluminescence output of polyethylene as a function of ultraviolet dose at three dose rates (1.0, 2.8 and 6.2 x 10^{20} photons m^{-2} s^{-1}). Experimental values taken from Ref. 1; theoretical values calculated from equation (9). (*Figure* reproduced from Wintle, H. J. *Polymer* 1974, **15**, 425 by permission of the publishers)

polyethylene is put forward here which has the following advantages:

(1) Explanation in terms of known or very probable reactions
(2) Mathematical similarity to the Wintle model, so providing the same good fit to the dose curve data.
(3) Correlation with alkyl radical production, which is one of the primary effects of the irradiation of polyethylene.
(4) Synthesis of the data on thermoluminescence as produced by u.v. radiation and by ionizing radiation.

In this model it is assumed that the luminescent molecules are ionized by the same double excitation mechanism described earlier but that the ejected electrons are then captured by two different types of traps, 'shallow' and 'deep', in competition with one another. The shallow traps are those that on warming release their electrons back to the ionized luminescent molecules to produce thermoluminescence, while the deep traps remove the electrons completely from the thermoluminescence process. The shallow traps are often likely to be permanent and intrinsic features of the polyethylene structure, probably 'cavities' of various types[4] formed by particular local configurations of the polymer chains, whereas the deep traps are assumed to be radiation-produced free radicals (later identified as alkyl radicals) which are produced, like the ionized luminescent molecules, at a rate proportional to the square of the dose rate. Electrons in the shallow traps are assumed to be released also by the actual radiation that is responsible for production of the thermoluminescence (optical bleaching of polyethylene thermoluminescence is well established[4]) but electrons in deep traps are taken to be unaffected by this. Note that in this model there is no destruction of luminescent molecules during irradiations at liquid nitrogen temperature; any destruction that does occur is assumed to be during or after the warming to room temperature when radicals and ions become unfrozen and are able to react.

The mathematical treatment of this model generally follows that already given by Partridge[4] for a similar system subjected to true ionizing radiation, except that in the u.v. radiation case the rates of both deep trap production and luminescent molecule ionization are proportional to the square of the dose rate instead of to just the dose rate as in the ionizing radiation case. Using the notation of the previous treatment as far as possible let s, f and i be the concentrations of electrons in shallow traps, free radicals and ions (i.e. electrons trapped on free radicals) respectively at time t during an irradiation at dose rate r (but note that previously[4] r signified dose not dose rate). Let D be the product of the capture cross section of the shallow traps and the concentration of empty shallow traps (empty shallow traps being assumed to always greatly outnumber filled ones) and E be the capture cross section of the free radicals. Untrapping of electrons from shallow traps by the radiation is assumed to occur at a rate proportional to the dose rate and to the concentration of shallow trapped electrons, s, with a rate constant of F. Finally, both the ionization of luminescent molecules and the production of free radicals occur at rates proportional to the square of the dose rate, with rate constants of M and N respectively. The thermoluminescence output for any irradiation lasting a time, t, will be proportional to the concentration of shallow trapped electrons at that time, s, since only these are involved in thermoluminescence production on subsequent warming.

With these definitions the total number of free radicals produced initially by a radiation dose of $d(=rt)$ is given by $(i+f)$ where:

$$(i+f)=rdN \tag{1}$$

The probability of an ejected electron being captured by a free radical after ionization of the electron's parent molecule will be $Ef(D+Ef)^{-1}$ and so the rate of electron trapping by free radicals will be:

$$\frac{\mathrm{d}i}{\mathrm{d}t}=Mr^2\left(\frac{Ef}{D+Ef}\right) \tag{2}$$

Similarly the net rate of electron trapping by shallow traps, allowing for release of the electrons by radiation (release is assumed to be back to their parent ions and not to other traps) will be:

$$\frac{\mathrm{d}s}{\mathrm{d}t}=Mr^2\left(\frac{D}{D+Ef}\right)-rsF \tag{3}$$

Eliminating i between (1) and (2) and integrating from zero time gives:

$$(N-M)r^2t=f-\left[\frac{DM}{E(N-M)}\right]\mathrm{Log}_e\left\{1+\left[\frac{E(N-M)}{ND}\right]f\right\} \tag{4}$$

Examination of the asymptotic values of equation (4) shows that the net rate of free radical production varies from Nr^2 at low doses, where the amount of electron capture by free radicals will be small due to the low radical concentration and hence $i \ll f$, up to $(N-M)r^2$ at very high doses, where essentially all electrons will be captured by free radicals if $n>M$.

Differentiating equation (4) with respect to time, eliminating time with equation (2) and integrating gives the relation between i and f as:

$$i=\left(\frac{M}{N-M}\right)\left\{f-\left[\frac{ND}{E(N-M)}\right]\mathrm{Log}_e\left(1+\left[\frac{E(N-M)}{ND}\right]f\right)\right\} \tag{5}$$

When f is very small equation (5) reduces to:

$$i=\left(\frac{EM}{2ND}\right)f^2$$

Use of this with the low dose asymptotic value of equation (4) yields:

$$i=\left(\frac{EMN}{2D}\right)r^2d^2 \tag{6}$$

Thus the concentration of electrons trapped on free radicals is predicted to be proportional to the square of both dose and dose rate at low doses. Conversely, when f is very large the limiting value of i, using equations (4) and (5), becomes:

$$i=\left(\frac{M}{N-M}\right)f=Mrd \tag{7}$$

and so i changes from being quadratic with dose at low doses to being linear with dose at high doses.

By differentiation of equation (4) and combining it with equation (3) it is possible[4] to obtain an exact solution for s in terms of a series expansion. Alternatively, however, the approximation $f \gg i$ can be made, which assumes that the concentration of electrons trapped on radicals is always much smaller than the concentration of free radicals. This is certainly true for low doses, from the asymptotic values just considered, and it is shown later that it is likely to be true in practice also for high doses. Neglect of i compared with f in equation (1) then allows equation (3) to be written as:

$$\frac{\mathrm{d}s}{\mathrm{d}t}=-rsF+Mr^2\left[1+\left(\frac{ENr^2}{D}\right)t\right]^{-1} \tag{8}$$

Equation (8) is identical in mathematical form to that obtained by Wintle[3], using a very different model, and therefore the same excellent fit to the u.v.-induced thermoluminescence data can be obtained (see *Figure 1*) by use of his two curve shape parameter values which, in the present notation, are:

$$F=4\times10^{-22}\ \mathrm{m}^2\ \mathrm{photon}^{-1}$$

$$\frac{EN}{D}=1\times10^{-43}\ \mathrm{m}^4\ \mathrm{s\ photon}^{-2}$$

The solution to equation (8) can be written in terms of exponential integrals as:

$$s=\left(\frac{MD}{EN}\right)\left[Ei(y)-Ei\left(\frac{\varphi}{r}\right)\right]\mathrm{Exp}-\left[Fd+\frac{\varphi}{r}\right] \tag{9}$$

where $y=\frac{\varphi}{r}\left\{1+\left(\frac{rF}{\varphi}\right)d\right\}$

and $\varphi=\frac{FJ}{EN}$

For the smaller argument of the two exponential integrals, φ/r, use can be made of the parameters F and EN/D above together with the three original dose rates of Charlesby and Partridge[1] of 1.0, 2.8 and 6.2×10^{20} photons $\mathrm{m}^{-2}\ \mathrm{s}^{-1}$ to obtain arguments of 40, 14.3 and 6.45 for these dose rates respectively. For these relatively large arguments, an exponential integral can be written without too much error in its asymptotic form:

$$Ei(x)\rightarrow\frac{e^x}{x}$$

and in practice the error involved in doing this is about 11% for an argument of 10 and falls to just over 5% for an argument of 20. Thus there is not a large error in using the asymptotic form for the integrals in equation (9), which then gives the simple but approximate solution:

$$s=r\left(\frac{M}{F}\right)\left\{\frac{1-\left[1+\left(\frac{Fr}{\phi}\right)d\right]e^{-Fd}}{1+\left(\frac{Rr}{\phi}\right)d}\right\} \tag{10}$$

Although it is approximate, equation (10) does have the correct asymptotic values of Mrd and $\left(\frac{MD}{EFN}\right)\frac{1}{d}$, for doses tending to zero or infinity, that come from the exact solution of equation (8). Note that the high dose asymptote is independent of dose rate, as indicated from the experimental data, despite the dose rate dependence of both ionization and radical production.

Differentiation of equation (10) gives an expression for the dose, d_m, at the maximum of the thermoluminescence output *versus* dose curves of:

$$r\,\mathrm{Exp}(Fd_m)=\varphi\left[1+\left(\frac{Fr}{\varphi}\right)d_m\right]^2 \tag{11}$$

from which d_m can be obtained by iteration.

The values of d_m found in this way for the three experimental dose rates are 9.68, 7.61 and 6.31×10^{21} photons m^{-2} in order of ascending dose rate, which compare quite well with the true values obtained by computer evaluation of equation (9), using a series expansion for the exponential integrals, of 9.63, 7.46 and 5.98×10^{21} photons m^{-2}.

An approximate empirical relationship for the maximum of the dose curve exists in the form[4]:

$$(d_m)^{-4}\simeq KrF^3\left(\frac{EN}{D}\right)$$

where K is a dimensionless constant with, in the case of u.v.-induced thermoluminescence here, a value of about 0.17. From this relation it is apparent that the value of d_m is considerably more sensitive to the electron untrapping constant F than it is to the deep trap production constant N or the ratio E/D (which reflects the competition for electrons between shallow and deep traps).

DISCUSSION

The two new elements in this model are the radiation-induced untrapping of electrons from shallow traps and

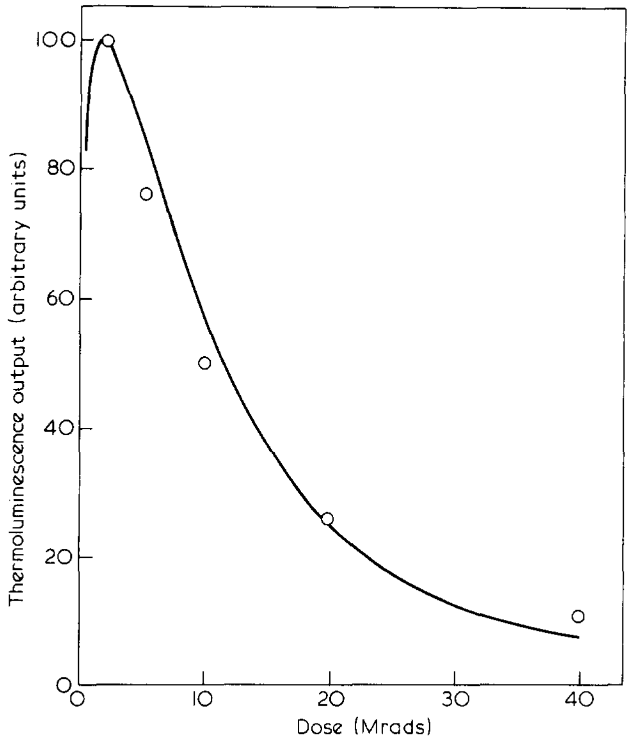

Figure 2 Thermoluminescence output of polyethylene as a function of electron irradiation dose. Experimental values taken from Ref. 6; theoretical values calculated from equation (9) as modified for ionizing radiation

the existence of deep traps which are produced by the radiation at a rate proportional to the square of the dose rate. The evidence for the first of these already exists since the thermoluminescence induced in polyethylene by warming it from 77 K after exposure to ionizing radiation can be substantially reduced or even eliminated by exposing the polymer to near-ultraviolet, visible or near-infrared radiation before warming commences[5-10].

Recombination luminescence is seen during this optical irradiation[11] as the trapped electrons recombine with the luminescent molecule cations. At the same time the broad absorption spectrum of the trapped electrons (and possibly other ionic species) fades as the trapped electrons are removed[12]. The efficiency of this untrapping process varies somewhat with wavelength[8,9], but as the original u.v.-induced thermoluminescence studies were performed with an unfiltered mercury lamp there was much visible as well as u.v. radiation available for this untrapping.

The second postulated reaction, deep trapping by radiation-produced species, can be plausibly established if the deep traps are identified as alkyl radicals. Alkyl radicals are well known to be a major product in polyethylene subjected to ionizing radiation and indeed are the only free radicals detected in it for irradiation at 77 K or lower[13]. Furthermore, Charlesby and Partridge[4] showed that these radicals could be produced by u.v. radiation and at a rate which is probably proportional to the square of the dose rate. Alkyl radicals are likely to have quite a high electron affinity, since the affinities of methyl, ethyl and propyl radicals have been estimated at around 1 eV[14], and thus it is very likely that they will trap electrons and so form carbanions. Electron trapping on 3-methyl pentyl radicals due to the irradiation of 3-methyl pentane at low temperature has been postulated by Ekstrom *et al.*[15], and an ultraviolet absorption assigned to this anion was found to increase at a supralinear rate with dose as would be anticipated for trapping on a radiation-produced species (see for instance equation (6) here). Also electron trapping on radicals in polyethylene and other polymers has been postulated by Alfimov *et al.*[6]

With the deep traps now assigned as alkyl radicals, consider the approximation $f \gg i$ made earlier when solving the differential equation for the shallow trapped electron concentration, s. The approximation was shown to be valid for low doses, but in order to be valid also for high ones it is necessary, from equation (7), for $M \ll N$; that is, for the rate of luminescent molecule ionization to be much lower than the rate of deep trap (now alkyl radical) production. Charlesby and Partridge estimated[1] that at their maximum efficiency of u.v.-induced thermoluminescence production (maximum dose rate and low total dose) one thermoluminescence photon was emitted for about every 10^6 u.v. photons incident upon the sample. Using their comparison of the relative efficiencies of alkyl radical production by u.v. and γ radiation, together with their approximate u.v. penetration depth into the sample and the known efficiency of alkyl radical production by γ radiation (about 2.5 radicals per 100 eV absorbed), it can readily be calculated that at the highest dose rate each alkyl radical produced required about 10^3 u.v. photons to fall upon the sample. Therefore even allowing for the probability that not every shallow trapped electron will give rise to a thermoluminescence photon on subsequent warming it is still clear that the rate of alkyl radical production must far outweigh the rate of ionization and hence that the approximation $f \gg i$ is reasonable for all doses.

Of particular interest in this electron trapping model is the relationship between thermoluminescence induced by u.v. and by ionizing radiation. On Wintle's model there was no connection at all between these two types of thermoluminescence[3] but in the present case there is a clear overlap between the two. Indeed the only points of difference here are that for ionizing radiation the rates of ionization and alkyl radical production will be proportional to just dose rate and not to dose rate squared, and also that the untrapping rates for the shallow trapped electrons are likely to differ as between the two types of radiation.

The first of these points can be accommodated by replacing M and N by G/r and H/r in the case of ionizing radiation, where as before[4] G and H are rate constants for ionization and radical production respectively. By putting these new values in equation (8) the asymptotic solutions become Gd for low doses and $\left(\frac{GD}{HEF}\right)\frac{1}{d}$ for high doses and thus the thermoluminescence output loses its dependence on dose rate at low doses, but remains independent of dose rate at high doses, as observed in practice. Equation (9), modified in this manner, is shown in *Figure 2* as fitted to the data of Alfimov *et al.*[6] on the thermoluminescence output of polyethylene under ionizing (electron) radiation, using the parameters:

$$F = 0.13\ \text{Mrad}^{-1} \qquad \frac{HE}{D} = 57\ \text{Mrad}^{-1}$$

The fit is good, although unfortunately the experimental data does not include values in the low dose region where the output is known to increase rather than decrease with dose[16,17].

In comparing first the F values for the ionizing radiation and u.v. radiation cases, it might be expected that the latter one would be the higher since the u.v./visible radiation is directly absorbed by the trapped electrons, whereas the ionizing radiation probably has to interact indirectly through the degradation of the incident energy into local thermal motion of polymer chain segments which then 'shakes' free the electrons from their shallow traps[4]. This is indeed found since using the 2.3×10^{-2} cm effective absorption depth and 4.76 eV average photon energy of the original work[1], the F value becomes $1.2 \times 10^{-7}\ \mathrm{m^3\ J^{-1}}$ for the u.v. radiation case as compared to only $1.4 \times 10^{-8}\ \mathrm{m^3\ J^{-1}}$ for ionizing radiation (using $F = 0.13\ \mathrm{Mrad^{-1}}$, where a rad represents an energy absorption of $10^{-2}\ \mathrm{J\ kg^{-1}}$). The difference of nearly a factor of ten between the two values seems quire reasonable.

In considering the NE/D and HE/D values it is clear that, if the electron trapping model is correct, the value of E/D should be the same whether the thermoluminescence is induced by u.v. or by ionizing radiation since both D and E are parameters of the traps and not of the type of radiation. Thus if N and H can be obtained then E/D may be evaluated for each type of radiation and compared. For ionizing radiation, H is the concentration of alkyl radicals produced by unit radiation dose and this is known[17] to be about 1.5×10^{24} radicals $\mathrm{m^{-3}\ Mrad^{-1}}$. Combining this with the earlier HE/D value of 57 $\mathrm{Mrad^{-1}}$ gives E/D as $3.8 \times 10^{-23}\ \mathrm{m^3}$ radicals^{-1}. For u.v. radiation, N is the alkyl radical concentration produced per unit radiation dose per unit dose rate. Using the observation[1] that a u.v. dose of 3.7×10^{23} photons $\mathrm{m^{-2}}$ at a dose rate of 6.2×10^{20} photons $\mathrm{m^{-2}\ s^{-1}}$ gave a total number of alkyl radicals equivalent to a 130 krad γ-irradiation of the same sample, together with the estimated fractional u.v. penetration into the sample of 0.15, then an N value is obtained of 5.6×10^{-21} radicals m s photon^{-2}. This can be combined with the earlier NE/D value of $1 \times 10^{-43}\ \mathrm{m^4}$ s photon^{-2} to yield an E/D value of $1.8 \times 10^{-23}\ \mathrm{m^3}$ radicals^{-1}. Therefore despite the use of different polyethylene samples in the two sets of thermoluminescence studies and despite also a rather approximate calculation of the efficiency of alkyl radical production by u.v. radiation it is found that the two calculated E/D values are only a factor of two different from one another. This degree of correspondence obtained from two systems with such very different types of thermoluminescence behaviour with respect to dose rate provides strong support for the basic features of the electron trapping model.

It should be noted that the experimental data used here for the u.v.-induced[1] and, apparently, the ionizing radiation-induced[6] thermoluminescence of polyethylene were obtained from observation of the ε glow peak, which is a peak arising from shallow trapping of electrons by oxygen molecules[4] rather than by the polymer itself. However since the other polyethylene glow peaks associated with polymer traps seem to have much the same behaviour, with both u.v. dose[4] and ionizing radiation dose[16,17], as the ε peak, and since likewise the ε peak declined at much the same rate as the other peaks under visible light irradiation prior to warming[4], it may be concluded that similar results would have been obtained by use of any of the other thermoluminescence peaks.

There are many ways in which the electron trapping model could be extended; for instance by allowing for re-trapping of electrons that have been untrapped by radiation or for radiation-induced untrapping from radicals as well as shallow traps or for permanent destruction of some luminescent molecules, or by assuming only a limited number of shallow traps. However, as the simplest model fits the available data quite adequately, such extensions are not warranted until more exact data becomes available. Such data should clearly include both u.v. and ionizing radiation measurements on the same set of polyethylene samples, together with the use of luminescent molecules deliberately added to the samples rather than relying on molecules fortuitously present in the polymer[4].

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