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AN IN-DEPTH STUDY OF THE EFFECTS OF THE ELECTRIC FIELD ON CHARGE CARRIER MOBILITIES IN MOLECULARLY DOPED POLYMERS

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Abstract It is well known that charge carrier mobilities μ in molecularly doped polymers (MDP) determined by transient photoconductivity experiments depend on three variables, the temperature T, the mean distance between dopant molecules ρ, and the electric field E. Recently introduced deconvolution procedures have made possible the first systematic determination of the dependence of μ on T, ρ, and E. This determination led to the suggestion that the T and ρ dependencies are consistent with small polaron theory. However, the electric field dependence of μ remains unexplained. In this paper we present an in-depth study of the electric field dependence of charge carrier mobilities in MDP.

Gill,[1] in his study of PVK-TNF, suggested that the electric field dependence of ln μ can be empirically described by $\sqrt{E}\,(1/T - 1/T_0)$ where T_0 is a constant. T_0 has, up until now, always been obtained by extrapolation because it is usually above the glass transition temperature T_g of the polymer. $\sqrt{E}/T_0$ is a field dependent term which is independent of temperature. Such a term is not predicted by any hopping theory,[2] including small polaron theory.[3] Some workers have suggested that T_0 is associated with the glass transition temperature.[4] Hirsch[5] suggested T_0 is the result of a temperature dependent dielectric constant. Recently Bässler[6] suggested that T_0 is an artifact resulting from the way data were being plotted. He predicted, assuming a Gaussian distribution of energy transport levels, that ln μ should be proportional to $-(T_1/T)^2 + E/c_1T^2$ where T_1 and c_1 are constants, i.e., no parameter like T_0 is needed to describe the data. We have recently[7] directly observed T_0 for the first time in a MDP (10% pyrazoline:polycarbonate). In this MDP, $T_0 < T_g$ and data in the temperature range between T_0 and T_g are characterized by a mobility that decreases with increasing E, consistent with Gill's empirical equation (see Figures 1 and 2). Such data clearly demonstrate that the T_0 parameter is not an artifact. In addition, the data shown in Figures 1 and 2 are inconsistent with Hirsch's predictions. Furthermore, we have shown in several MDP's that T_0 decreases with ρ, while T_g increases with ρ (see Figure 3), suggesting T_0 is not associated with rheological properties.

The obvious explanation for the $\sqrt{E}$ dependence is the Poole-Frenkel effect, the lowering of a Coulomb barrier by an applied electric field. None-the-less, most workers have ruled out this explanation because of the unreasonable number of charged

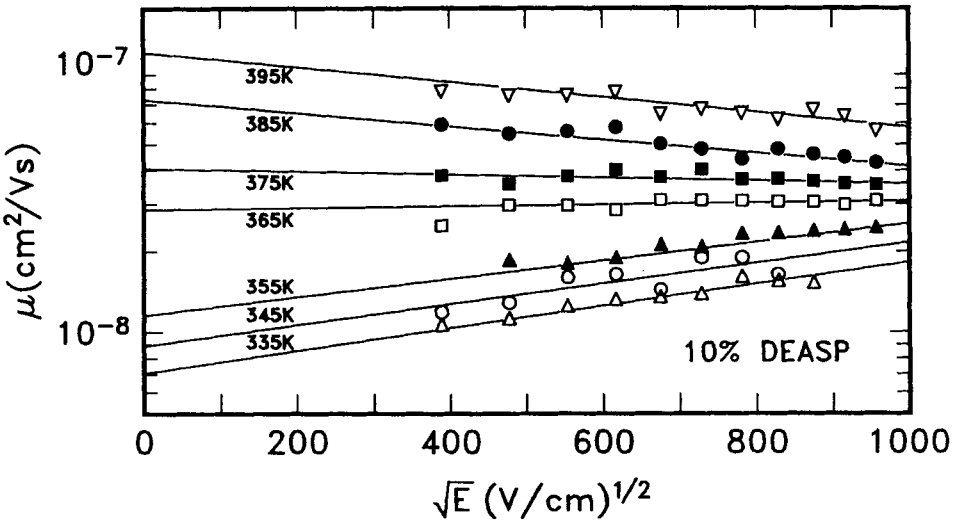

Figure 1. The hole mobility in 10% DEASP:polycarbonate plotted semilogarithmically versus the square root of the electric field. The different curves represent temperatures ranging from 335 to 395K. Note that above 375K, the mobility decreases as the electric field increases.

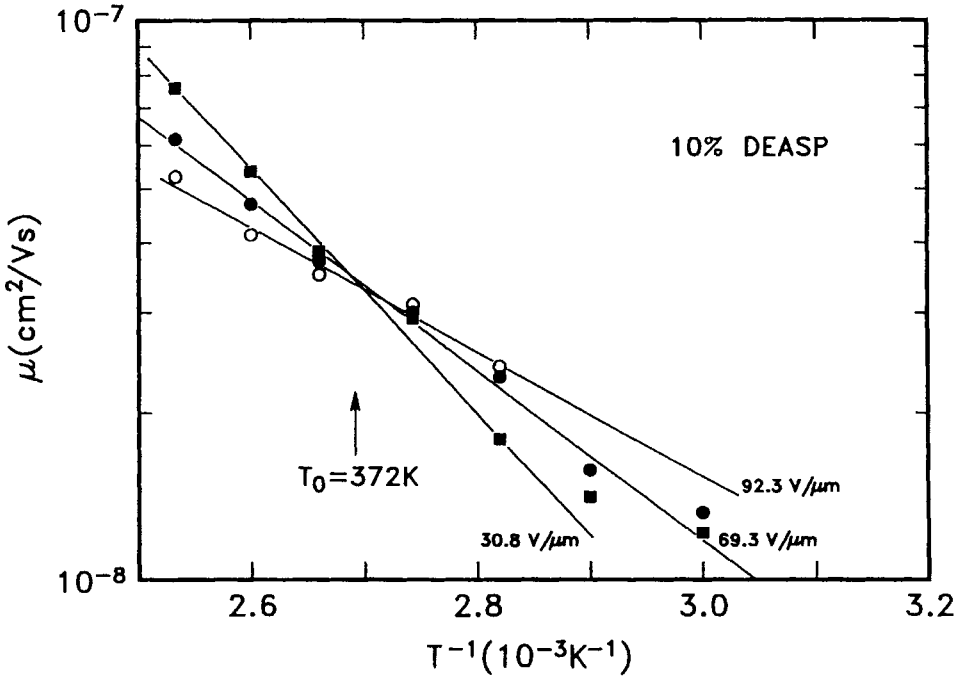

Figure 2. Another method of obtaining T_0 is to plot the mobility data shown in Figure 1 versus T^{-1} as a function of E and obtain the temperature at which the field dependence vanishes. The value obtained from the plot is 372K.

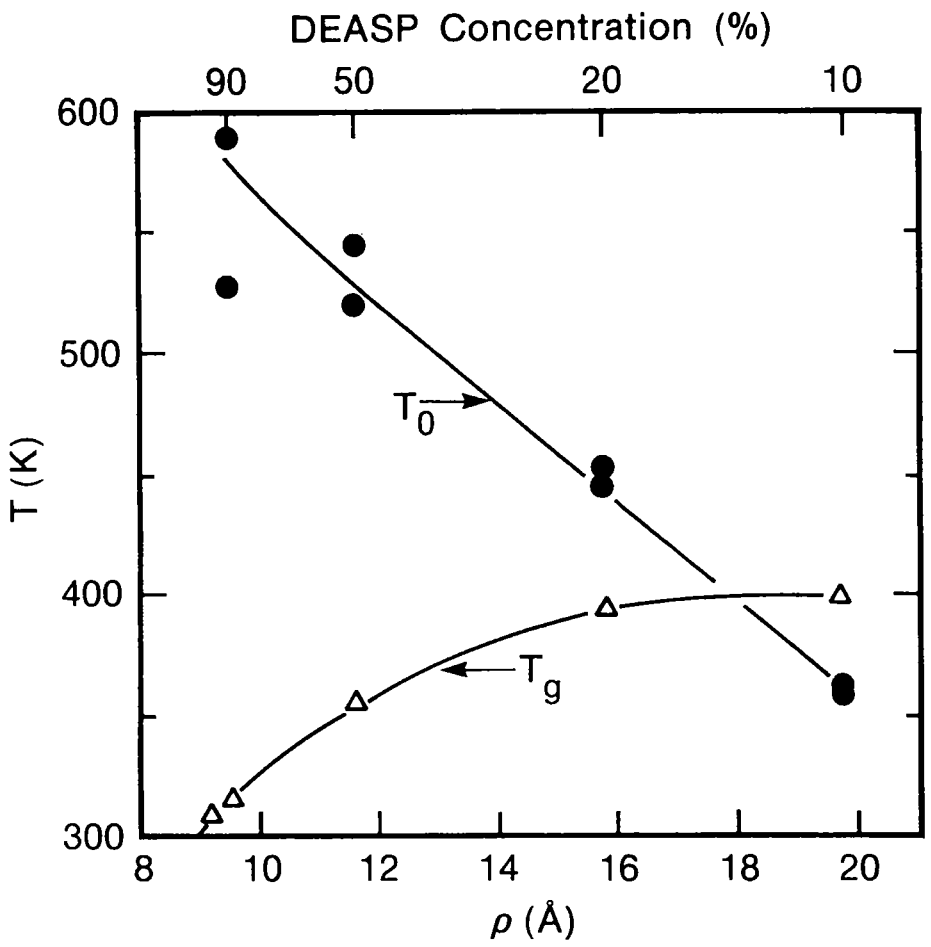

Figure 3. T_0 and T_g plotted against the calculated average distance between DEASP molecules ρ. Note that T_0 and T_g have different dependences on ρ, suggesting the physical significance of T_0 is not associated with rheological properties.

Coulomb centers that would be required in the sample. Because of this, many other alternative physical explanation for the field dependence (all involving energy shifts of the hopping energy level) have been suggested, and data over a limited E range have been fit to functions suggested by these alternative explanations. We have obtained data over the widest electric field range reported to date and performed a thorough linear and non-linear statistical analysis of the data[8] (see Figure 4). Of all the functions suggested in the literature, only the $\sqrt{E}$ is consistent with the data with a correlation coefficient (R^2) of 0.998.

So far we have discussed only the electric field dependence of the transit time, one point on the full current-time curve. This curve is known to have an initial peak followed by a slowly decreasing current until a shoulder (the transit time) when a large fraction of the carriers leave the sample. Over the years, as sample preparation has

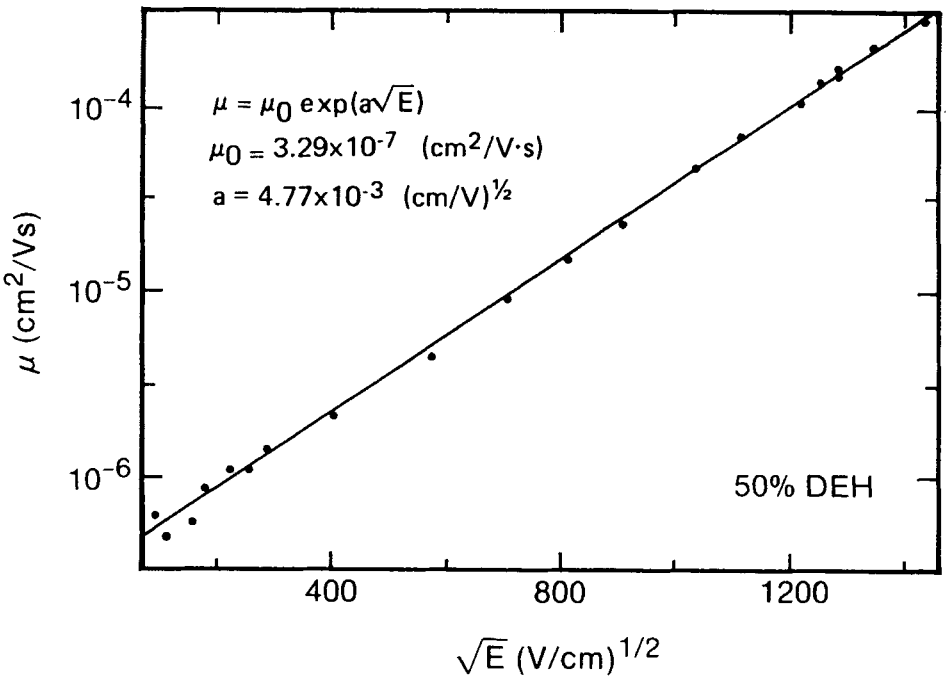

Figure 4. Hole mobility data for 50% DEH:polycarbonate plotted on log $\mu - \sqrt{E}$ axes. The data are least squares fit a straight line; the parameter shown describe the data with a correlation coefficient of 0.998.

improved, the general shape of this curve has approached those obtained in molecular crystals. A measure of this shape is the dispersion d, defined as the ratio of the time for the current to decrease to half the value at the shoulder, to the transit time. We have carefully analyzed an MDP system which exhibits clear evidence for a transit time in linear time-linear current curves, has $d = 0.72$, and has continually decreasing current-time curves. We found that it has the three characteristics of dispersive transport as defined by Scher and co-workers,[9] namely, universality of current shape with field, a time dependence t of $t^{-(1-\alpha)}$ for one time decade before the transit time and $t^{-(1+\alpha)}$ after the transit time, and a thickness dependent mobility with α of 0.86. This again can be viewed as an unexpected field dependence, namely the current-time curve is field independent. A similar field independent current-time curve has been reported by Yuh and Stolka[10] for another MDP with a dispersion of 0.52 which shows no decrease in current with time before the transit time. Such results have been explained in terms of wide distributions of transport states, either in energy or space. However, such models do not account for the T_0 or the $\sqrt{E}$ dependence of μ. It also is not clear that wide distributions of transport states should still exist in systems with d as small as 0.52 or 0.72 which is equal to or better than d's obtained in most molecular crystals.

In summary, while the recently introduced deconvolution procedures[11,12] that have allowed a systematic determination of the dependence of μ on T, ρ, and E represent significant progress in understanding the microscopic hopping mechanism in MDP, the physical significance of the electric field dependence remains puzzling. It appears that the usual picture of the electric field bringing hopping energy levels into closer coincidence is inadequate to account for the data.

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