

CHARGE TRANSPORT AND CARRIER MOBILITIES IN INSULATING POLYMERS*

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Results of drift mobility measurements by the recent method of the authors⁴⁾ on three common organic polymers are given and compared. At 80°C the hole mobility in practically amorphous polystyrene ($5 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$) is 5 orders of magnitude greater than in 95 % crystalline polyethylene. It is suggested that this is not due to the differences in chemical structure, but that the characteristic chain folding in polyethylene produces strong localisation. The temperature dependence of the hole mobility in polystyrene and of the electron mobility in polyethylene terephthalate is shown to correspond neither to a single process with constant activation energy nor to Mott's relation $\log \mu = \text{const} (-1/T^4)$. The tentative conclusions drawn from the temperature dependence in⁴⁾ are revised, and it is suggested that chain-hopping and trap-hopping must be considered separately, the first contributing a weak and the second a strong dependence on temperature.

At Bucarest, in 1967, we reported preliminary experiments on the conduction in some of the best-known commercial insulating plastics, induced by an electron beam, this being the most efficient method of excitation available. The response of these plastics, while small, was on the whole so similar to that of insulating inorganic glasses such as As_2S_3 that we concluded that the conduction was limited by the lack of long-range order rather than by any specific properties of the organic chain molecules. We distinguished between a "prompt" and a "long-lived" conduction process, and proposed a tentative model in which the prompt current results from the drift of the excited carriers along the chain in which they are created until trapped for the first time, and the long-lived current from subsequent thermal detrapping followed by a further drift along the same chain or by a hop into an adjacent chain^{1, 2)}. We were, and still are, unable to distinguish between the last two processes which are probably closely related, in that the most numerous traps will be kinks or folds in the chains which also form the springboards for interchain hopping. We are about to attempt an experimental separation of these processes by compressing the samples during bombardment.

More recently, we found that the long-lived current is essentially a one-carrier current²⁾, and developed a method for determining the carrier mo-

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TABLE I

	Atactic polystyrene (Styrafoil)		Polyethylene-terephthalate (Melinex)		Linear polyethylene (Rigidex)	
	20°C	80°C	20°C	80°C	80°C	95°C
Estimated crystallinity %						
Mobile carrier type		negligible		60	95	
Effect. mobility μ ($\text{cm}^2 \text{sec}^{-1} \text{V}^{-1}$)	1×10^{-6}	5×10^{-5}	1.5×10^{-6}	2×10^{-5}	4.5×10^{-10}	9×10^{-10}
Activation en. E (eV) if $\mu = \mu_0 \exp(-E/kT)$	0.2	0.75	0.2	0.3		
Bimolecular recomb'n coeff. ($\text{cm}^3 \text{sec}^{-1}$)	3×10^{-8}	1.5×10^{-6}	1×10^{-8}	1.3×10^{-7}	1×10^{-13}	2×10^{-13}
Eff. pair ion. en. (eV) at 0.5 MV/cm						
Prompt displacement (μm) at 0.5 MV/cm		120	40			30
Total displacement (μm) at 0.5 MV/cm	0.5	0.03	0.03	1.0	0.5	0.01
						0.5

bility in a relatively direct way. Straightforward time-of-flight measurement³⁾ is impracticable because the long-lived current offers no mark which could be used for timing. The method is explained in a published note⁴⁾ and should be applicable to other amorphous non-conductors. We are about to use it on As_2S_3 . The mobilities determined are the effective, trap- or hop-controlled values; we have so far found no way of measuring intramolecular mobility, only the schubweg before trapping.

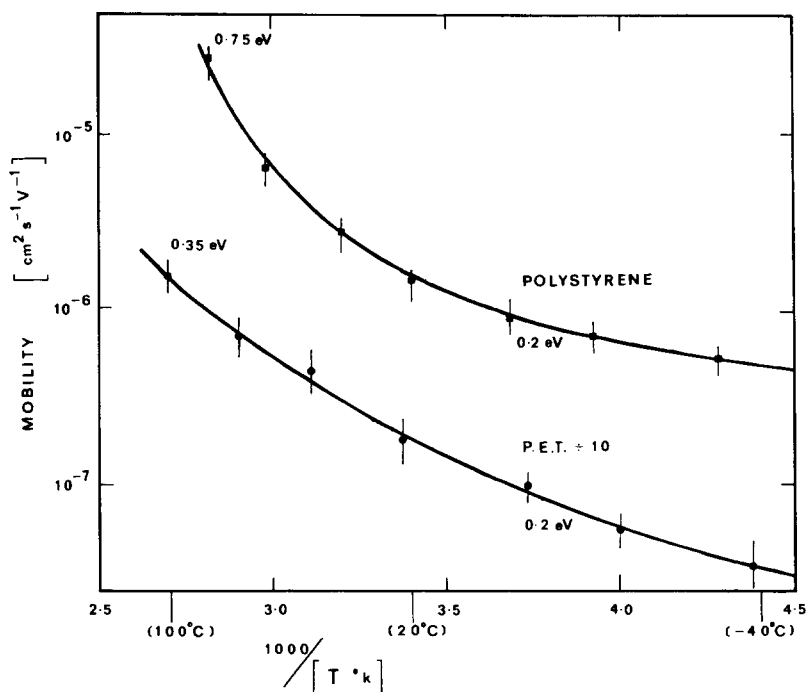


Fig. 1. Variation of mobility with temperature in polystyrene and polyethylene terephthalate. Bias field 1.2 MV/cm; for other conditions see ref. 4.

Plastics in general are neither wholly amorphous nor crystalline, but consist of spherulitic microcrystals formed of aggregates of chains folded back on themselves, and embedded in a less dense amorphous phase. Table I shows the parameters determined for three common plastics which differ not only chemically but also in crystallinity. The main difference between polystyrene and polyethylene terephthalate (p.e.t.) is that in the first, electrons are more deeply trapped than holes, whereas in the second the converse applies. Numerically the parameters of these two plastics are surprisingly similar despite the different chemical structure and crystallinity. It

is hard to understand why the (hole) mobility in the highly crystalline linear polyethylene should be so much lower. Our value is in order-of-magnitude agreement with that given by Davies⁵⁾ for injected carriers, although the experimental conditions differ: we measure mobility of one carrier with the other present but localised, a situation similar to impurity conductivity. At lower temperatures, the mobility was too low for measurement with our apparatus. We could not measure the mobility in ordinary low-density, low-

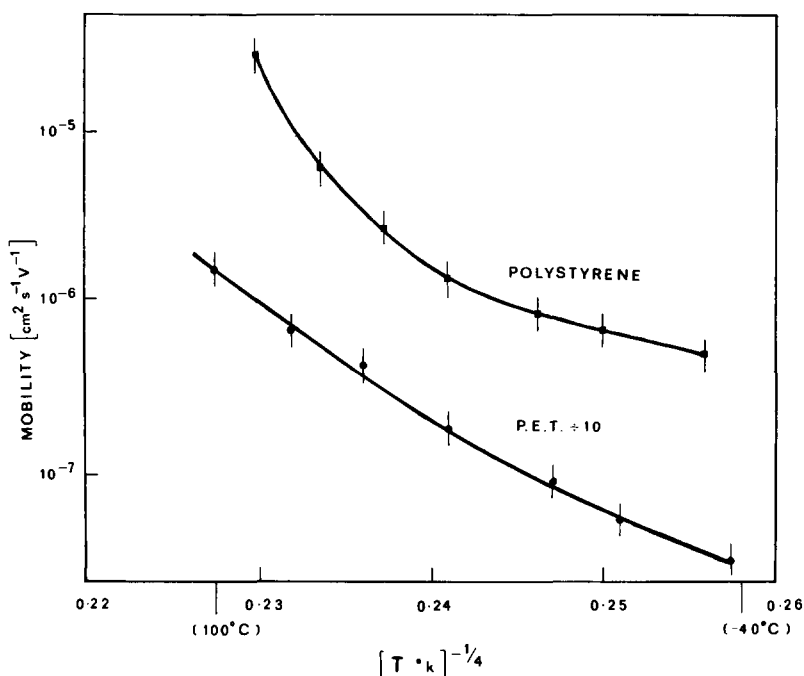


Fig. 2. The points in fig. 1 replotted in the form $\log \mu$ against $1/T^{\frac{1}{2}}$.

crystallinity polyethylene at all because, at low temperatures, it was again too low for the apparatus to cope, and at 80°C the material was already mechanically too soft. Nor did we have any success with single crystal mats kindly given us by Dr. Keller of Bristol University.

As we can see no chemical property which could account for the vast difference in mobility between polystyrene and polyethylene, we conclude that the morphology is largely responsible. In polymers, crystallinity may have little effect on conductivity owing to the weak bonding between parallel chains. An *adverse* effect was already noticed by Amborski⁶⁾. The shorter

prompt schubweg in polyethylene (table 1) suggests that the traps are denser, and we believe that they are also appreciably deeper, than in polystyrene on account of the chain folding which is such a prominent feature of polyethylene, especially the linear kind. Intuitively, a 180° fold should produce a greater perturbation, i.e. a deeper trap, than the low-angle kinks common in the amorphous phase of polymers. On this picture, the mobility in polyethylene is essentially limited by traps rather than by hops.

Fig. 1 shows the dependence of the mobility on temperature for polystyrene and p.e.t. This cannot be described by a single activation energy. On the assumption that, at least in low-crystallinity polymers, conduction is controlled by activated hopping, we have replotted the data of fig. 1 in the form $\log \mu$ (mobility) against $1/T^\ddagger$ (temperature) as suggested by Mott⁷⁾ (fig. 2). It is seen that this law might possibly, approximately, apply to the part-crystalline p.e.t. but not to the amorphous polystyrene. However, the comparison is inconclusive because, even in polystyrene, chain-hopping and trap-hopping may be separate and distinct processes, the first contributing a weak and the second a strong dependence on temperature.

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