

Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60th birthday

SIMULTANEOUS THERMALLY STIMULATED LUMINESCENCE AND DEPOLARIZATION CURRENT IN LOW DENSITY POLYETHYLENE

A. Markiewicz¹ D. V. Balbachas² and R. J. Fleming²

¹SCHOOL OF APPLIED SCIENCE, MONASH UNIVERSITY COLLEGE GIPPSLAND,
CHURCHILL, VICTORIA 3842, AUSTRALIA

²DEPARTMENT OF PHYSICS, MONASH UNIVERSITY, CLAYTON, VICTORIA 3168,
AUSTRALIA

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Thermally stimulated luminescence (TSL) and thermally stimulated depolarization current (TSD) measurements were made simultaneously on low density polyethylene samples 0.175 mm thick, carrying evaporated gold electrodes. The samples were dc-polarized at room temperature at a field strength of 90 kV/cm, cooled to -190°C and X-irradiated with the field still applied, and then heated in short-circuit at 3 deg/min. Comparing the TSL and TSD data, particularly the effects of oxidizing the samples and immersing them in fuming nitric acid, it was shown that (1) the space-charge transport component of the TSD current between -190 and 30°C is negligible, (2) charge injection begins around -10°C (for evaporated gold electrodes) and increases rapidly with increasing temperature, and (3) all the injected charge is transported through the sample to the opposite electrode. Such transport takes place only through the amorphous regions of the sample.

When an insulator is polarized, i.e. a dc voltage is applied across it, three main processes may take place. These are (1) orientation of dipoles in the bulk of the sample, (2) injection of electrons/holes from the electrodes, followed by transport and trapping, and (3) transport of free charge already present in the sample bulk, particularly ions. If the field is applied for several minutes at some temperature T_p , and the sample is then cooled well below T_p , short-circuited and heated, a current commonly called the thermally stimulated depolarization (TSD) current will usually be observed [1]. Several workers have presented TSD data for polyethylene. Of these we select the following: (1) Amakawa and Inuishi [2] explained their data for

*John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest*

high and low density samples in terms of detrapping and movement of space charge injected during polarization, for polarization temperatures between -153 and 80° . (2) Fischer and Rohl [3] interpreted the TSD current in oxidized low density samples polarized at various temperatures between -180 and 20° in terms of relaxation (reorientation) of dipoles. They believed that a very small contribution to the TSD current from the motion of detrapped space-charge was present but was swamped by the much larger dipole relaxation component. (3) Varlow [4] found a single TSD peak around 10° in low density samples polarized at 20° , and concluded that it was due to the motion of injected space charge thermally released from traps. (4) Doughty *et al.* [5] measured TSD current in cross-linked polyethylene and found two peaks around 50 and 66° , following dc polarization at 56° . They suggested charge injection into two different types of trap. Polarization at 20° and cooling to 0° with the field applied yielded a featureless TSD plot between 0 and 60° .

Fischer and Rohl [3] presented a range of experimental data strongly supporting their preference for the dipole relaxation interpretation, e.g. a linear dependence of the TSD current on polarizing voltage, but the other authors listed above offer little or no justification of the detrapped space charge model. Whilst there is a difference of opinion on the origin of TSD current observed between liquid nitrogen temperature and room temperature, following polarization at room temperature (Amakawa and Inuishi versus Fischer and Rohl), there seems to be general agreement that injected space charge dominates the TSD current when the sample is polarized at or above room temperature.

Thermally stimulated luminescence (TSL) is the emission of light from a sample when it is heated, after exposure to some form of ionising radiation. TSL in polymers has been studied since the early 1960s [6], and is now firmly established as a technique for the investigation of electron trapping and transport in polymers [7, 8] and in insulators in general [9].

In this paper we present TSL and TSD data collected simultaneously for low density samples polarized at room temperature and X-irradiated at -190° . To our knowledge this is the first time this type of data has been reported for polymer samples. We show that, contrary to expectation, the space-charge transport component of the TSD current between -190 and 30° is negligible, although injection of space-charge commences around -10° under a dc applied field of order 10^7 V/m and increases rapidly with increasing temperature. The injected charge does not generate a significant concentration of trapped space-charge, most if not all of it being transported through the sample bulk to the opposite electrode.

Experimental

The apparatus and samples (XJG 143 grade 175 μm thick) were as described previously [10], as also were the procedures for immersion in fuming nitric acid and exposure to an oxygen/ozone mixture. Fuming nitric acid is known to "digest" the amorphous regions of polyethylene [11], while oxygen/ozone produces heavy oxidation in the amorphous regions [12]. Prior to simultaneous TSL/TSD measurements, the measurement cell was evacuated and held at a pressure less than 10^{-5} torr for several hours at room temperature in order to remove absorbed air from the samples. The samples were then dc polarized at room temperature ($20 \pm 2^\circ$) for 30 min at a field strength of 90 kV/cm, cooled to -190° and X-irradiated to doses up to 7 kGy with the field still applied. The dose rate was 23 Gy/min. After short-circuiting the samples were heated to 30° at a constant rate of 3 deg/min, the TSL emission and TSD current being recorded during heating. Heating was not continued above 30° in order to avoid possible complications arising from loss of crystallinity commencing above 40° [12]. The samples carried evaporated gold electrodes, 20 nm thick (semi-transparent) on the surface facing the photomultiplier and 100 nm thick on the other.

Results and discussion

Simultaneous TSL/TSD

Figure 1 shows a typical TSL glow curve and a typical TSD current plot obtained simultaneously from the same sample. In this case the sample was X-irradiated to a dose of 700 Gy over a period of 30 min at liquid nitrogen temperature. Each curve shows three main peaks, labelled L1, L2 and L3 for TSL and D1, D2 and D3 for TSD. In some samples the D1 and D2 peaks merged into a single peak; Fischer and Rohl [3] also observed only two peaks, around -140 and -30° , in heavily oxidised low density samples polarized at 20° and heated from -180° at 6.6 deg/min.

Displacement and injection current

In order to investigate the possibility of charge injection during polarization, we measured the current flowing in the sample during heating from -190 to 30° with the field applied, after polarization at room temperature and cooling (also with the field applied). The dipole relaxation contribution

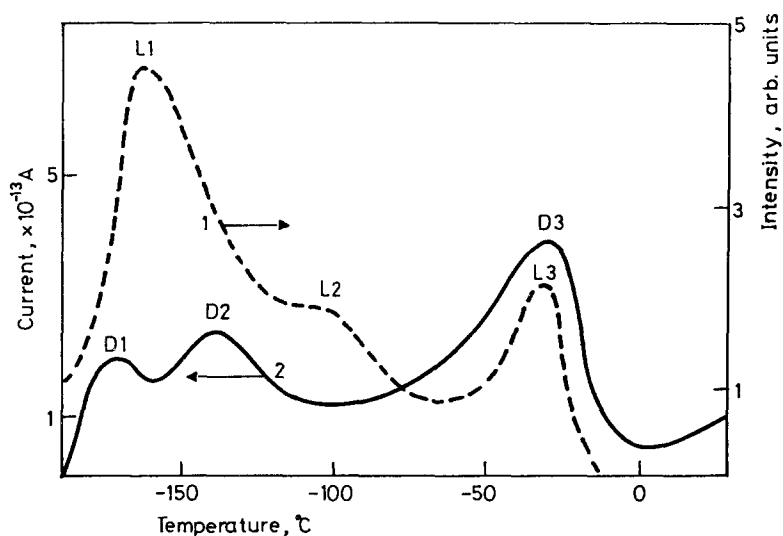


Fig. 1 Typical TSL (—) and TSD (---) plots for an unoxidised sample, polarized at room temperature for 30 min at a field strength of 90 kV/cm, and then X-irradiated at -190°C to a dose of 700 Gy. The polarizing field was maintained during the irradiation. The heating rate was $3^{\circ}\text{C}/\text{min}$

to the total current was thus negligible, the principal components being the displacement current and transport of injected charge. The results are shown in Fig. 2, for a virgin sample and one which had been exposed to the oxygen/ozone mixture for 100 hrs at 40° . In both cases a fairly constant negative current is evident up to about -25° , followed by a small increase (in the negative direction) probably due to the glass transition, and finally a reversal in direction and extremely rapid growth. It is difficult to explain this reversal and rapid growth other than in terms of charge injection. The nearly constant current up to -25° is probably a displacement current.

Effects of X-irradiation

TSL and TSD were measured for increasing X-ray doses up to 7 kGy. It was found that the intensity of each TSL peak increased with dose, tending to saturate at the higher doses, but the TSD current peaks were unaffected by the irradiation (within the limits of run-to-run reproducibility, estimated as $\pm 5\%$).

Charge injected into a sample during polarization at temperature T_p , and trapped, will usually begin escaping from the traps at temperatures slightly below T_p , when the sample is heated in short-circuit after having been

cooled well below T_p . Since in the present measurements the field was maintained during cooling to liquid nitrogen temperature after polarization at room temperature, we would expect to measure TSD current at all temperatures between liquid nitrogen and room temperature, assuming charge injection and a quasi-continuous distribution of trap activation energies. Thus if the injected space-charge is confined to a thin slice of the sample close to one electrode, say the cathode, then in the absence of pre-existing space-charge and dipoles with significant dipole moment, the TSD current in the short-circuited sample will originate entirely in the flow of injected electrons back to the cathode. Such a near-electrode confinement of the injected space-charge might be expected because of the high density of traps in polymers (expected to be in the range 10^{17} to 10^{19} cm^{-3} , [13, 14] although Andress [15] prefers a volume distribution.

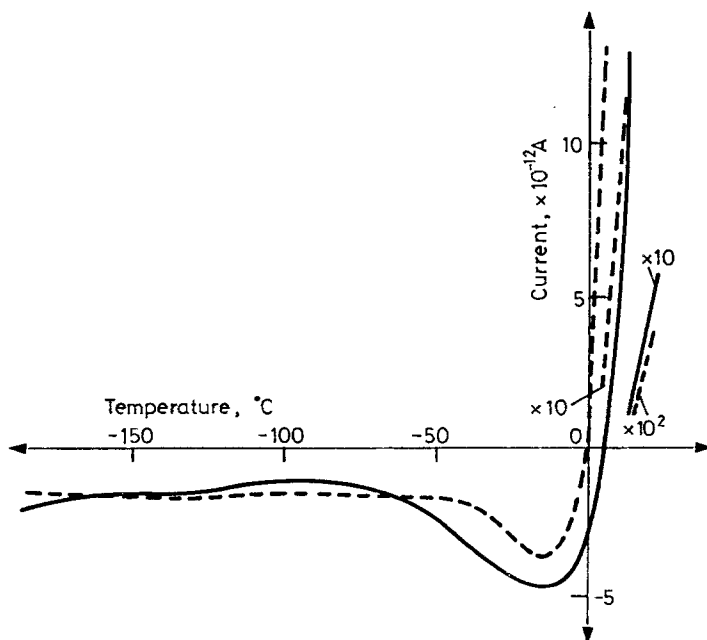


Fig. 2 Current vs. temperature for samples polarized at room temperature for 30 min at a field strength of 90 kV/cm, cooled to -190°C , and heated with the field still applied.

Unoxidized sample —, sample exposed at 40°C to an O_2/O_3 flow for 100 hrs - - -

If the sample is X-irradiated at liquid nitrogen temperature after polarization, additional filling of electron traps throughout its volume will take place. On escaping from the traps when the sample is heated in short-

circuit, the electrons will recombine with their geminate positive ions under the influence of the Coulomb field between each pair, assuming that the concentration of ion pairs is not large enough that adjacent pairs interact. Although such geminate recombination generates TSL (the neutral molecules formed by recombination are taken to be the luminescence centres), it will not increase the TSD current, since presumably as many electrons will move from right-to-left to recombine as move from left-to-right, and the distribution of luminescence centre/trap separations at the end of the irradiation will be isotropic. However one would expect that some of the X-rays would interact with any electrons injected and trapped during polarization, detrapping them and thus enabling them to move through the sample bulk under the influence of the applied field until retrapped. Thus one would in general expect a change in the profile of the TSD current generated by the re-distributed space-charge, when released from the traps during heating in short-circuit.

In the same way, if the TSD current is due to dipole relaxation, we would expect to see some change in the current profile as a result of X-irradiation. This is because ionization of an atom forming part of a dipole would alter the local electric field and hence the orientation of the dipole.

Since the TSD current at all temperatures between -190 and 30° was unchanged by the X-irradiation, it follows that the fraction of trapped electrons or oriented dipoles suffering "direct hits" during irradiation was too small to cause a detectable change in the TSD current. This is confirmed by the simple order-of-magnitude calculation set out in the Appendix.

Optical bleaching of TSL

When a polarised X-irradiated sample at -190° was exposed to the light from a 60 W incandescent filament for 15 minutes before being heated, the subsequent TSL glow curve intensity was reduced by about 40% at all temperatures, but the TSD current was unchanged.

The reduction in the TSL is almost certainly due to optical excitation of some of the trapped electrons out of the traps [16]. Since each of the three peaks in the TSL glow-curves was reduced by about 40% by the optical excitation, it seems that (a) much the same range of trap depths is associated with each peak, and (b) more than half the traps have depths (activation energies) greater than about 3 eV, corresponding to the short wavelength end of the visible spectrum (assuming negligible uv-content in the filament emission). The deeper occupied traps which are not emptied by the optical excitation are then broken up by the onset of various modes of molecular

motion at higher temperatures, yielding the same three peaks as in the normal TSL glow-curve. Thus the profile of the latter is heavily influenced by the molecular motion modes. [The concepts of thermally induced trap disintegration, and "intrinsic" traps formed by the polymer chains themselves (cavity traps) rather than by impurities or structural imperfections, are now widely accepted in the context of TSL originating in the amorphous regions of semi-crystalline polymers [17, 18]. Optical (or thermal) excitation out of stable traps is of course usually assumed in inorganic phosphors.] Since the TSD current was unaffected by the optical excitation, it seems unlikely that it originates in the motion of injected space-charge; presumably the traps occupied by such space-charge would be of the same type as those associated with the TSL emission, and so we would expect a significant reduction following optical excitation. On the other hand, the absence of change following optical excitation is consistent with a dipole relaxation origin of the TSD current, provided that the minimum energy required to ionize each dipole is more than about 3 eV. This condition is almost certainly satisfied, since the ionization potential of many low molecular weight organic compounds is of order 8-10 eV [19]. The absence of a space-charge contribution to the TSD current indicates that (1) no space-charge was injected into the sample during polarization or cooling, or (2) the spatial distribution of the injected space-charge was uniform through the sample volume, so that it discharged equally to both electrodes, or (3) all the injected space-charge was transported through the sample volume to the opposite electrode and neutralized or extracted there. Now the data of Fig. 2 suggest copious injection, and one would expect the injected space-charge concentration to decrease with increasing distance from the injecting electrode [20, 21] as a result of trapping. However, the observation of a nearly constant current towards the end of the polarization period is consistent with transport of most of the injected charge to the opposite electrode (assuming injection from only one electrode).

Our earlier measurements [10] on samples X-irradiated at -190° showed an easily measurable TSC current at all temperatures between -190 and 30° , suggesting a quasi-continuous distribution of trap activation energies. In particular, the TSC current between -50 and 30° was shown to involve release of charge from traps formed within the crystalline lamellae of the samples. Charge injection and transport at temperatures above -10° (see Fig. 2) would be expected to fill some of these traps during cooling with the field applied, and hence the TSD current above -10° would be expected to have a space-charge component. Since this is not the case, it follows that transport of the injected charge to the opposite electrode proceeds only

through the amorphous regions of the sample. This is in agreement with the findings of Cooper *et al.* [22].

Oxidation

Figure 3 shows TSL and TSD plots recorded simultaneously for three samples cut from the same sheet of stock material. The plots numbered 1 were obtained before exposure to the oxygen/ozone mixture, and plots 2 and 3 after exposures of 25 and 150 hrs respectively. Large increases in TSD current with increasing oxidation time will be seen. It should also be noted that plots 2 and 3 contain an additional peak D4. On the other hand the TSL intensities decrease with increasing exposure time. The IR absorption spectra of these samples showed a continuous increase in absorption at 1720 cm^{-1} , from very nearly zero before exposure to 93% after 150 hrs exposure (Fig. 4), with smaller increases around 1880, 2010 and 2140 cm^{-1} . The effects on the TSL glow curves of exposure of the samples to an oxygen/ozone mixture were reported earlier [10] and are in good agreement with the present data. Comparing TSL and TSC data recorded simultaneously from the same sample, a marked reduction in the intensity of all TSL and TSC peaks for exposures up to 25 hr was ascribed to a reduction in the concentration of the electron traps. A continuing reduction in the TSL peaks alone at longer exposures was considered due to a reduced efficiency of the luminescence centres. In the present work oxidation again decreased the TSL peaks but increased the TSD peaks, suggesting strongly that the two phenomena originate in different physical processes. The obvious explanation is that the TSD peaks are generated by dipole relaxation. More specifically, given the large increase in optical absorption around 1720 cm^{-1} , the stretching frequency for C=O groups attached to the polymer chains [23], we suggest that oxidation generates additional C=O groups attached to the polymer chains and the associated increase in dipole moment per unit volume leads to an increased TSD current. Note that the additional C=O groups cannot be formed within the crystalline lamellae, since gases cannot penetrate the relatively dense molecular packing within the lamellae [24]; it follows that they are formed either on the surfaces of the lamellae or in the remainder of the amorphous volume. The temperature correlation between the $(D1-D2)/L1$ and $D3/L3$ peaks suggests that they originate in the same regions of the samples, and are driven by the same molecular motions. We deduced in earlier papers [7, 8] that peak $L1$ originates in the motion of side-groups attached to the main chains in the chain-fold regions, and $L3$ in the glass transition, also in the chain-fold regions. Thus we suggest now that

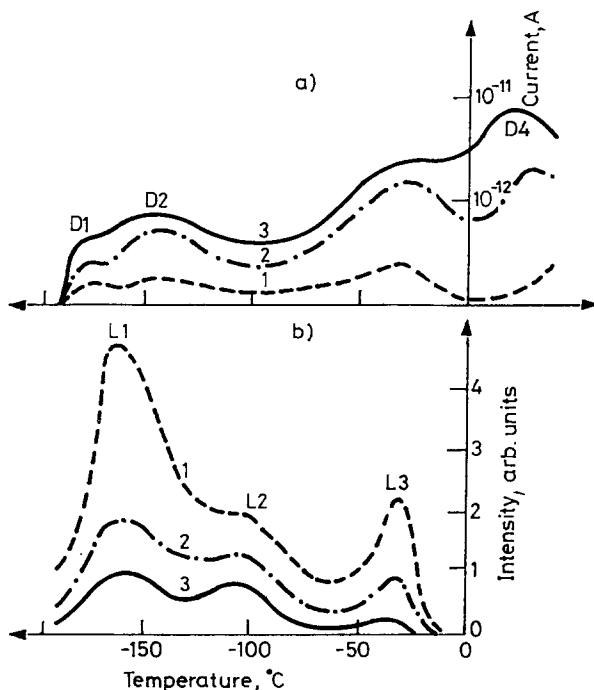


Fig. 3 (a) TSD plots for three samples after exposure at 40°C to an O_2/O_3 flow for various times. Curve 1 - 0 hr, Curve 2 - 25 hr, Curve 3 - 150 hr.
(b) TSL plots for the same samples and the same exposures as in (a), recorded simultaneously

peaks *D1* and *D3*, assumed due to C=O dipole relaxation, are driven by the same two molecular motions. The *D1/D2* split might also correspond to C=O groups formed in slightly different molecular environments within the chain-fold regions. The TSL *L2* shoulder is thought to originate in the "crankshaft" motion of short segments of the polymer backbone; the absence of a TSD peak in this temperature range is surprising, since a TSC peak was observed [10]. The origin of the TSD current peak *D4* observed in oxidized samples [curves 2 and 3 of Fig. 3(a)] is also presumably the additional C=O dipoles created by the oxygen/ozone mixture. However, the lowering of the peak temperature with increasing oxidation time is not consistent with an increasing concentration of only one type of dipole situated in only one particular molecular environment. We therefore suggest that the *D4* peak originates in the relaxation of C=O dipoles formed at a number of slightly different sites, and that the formation rate is not the same for all sites. Since no new form of molecular motion commences around the *D4* peak temperature, we very tentatively identify the relaxation mechanism as the early

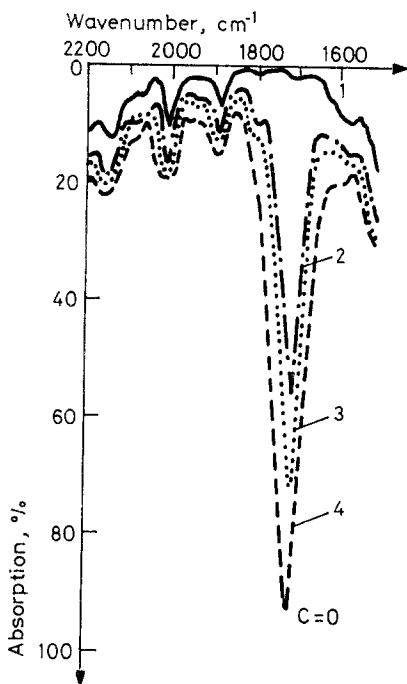


Fig. 4 IR absorption spectra for samples nominally identical to those of Fig. 3, after exposure at 40°C to an O₂/O₃ flow for various times. Curve 1 – 0 hr, Curve 2 – 25 hr, Curve 3 – 50 hr, Curve 4 – 150 hr

stages of pre-melting of the crystalline lamellae; this implies that the dipoles are formed on the lamellae surfaces. (The Vicat softening point of low density polyethylene is around 95°, and a plot of specific volume against temperature shows a rapid increase commencing at the same temperature [25]).

Immersion in nitric acid

Curve 1 of Fig. 5 is a typical TSD current plot for a virgin sample, and curves 2 and 3 are corresponding plots after 65 hrs and 45 days immersion in nitric acid respectively. A large increase in the magnitude of all peaks can be seen. However, no TSL was observed after 65 hrs immersion, in agreement with our previous work [10]. The IR absorption spectra of these samples (Fig. 6) showed significant increases in absorption around 1720, 1640 and 1560 cm⁻¹.

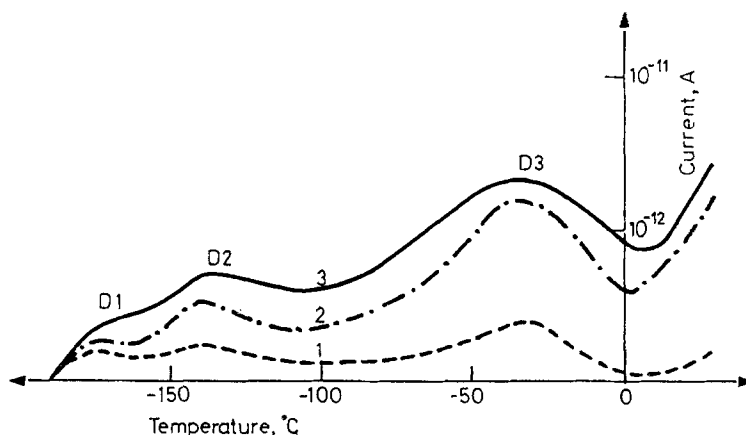


Fig. 5 TSD plots for three samples after immersion in fuming nitric acid at room temperature for various times. Curve 1 - 0 hr, Curve 2 - 65 hr, Curve 3 - 45 days

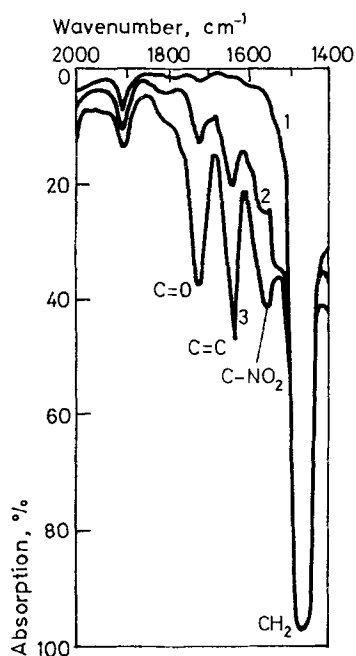


Fig. 6 IR absorption spectra for the samples of Fig. 5, after immersion in fuming nitric acid for the times quoted

The total suppression of the TSL emission at relatively short immersion times is thought to be due to the removal of electron traps from the chain-

fold regions [10]. The increase in TSD current following immersion is in striking contrast, suggesting that the nitric acid generates additional permanent dipoles in the regions accessible to it. During the first stages of immersion, chains are randomly cut in the chain-fold and amorphous regions of the samples, producing ethylenic ($C=C$) linkages [26,27] consistent with the increased IR absorption around 1640 cm^{-1} shown in Fig. 6 [28]. At the same time chemical reactions occur which produce $C=O$ and $C-NO_2$ groups at the ends of the cut chains [11], leading to increased IR absorption around 1720 cm^{-1} and 1560 cm^{-1} respectively [28], again as shown in Fig. 6. It is of interest to compare Fig. 3(a) with Fig. 5. Although the $D1$, $D2$ and $D3$ peak temperatures and magnitudes are very similar, the IR absorption at 1720 cm^{-1} is always much larger for the oxidised sample (Figs 4 and 6). This suggests that the $C-NO_2$ and $C=C$ groups created as a result of immersion in nitric acid have significant dipole moments [29] and contribute significantly to the TSD current. The fact that very similar TSD current peak temperatures ($D1$, $D2$ and $D3$) are observed in virgin samples, in samples oxidized by an O_2/O_3 mixture, and in samples immersed in nitric acid, strongly supports the contention that the TSD current originates in dipole disorientation driven by particular forms of molecular motion, the peak temperatures being determined by the characteristics of this motion rather than the physical/chemical properties of the dipoles themselves.

Dependence of TSD current on polarization voltage

The dependence of the TSD current on the polarization voltage is shown in Fig. 7, for a sample which had been exposed to the oxygen/ozone mixture for 150 hrs at 40° . All peaks were linearly dependent on the polarization voltage over the range 0-2500 V, except at 2000 V where the $D3$ and $D4$ peak currents were approximately 7% greater than would have been expected from a linear relationship. In addition, the $D3$ peak temperature decreased by about 8° between 500 and 2500 V. A linear relationship between peak current and polarizing voltage is expected for a dipole relaxation current [1], while a space-charge limited current usually increases as the square of the polarizing voltage [30]. We have no explanation for the isolated departure from linearity at 2000 V, but overall the data are strongly supportive of a dipolar relaxation mechanism. Such a mechanism should also yield a peak temperature independent of polarizing voltage, assuming (1) a single type of dipole and so a single relaxation time, and (2) a sufficiently long polarization time so that polarization equilibrium is attained. If the dipoles ($C=O$) are covalently bonded to the polymer chains, then the equilibrium con-

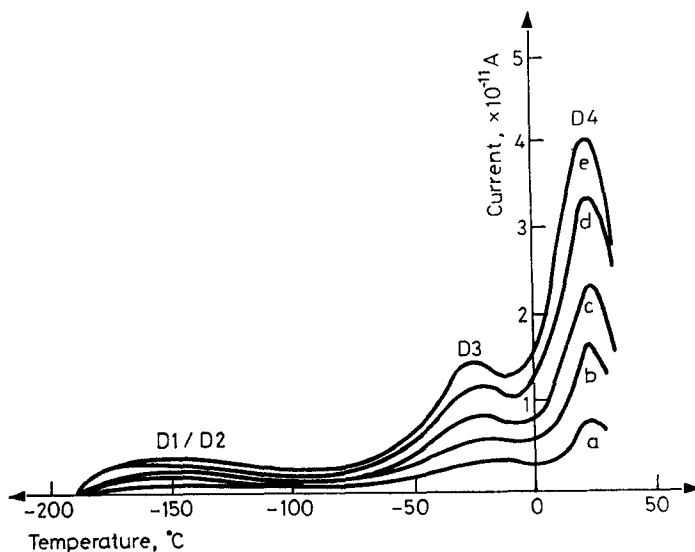


Fig. 7 Polarization voltage dependence of TSD current for a sample exposed at 40°C to an O_2/O_3 flow for 150 hr. Polarizing voltages applied at room temperature for 30 min were (a) 500 V, (b) 1000 V, (c) 1500 V, (d) 2000 V, (e) 2500 V

figuration of that part of a chain immediately adjacent to an oriented dipole may depend on the orientation, and therefore so also may the relaxation time. In this way a field-dependent relaxation time could eventuate. However it is not clear why such a mechanism should be associated only with the glass transition.

Conclusions

The following conclusions may be drawn from the data presented in this work:

(1) TSD current measured in the approximate range -190 to 30° originates in dipole relaxation processes, i.e. the space-charge transport component is negligible.

(2) Charge injection commences around -10° at a field strength of 90 kV/cm applied via evaporated gold electrodes, and increases rapidly with increasing temperature.

(3) Charge injection does not generate a sufficient concentration of trapped space-charge to yield any readily measurable TSD current, since nearly all the injected charge is transported across the sample to the op-

posite electrode without being deeply trapped. It follows that such transport occurs only through the amorphous regions of the samples, since traps which can immobilise electrons above -10^0 are known to exist in the crystalline regions.

Appendix

In order to calculate the fraction of trapped electrons or oriented dipoles "hit" during the X-irradiation, we must first calculate the total number of X-rays incident on the sample. We will assume a cross-sectional area of 1 cm^2 , and take the density of polyethylene to be 0.925 gm cm^{-3} [31]. We have $I(x) = I_0 \exp(-\mu x)$, where I_0 is the incident intensity of the X-ray beam, $I(x)$ is its intensity at depth x in the sample, and μ is the linear absorption coefficient for the photoelectric effect. This coefficient appears not to have been measured for polyethylene $[-(\text{CH}_2)_n-]$, but we can estimate it from the corresponding values for water and boron which have similar densities and are composed of light atoms. Selecting a mean X-ray energy of 12.5 keV, since the X-ray tube was operated at 25 keV, we find $\mu = 2 \text{ cm}^{-1}$ for water [32] and 1.75 cm^{-1} for boron [33]. Taking $\mu = 2 \text{ cm}^{-1}$ and a sample thickness of $175 \mu\text{m}$, it follows that the energy deposited in the sample by the X-rays is $3.4 \cdot 10^{-2} I_0$. Assuming that this energy is homogeneously deposited through the sample volume, then a dose of 7 kGy ($= 4.4 \cdot 10^{19} \text{ eV/gm} = 4.07 \cdot 10^{19} \text{ eV} \cdot \text{cm}^{-3}$) corresponds to $7.12 \cdot 10^{17} \text{ eV}$ incident on the sample and hence $1.68 \cdot 10^{15}$ X-rays. We are assuming that the energy of every X-ray extracted from the beam is totally absorbed within the sample.

Now let the total number of trapped electrons in the sample be n_t . Then the number of trapped electron/X-ray interactions will be $1.68 \cdot 10^{15} \cdot n_t \cdot \Phi$, where Φ is the cross-section of each trapped electron for photoelectric interaction with an X-ray. We are assuming no "overlapping" between adjacent trapped electrons. Φ is not known precisely, since it depends on the binding energy of the trapped electron. However, it will certainly be greater than $6.65 \cdot 10^{-25} \text{ cm}^2$, the corresponding cross-section for a free electron [34], and, assuming that the trapped electron is attached to a carbon atom of the polymer chain, probably less than the corresponding cross-section for a valence electron in that atom. We can estimate the latter very approximately as one-sixth of the atomic photoelectric cross-section. The mass absorption coefficient for carbon is $1.40 \text{ cm}^2 \cdot \text{g}^{-1}$ [33], and its density (graphite) is

2.3 g/cm⁻³ [35], so that an upper bound for Φ is around $5 \cdot 10^{-24}$ cm². It follows that the fraction of the trapped electrons "hit" by the X-rays will be $8.4 \cdot 10^{-9}$. A fractional change in the TSD current of this magnitude would be much too small to be observed. The photoelectric cross-section for an electron in an atom forming part of a dipole with aldehyde or ketone structure would be very similar, so that again no change in the TSD current would be observed if it originated in dipole relaxation.

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33 *Handbook of X-rays*, Ed. E. F. Kaelble, McGraw-Hill, New York 1967, P. 1-26.

34 I. Kaplan, *Nuclear Physics*, Addison-Wesley Publishing Company, Inc., Cambridge Mass., 1955, p. 56.

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Zusammenfassung — Es wurden simultane TSL- und TSD-Messungen an 0.175 mm starken, über aufgedampfte Goldelektroden verfügende Polyethylenproben geringer Dichte durchgeführt. Die Proben wurden bei Raumtemperatur und einer Feldstärke von 90 kV/cm gleichstrompolarisiert, auf -190°C abgekühlt, bei noch anliegendem Feld röntgenbestrahlt und dann unter Kurzschluß mit 3 Grad/min erhitzt. Durch einen Vergleich der TSL- und TSD-Daten, insbesondere der Wirkung der Oxydation der Proben bzw. des Eintauchens in rauchende Salpetersäure, zeigten, daß (1) die Raumladungstransport-Komponente des TSD-Stromes zwischen -190 und 30°C vernachlässigbar ist, (2) die Ladungsinjektion bei etwa -10°C beginnt (für aufgedampfte Goldelektroden) und mit steigender Temperatur schnell anwächst und (3) die gesamte injizierte Ladung durch die Probe hindurch an die gegenüberliegende Elektrode transportiert wird. Ein derartiger Transport erfolgt nur in den amorphen Regionen der Probe.