Thermoluminescence and Triboluminescence in Trioxane Crystals

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Polymerised trioxane crystals, irradiated at liquid nitrogen temperature show a single thermoluminescence peak on warming. Corresponding trioxane monomer crystals show a thermoluminescence spectrum of five peaks, and a series of sharp spikes at irregular intervals. On warming an unirradiated crystal, a two-peak spectrum plus spikes is obtained. The spikes are associated with strong electrical discharges and tentatively ascribed to dislocation of crystals under thermal stress.

1. Introduction

Recent work has shown that many polymeric and biochemical systems, when subjected to high energy radiation at low temperature, emit visible and ultra-violet light on subsequent warming (thermoluminescence) [1]. The light intensity/temperature curves (glow curves) show one or more peaks which are characteristic of chemical structure and molecular arrangement of the macromolecule. The emission spectrum within each glow peak is closely related to the fluorescence and phosphorescence of the specimen, and is often attributable to impurities within the base polymer. These observations can be explained in terms of three distinct processes: (i) trapping of electrons by the polymer; (ii) thermal release of trapped electrons at various temperatures depending on trap depth; (iii) capture of these electrons by luminescence centres to give excited species, which then decay to the ground state by radiative and non-radiative transitions.

Experiments with irradiated trioxane (-CH$_2$-O-CH$_2$-O-CH$_2$-O-) monomer crystals have shown, superimposed on the usual type of glow curve, a series of extremely sharp peaks (spikes). It is found that these flashes of light are not due to irradiation, but to temperature changes in the crystal, and they have been tentatively ascribed to triboluminescence (i.e. luminescence caused by stresses within a crystal).

2. Experimental

Trioxane powder in the form of small crystal-
lites was obtained from Kodak Ltd and two main types of specimens were prepared.

Polycrystalline pellets 1.5 cm diameter × 0.5 cm thickness were pressed from the powder at room temperature under a pressure of 8000 psi (1 psi = 1 lb/in.^{2} = 7 × 10^{-2} kg/cm^2).

Single crystals were grown by evaporation of the powder from one limb of an evacuated and inverted U-tube held at room temperature, into the other limb, the bottom part of which was maintained at solid CO$_2$ temperature. A large crystal was formed halfway up this limb, the bottom part being translucent, the top part transparent. X-ray diffraction showed that the latter was usually a single crystal, about 1.5 cm diameter × 2 cm length, and only such transparent crystals were used for cutting specimens about 0.5 cm thick. A small residue from the initial powder was left in the warmer limb, and may have been polymer.

Specimens with a buried, thin copper-constantan thermocouple were irradiated at liquid nitrogen temperature, with ^{60}Co gamma rays at dose rates of 0.5 or 1.8 Mrad/h. After irradiation the crystals showed a milky appearance.

For glow curve measurements, the crystals were exposed 1 cm from an IP28 photomultiplier in a light-tight enclosure, and the output fed via an EEL microphotometer amplifier to a recorder. The temperature was recorded separately on another recorder. The light intensity was insufficient to provide a good emission spectrum, but was faintly visible to a dark adapted eye, which could also note frequent

brighter flashes.

The irradiated monomer evaporated if left standing overnight at room temperature. On warming to 50° C, polymerisation occurred; the specimen was then washed in ethanol to remove residual monomer, leaving a milky-white shining specimen, which is polyoxymethylene, the polymer of trioxane.

3. Results

3.1. Thermoluminescence of Irradiated Polymer

Trioxane, polymerised from a pellet by irradiation and heating and subsequently re-irradiated at liquid nitrogen temperature, gives a glow curve with a single very broad peak (maximum at 180° K, half heights at about 170 and 200° K, extending at low intensity to above 240° K*, fig. 1). The intensity of the peak is linear with

Figure 2 Effect of dose and prior dose on peak at 180° K (trioxane polymer, dose rate 0.5 Mrad/h); prior dose in brackets.
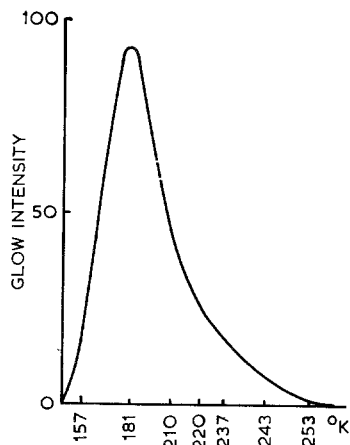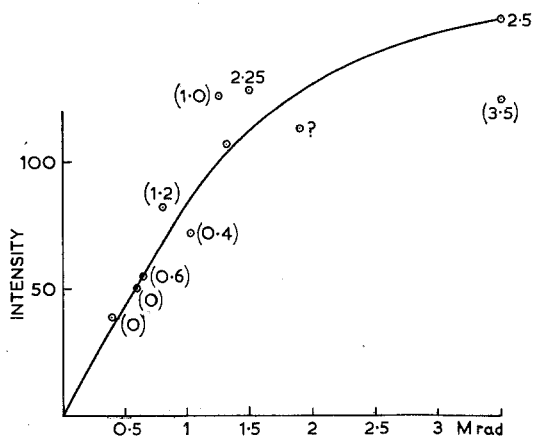
Figure 1 Glow curve of irradiated trioxane polymer (dose 1 Mrad; warming rate 120 to 220° K in 1.4 min).

dose up to 1.5 Mrad, and then tends to saturate. This tendency to saturation may be due to a loss in intensity due to emission during the extended exposure time. However, the intensity does not diminish if the specimen has previously been irradiated and then warmed, showing that high doses of radiation do not permanently destroy the luminescent centres (fig. 2).

The temperature at the peak varied slightly with rate of warming as is expected from an activation energy.

3.2. Thermoluminescence of Monomer

The glow curves of irradiated, then warmed,

monomer crystals show five peaks (fig. 3; see also fig. 7a) of which the most prominent are those at 133 and 150° K which overlap at the warming rate used. Other peaks are found with maxima at 188, 250 and 270° K approximately. These peaks are found in both polycrystalline
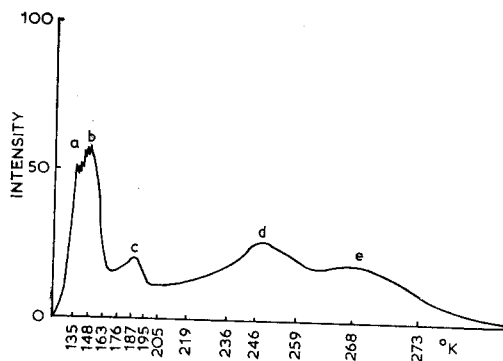
Figure 3 Glow curve of irradiated trioxane monomer (dose 0.5 Mrad; warming rate 120 to 220° K in 1.5 min).

pellets and single crystals, but their relative intensities vary widely from one specimen to another. Superimposed on these broad peaks is a large number of irregularly spaced sharp spurs, whose recorded period is in fact limited by the response time of the recorder. These spurs or spikes do not occur much at temperatures above 200° K.

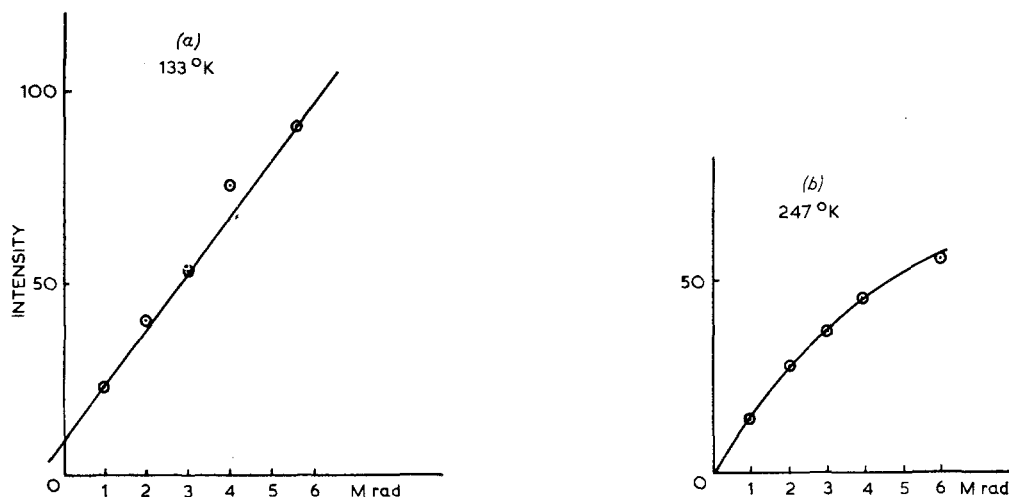The intensities of two peaks have been plotted against the radiation dose (fig. 4). That

*The above values represent an approximately logarithmic temperature rise from −155 to −50° C in 1.5 to 2 min.

Figure 4 Effect of dose on light intensity. Glow curve peaks of monomer crystal.

at 133° K is proportional to dose, but extrapolates to a finite value at zero dose. This may be interpreted as due to an additional contribution from triboluminescence and is discussed below. Up to doses of 6 Mrad there is no evidence of saturation. For the peak at 247° K there is no contribution from triboluminescence, and the curve extrapolates to zero at low doses. However, there is a tendency to saturate at high doses.

3.3. Triboluminescence

Following the experiments outlined above, a series of measurements was made with both pellets and single monomer crystals, unirradiated but allowed to warm as for the irradiated specimens. For a large crystal, held in a pyrex test tube, glow curves were observed with two main peaks, with maxima at about 130 and 180° K, and a series of extremely sharp spikes at irregular times, up to a temperature of 210° K (warming rate −155 to −50° C in 5 min). For smaller single crystal samples held only by the thermocouple, a higher rate of warming was possible (1.6 min from −155 to −50° C) and the temperatures of the maxima were correspondingly displaced to 130 and 185° K, with a broad tail up to 233° K (fig. 5; also fig. 7b). Pressed pellets suspended by a thermocouple gave peaks at 120 and 170° K (1.4 min from −155 to −50° C). Powder monomer as originally obtained from Kodak Ltd, and held in a test tube (2.1 min from −155 to −50° C) showed peaks at 120 and 170° K. These results, in each case from a number of specimens, show that crystal size has little effect. After con-
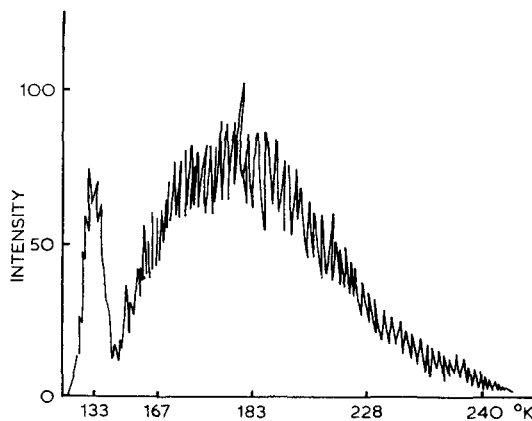

Figure 5 Triboluminescent glow curve from monomer single crystal (unirradiated).

tinuous cycles of warming and cooling, the same behaviour is observed; there is no tendency for either peaks or spikes to change in intensity, except after cracks have developed due to thermal cycling. The intensity is then increased. The same incidence of sharp spikes is observed when the crystal is cooled very rapidly.

In a further set of experiments, a single large crystal was subjected to a series of temperature cycles between liquid nitrogen and room temperature, alternate cycles involving radiation (0.5 Mrad at liquid nitrogen). The first luminescence peak occurred at 123° K (±10° K) with no significant difference in temperature as between the irradiated and unirradiated runs. We may therefore consider this peak as equivalent to the superposition of the luminescence

(133 and 150° K) peaks. The 180° K tribo-luminescent peak would appear to correspond to the 188° K thermoluminescence peak. However, the unirradiated specimen showed no evidence of peaks at 240 and 270° K as are revealed in the irradiated samples. We must therefore consider the monomer thermolum-inescence spectrum as consisting of the tri-boluminescent spectrum plus some additional components.

The very sharp flashes can be seen optically; their incidence varies from specimen to speci-men, and is also affected by warming rate. They produce strong electrical discharges whose presence can be readily revealed, e.g. by allow-ing the crystal to warm up inside a coil con-nected to a cathode ray oscillograph (fig. 6). The rise time of each flash is less than a few microseconds, and the decaying sinusoidal wave-form is determined by the electrical con-stants of the circuit. However, direct measure-ment of the potential between the crystal faces, with an electrometer valve, did not show changes of more than 1 V. The voltage breakdowns must have occurred within the crystal.
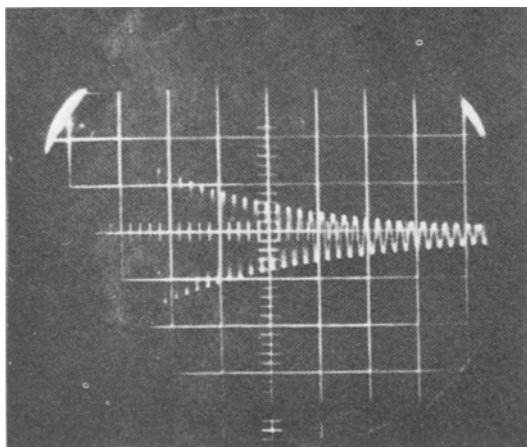

Figure 6 Oscillating discharge initiated by flash from warming monomer crystal (1 horizontal square = 100 μsec).

4. Discussion

Although trioxane can polymerise from solution or from the vapour, or during sublimation, its polymerisation under radiation gives rise to polymer crystals whose structure is closely related to that of the monomer. It has been concluded [2] that the matrix plays an essential part in the polymerisation, which occurs by some co-operative growth mechanism, so that con-cepts normally used in describing the usual polymerisation reactions are not applicable. The explanation involves the electrical properties of the crystal. Each molecule has a permanent dipole moment (2.18 Debye units [3]) and these are lined up in the crystal to form a permanent electret, which gives trioxane its pyro- and piezoelectric properties. Surface charges are greatly modified by the presence of condensed water. The rhythmic, spontaneous poly-merisation of trioxane crystals, growing from dry vapour, has been ascribed to electrical break-down between these charges.

The internal field of a trioxane crystal has been calculated by Nauta [4], and is largely due to the dipole field of neighbouring molecules along the c axis. It comprises two components, one being the permanent dipole of each mole-cule, multiplied by a factor allowing for thermal motion; the second involves the polarisation of the molecule under the influence of this field. At room temperature these are comparable (2.04 and 2.88 Debye units), and the internal field is 90.3 MeV/cm. As the temperature is lowered, a higher degree of molecular orientation becomes possible, and the field increases to a calculated maximum value of 96.4 MeV/cm at 0° K. The increase in field strength between liquid nitrogen and about −50° C would appear inadequate to account for electrical breakdown due to a temperature change.

It has already been shown that there is no second order transition between 19 and 61° C. We have also found, from X-ray diffraction studies, that there is no change in crystal structure down to liquid nitrogen temperature, other than small changes in lattice spacings expected from thermal contraction. It would not appear, therefore, that a second order transition is involved. However, other changes must be taking place in a monomer crystal even on standing at room temperature, since it is found that freshly crystallised trioxane gives much lower yields of polymer than aged crystals, irradiated under identical conditions. One possibility is the exudation of water from the lattice [4]. Trioxane with a water content above 500 ppm is turbid, whereas with much lower water concentration trioxane is highly trans-parent, and fairly strong mechanically. Our crystals were selected from the latter type of material – probably with less than 1 ppm of water inside. During the measurement of
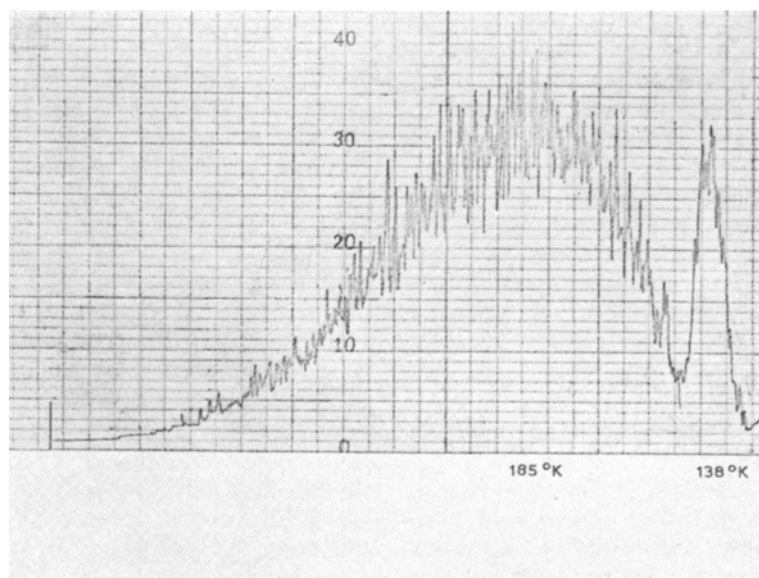
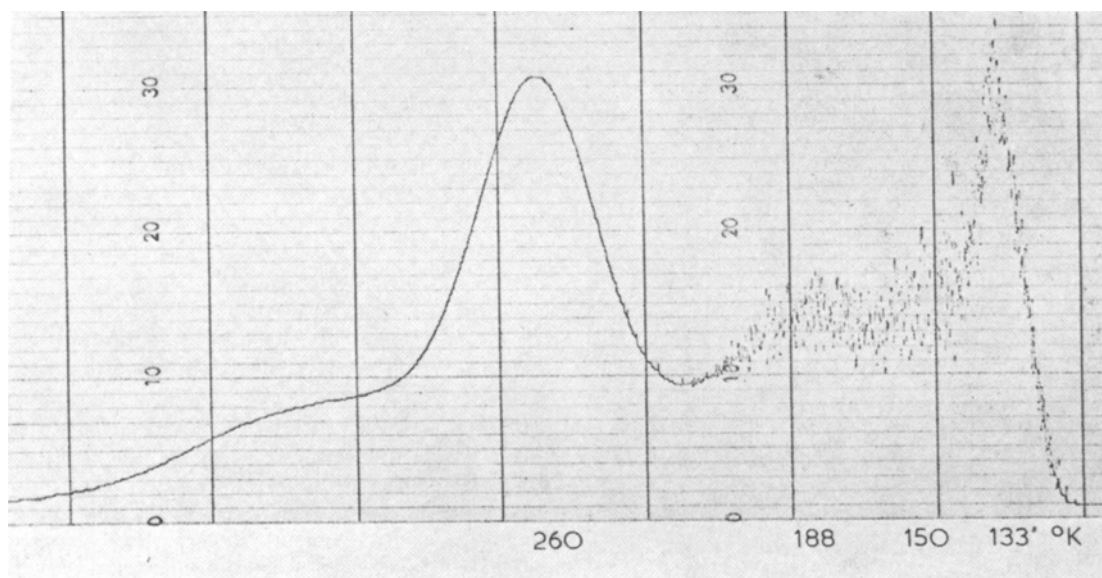*Figure 7a* Glow curve from irradiated monomer crystal.

Figure 7b Glow curve from unirradiated crystal during warming.

luminescence the cold crystal was exposed to air, and layers of ice formed on its surface, but apart from decreasing the overall light intensity these had little effect. It would therefore appear that the luminous effects observed are not related to a surface phenomenon.

We can envisage the following explanation for the sudden electrical discharges, accompanied by light, which occur on rapid warming or cooling. Unequal expansion or contraction causes internal disruptions between adjacent oriented crystallites, or even within a single one. The separation of two faces orthogonal to the c axis, and hence to the internal electrical field will cause a sudden decrease in this field. Calculations based on the method of Nauta [4] show that a separation of one molecular spacing in the c axis, i.e. 4.175 Å, will approximately halve the field, and cause a violent change in polarisation of a string of molecules. Charges

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on the newly-formed surface will then be able to produce an electrical discharge. It is necessary to assume that, on cooling, a reorientation of crystallites produces a somewhat similar change in charge separation.

The broad peaks must be assigned to a different mechanism. Here we may assume that internal crystalline defects can serve as electron traps, the electrons being liberated at different temperatures corresponding to the nature of the trap. The existence of several types of traps would account for the several peaks observed, while differences in their concentrations explain the wide differences in the relative peak intensities in successive experiments. These traps are not necessarily those resulting from radiation-induced structural changes, so that the temperatures at which electrons are released may also be different. That changes in structure occur on irradiation, even in the absence of polymerisation, has already been reported [5]; they may be revealed by a visible turbidity ascribed to the segregation of radiolytic products into droplets.

Low doses give rise to cracks and further changes occur on standing. No consistent changes in thermoluminescence pattern on standing has been observed as yet.

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