

DETERMINATION OF CARRIER MOBILITY IN PLASTICS BY A TIME-OF-FLIGHT METHOD *

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Carriers are volume-generated by electron bombardment, and flight-times of the predominantly mobile carriers to the bombarded surface determined. Mobilities found at 20°C are: $1.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ (holes) in polystyrene, and $1.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ (electrons) in polyethylene terephthalate. The temperature dependence of mobility cannot be expressed by a single activation energy.

IT WAS recently shown¹ that the electrical current induced by electron bombardment in polystyrene is carried predominantly by holes, and that in polyethylene terephthalate (p.e.t) by electrons, with drift ranges $\geq 1 \mu\text{m}$ at a field of 1 MV cm^{-1} . The preliminary mobility estimates are now shown to be a factor of 5 high.

Time-of-flight experiments using Spear's method² on specially drawn thin p.e.t. films were inconclusive because the conditions necessary for their success, viz. width of drifting carrier sheet $\ll$ specimen thickness $<$ drift range, could not simultaneously be satisfied. However, Reference 1, Fig. 1, suggests the possibility of timing the carrier transit from the end of the excited region to the bombarded surface.

The earlier observations are compatible with the following model. The exciting electron pulse creates carriers of both signs which drift along the chain of their origin.³ Both species are trapped in less (probably several orders of magnitude less) than 10^{-9} s within the same chain, one deeply, forming recombination centres, the other temporarily at shallow traps. At least some of the shallow traps are sites from which carriers may jump into adjacent chains. This

paper is concerned with the effective drift of the loosely trapped carriers, averaged over many jumps.

Such drift is terminated, either by deeper trapping after an effective drift lifetime $\tau_d \geq 0.1 \text{ ms}$, or by recombination characterised by a lifetime τ_r . τ_r depends on carrier density, and in the present experiments is $\leq 1 \mu\text{s}$. The difference in order of magnitude ensures that deep trapping and recombination are experimentally separable. A sheet of carriers, drifting across a distribution of recombination centres, then decays primarily by recombination.

As previously,¹ the specimen films had both surfaces metallised. They were bombarded, through one of the electrodes, with electrons of penetration $b \leq 1 \mu\text{m}$, in the form of pulses a few ns long. For technical reasons, although current transients are easier to interpret, induced charge was recorded. On the time scale considered, the 'prompt' carrier population¹ decays instantaneously, leaving at time $t = 0$ a loosely trapped carrier distribution

$$f_1(0) = \int_b^0 n_0(x) dx \quad (1)$$

where x is the distance measured from the bombarded surface. If the field draws these carriers towards the bombarded surface, the charge

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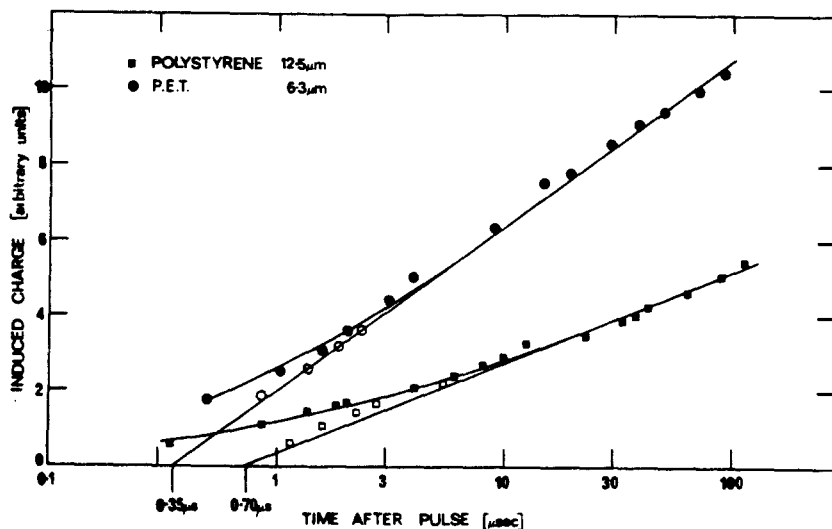


FIG. 1. Induced charge transients, carriers drawn into the bulk, in (a) polystyrene, (b) p.e.t. Bombarding dose: (a) 11 pC cm^{-2} at 6 kV, (b) 15 pC cm^{-2} at 5 kV; penetration: (a) $1.0 \mu\text{m}$, (b) $0.7 \mu\text{m}$; bias field: (a) 0.95 MV cm^{-1} , (b) 1.3 MV cm^{-1} . Solid circles: observed charge plotted against t , open circles, plotted against $t + \tau_r$.

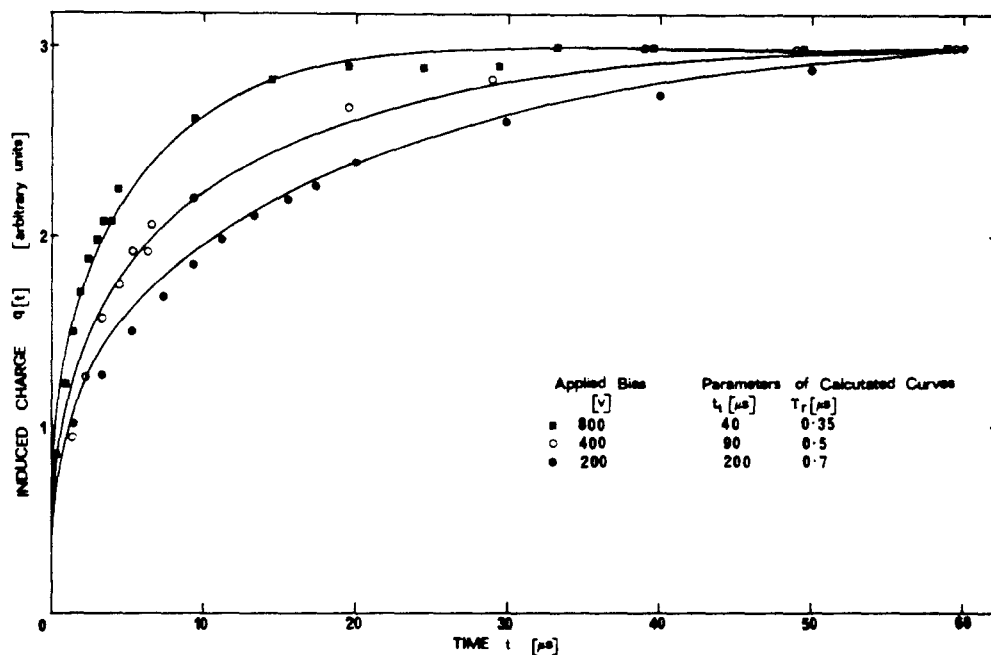


FIG. 2. Induced charge transients, carriers drawn to bombarded surface. P.e.t., conditions as in Fig. 1(b). Points plotted from photographs, solid curves calculated from (2).

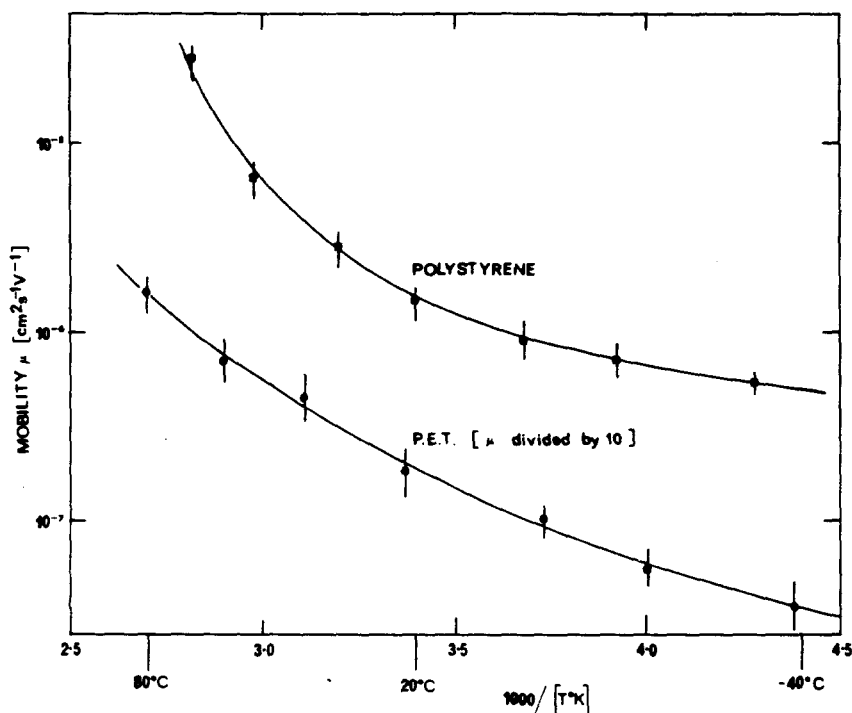


FIG. 3. Variation of mobility with temperature in polystyrene and p.e.t. Conditions as in Fig. 1, except bias field in polystyrene 1.2 MV cm^{-1} .

induced in the external circuit is

$$q(t) = (ev/L) \int_0^t f_1 f_2 f_3 dt, \quad (0 \dots t \dots b/v) \quad (2)$$

where v is the effective drift velocity, L the film thickness, e the electronic charge, and the f are functions of time. In the lowest approximation, $n_0(x)$ is constant and $f_1 = n_0(b - vt)$. f_2 represents the decay by recombination; if τ_r is taken as constant, $f_2 = (1 + t/\tau_r)^{-1}$. $f_3 = \exp(-t/\tau_d)$ describes the deep trapping; in this approximation $f_3 \approx 1$. Equation (2) then yields

$$q(t) = (evn_0 b \tau_r / L) [\ln(1 + t/\tau_r) - t/t_i], \quad (3)$$

$$(t_i \gg \tau_r),$$

where $t_i = b/v$ is the time taken by carriers which escape recombination to transit the entire excited region. Measuring time on a scale of τ_r by writing $t/\tau_r = \theta$ and $t_i/\tau_r = \alpha$, (3) becomes

$$q(\theta) = \text{const} [\ln(1 + \theta) - \theta/\alpha], \quad (0 \dots \theta \dots \alpha) \quad (4)$$

$q(t)$, found from the photographed charge transients, is first plotted against $\lg t$ to determine τ_r as

below. $q(t)$ is then expressed as $q(\theta)$, plotted against θ and matched against a set of standard curves (4) to determine α and hence t_i . Finally the effective mobility is calculated from $\mu = bL/Vt_i$ where V is the bias voltage applied. Space charge effects are negligible since about 95 per cent of the carriers recombine in transit. The greatest uncertainty is that in b .

The simple bimolecular form of f_2 is well substantiated for bulk excitation.⁴⁻⁶ Surprisingly, it holds well also in the present experiment. Figure 1 shows the induced charge growth after pulsed excitation as above, but with the field reversed so that carriers are drawn into the bulk. The charge varies linearly with $\lg t$ except at short times. The intercept of the straight line with the time axis is taken to be τ_r . If the curve is then replotted against $\lg(t + \tau_r)$, the wayward points also fall on the same straight line. The law should fail for $t \geq t_i$.

In practice, f_1 was calculated from Spencer's

table,⁷ which has been experimentally confirmed,⁸ for the energy loss in polystyrene scaled down⁹ to the lower energies used here. The penetration was taken as $0.7\mu\text{m}$ at 5 keV and $1.0\mu\text{m}$ at 6 keV. The same values were used for p.e.t. The integration (2) was carried out by computer. Figure 2 shows typical matches of charge transients against standard curves on a real time scale.

RESULTS

The following effective mobilities were deduced at 20°C: polystyrene (B.X.L. Styrafoil), holes, $1.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$; p.e.t. (I.C.I. Melinex), electrons, $1.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$; both to within a factor 2. The sensitivity of the existing arrangement was insufficient for reliable measurements on polyethylene (B.P. Rigidex); even at 70°C the mobility (holes) was at least an order of magnitude lower than those quoted above. Equation (1) leads to values for the effective ionisation energy per carrier pair, by

electron bombardment, of 100 eV in polystyrene and 50 eV in p.e.t., both at 1 MV cm^{-1} . These values are not absolute, since the yield is still unsaturated and varies approximately as $(\text{field})^{1/2}$ in the neighbourhood of 1 MV cm^{-1} . The mean bimolecular recombination coefficients $(n_0 \tau_r)^{-1}$ are $3 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ in polystyrene and $1 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ in p.e.t.

Figure 3 shows the variation of the mobility with temperature in polystyrene and p.e.t. At room temperature, the activation energy is about 0.2 eV in both cases (neglecting a slight field-effect not yet studied in detail). The form of temperature dependence suggests that the mobility is controlled by intermolecular barriers rather than intramolecular traps, and that in addition to the expected barrier-hopping mode of transport¹⁰ predominant at high temperatures, an unactivated process such as tunnelling¹¹ is present and becomes significant at low temperatures. A full report is in process of preparation.

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Ladungsträger werden im Volumen durch Elektroneneinstrahlung erzeugt, und die Flugzeiten der vorzüglich beweglichen Träger zur bestrahlten Oberfläche hin bestimmt. Die Beweglichkeiten bei 20°C sind: $1.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ (Löcher) im Polystyrol, und $1.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ (Elektronen) im Polyäthylenterephthalat. Der Temperaturabhang der Beweglichkeit kann nicht durch eine einfache Aktivierungsenergie ausgedrückt werden.