Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Carrier Mobility Studies of Carbazole Modified Polysiloxanes

D. M. Goldie [a] , A. R. Hepburn [a] , J. M. Maud [a] & J. M. Marshall [a]

[a] Molecular Electronics Group Abertawe, University College Swansea, Singleton Park, Swansea, SA2 8PP, Wales

Version of record first published: 05 Dec 2006.

To cite this article: D. M. Goldie , A. R. Hepburn , J. M. Maud & J. M. Marshall (1993): Carrier Mobility Studies of Carbazole Modified Polysiloxanes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 236:1, 237-242

To link to this article: http://dx.doi.org/10.1080/10587259308055234

Mol. Cryst. Liq. Cryst. 1993, Vol. 236, pp. 237–242
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

CARRIER MOBILITY STUDIES OF CARBAZOLE MODIFIED POLYSILOXANES

D.M. GOLDIE, A.R. HEPBURN, J.M. MAUD AND J.M.MARSHALL
Molecular Electronics Group Abertawe, University College Swansea, Singleton Park, Swansea SA2 8PP, Wales

ABSTRACT Carrier mobility data have been obtained for photogenerated holes in Carbazole Modified Polysiloxanes (CMPs). The data reveal a complex dependence upon temperature and electric field which may be interpreted in terms of either trap free or trap limited hopping transport, with the former providing the more consistent parameters for a range of structurally similar materials.

INTRODUCTION

Organic polymeric materials have found applications within the electronics industry, though largely in a passive role. However, the arrival of improved synthetic techniques has led to the development of new materials with potential applications as active elements. Therefore, it is becoming increasingly important that the fundamental charge transport mechanism(s) be understood. Given the limited temperature and field range available for many polymeric systems it is often not possible to obtain definitive agreement with a specific theory. However, it is possible to assess the sensitivity of fitted parameters for a range of structurally similar systems. In this paper we focus on the movement of photogenerated holes through polysiloxane polymers containing pendant carbazole groups and compare the extracted parameters with those obtained for polyvinylcarbazole (PVK).

EXPERIMENTAL DETAILS

CMPs synthesised in our laboratories (figure 1) were prepared via platinum catalysed hydrosilylation reactions between polymethylhydrosiloxane (Petrarch, Molecular Weight 2250, n=35 and 5105, n=80) and carbazol-9-ylalk-1-enes[1,2]. Thin films were spun from 0.015-0.03M solutions of CMPs and chloroform at speeds of 700 - 4000 RPM onto pre-patterned aluminium (Al) on glass substrates resulting in thicknesses in the range 6-1μm.

Semi-transparent top contacts were of sputtered Al. Reproducible experimental data could only be achieved subsequent to film vacuum baking at ≈ 50°C for ≈ 6 hours.

Owing to low glass transition temperatures, low photogeneration efficiencies (Figure 1) and high field electro-mechanical breakdown, our measurements were restricted to the m = 3 polymer within the field range 4 x 10^5 - 2 x 10^6 V cm^{-1} and the temperature range 250 - 310K. Carrier mobility measurements were performed utilising the standard time of flight technique (TOF) with a 337nm UV laser (absorption depth estimated < 0.1μm) producing 3ns pulses. Specimens were housed in an evacuated environmental chamber.

RESULTS AND DISCUSSION

Figure 1 shows the low photogeneration efficiency of CMP compared to PVK. This reflects the difficulty in generating and separating the charge carriers in systems of this

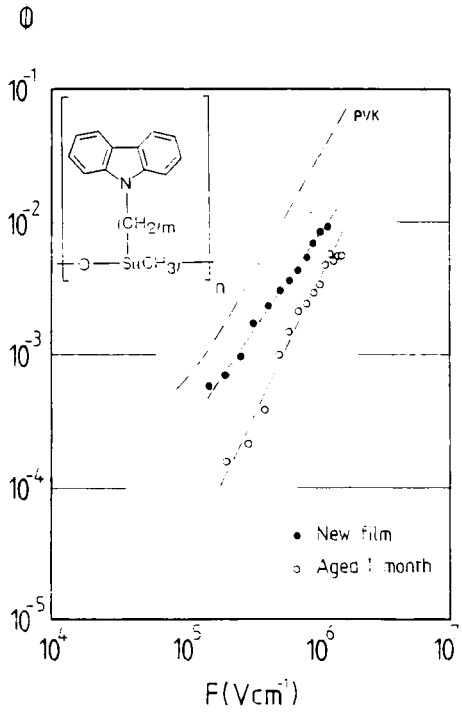

FIGURE 1 Photogeneration efficiency a function of field for CMPs and PVK. Inset : chemical structure of CMPs.

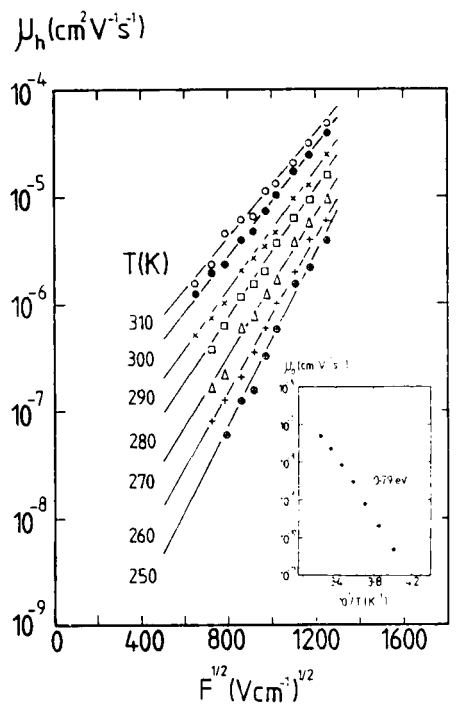

FIGURE 2 Logarithm of μ_h vs $F^{1/2}$ for CMPs (n=35). Inset shows logarithm of μ_0 vs 1/T.

type. TOF signals corresponding to the drift of charge carriers were only observed for holes. This is a consequence[3] of the transfer of electrons from neutral carbazole groups to adjacent cation radicals being more favourable than the formation of anion radicals. Consequently charge transfer is considered to occur via a series of redox reactions.

The hole mobility μ_h, is found to depend upon both the temperature, T and electric field, F. There have been two approaches[4,5] to explaining this behaviour. The first[4] considers transport to be trap limited (TL) by interactions with deep trapping centres an energy δ_o below the transport active states, while the second[5] considers trap free (TF) transport to occur via hopping within a gaussian distribution of localised states of characteristic temperature T_o (corresponding to an energetic width $\sigma = 1.5kT_o$) and relative spatial distribution Σ. The TL picture is phenomenological and the experimental data have been found to vary as (figures 2 and 3)

$$\mu = \mu_o \exp -[(\delta_o - \beta_{PF}F^{1/2})/kT] = \mu_o \exp - (\delta/kT) \quad (1)$$

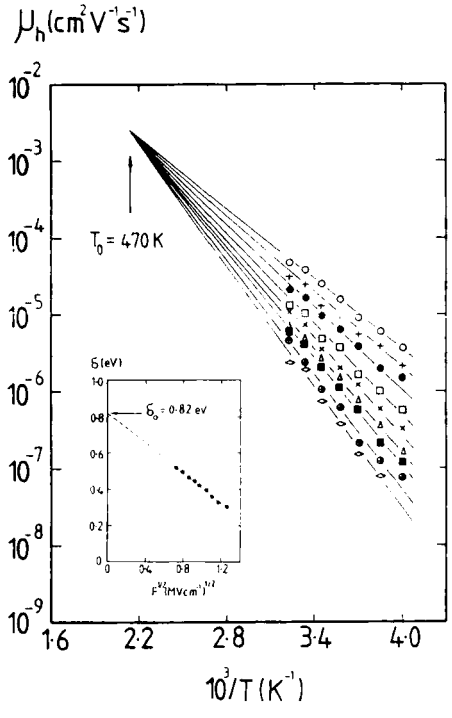

FIGURE 3 Log of μ_h vs 1/T for CMPs (n=35). Inset shows δ as a function of $F^{1/2}$.

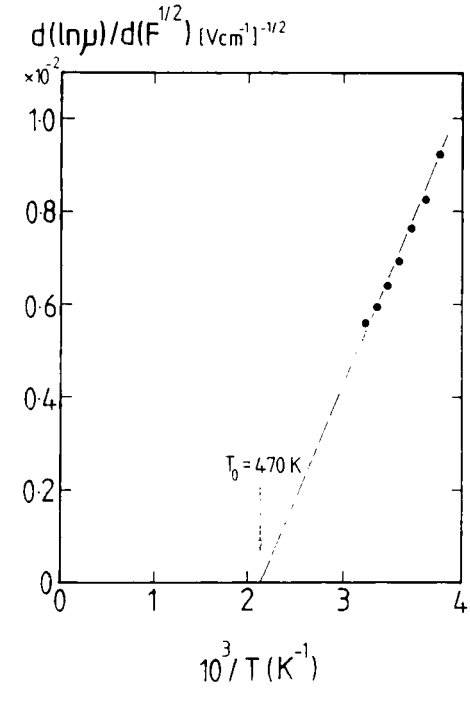

FIGURE 4 Slopes of curves in Figure 2 as a function of 1/T.

where β_{PF} is a constant of proportionality considered to be related to the Poole-Frenkel co-efficient and thus is given by $\beta_{PF} = (e^3/\pi\varepsilon_r\varepsilon_o)^{1/2}$ (e, the electronic charge, ε_r, the static dielectric constant and ε_o, the permittivity of free space). Assuming $\varepsilon_r = 3$ for CMPs, β_{PF} can be calculated to be 0.44meV $cm^{1/2}$ $V^{-1/2}$, which is comparable with the value obtained from the slope of figure 4. It is to be expected that an extrapolation of the best data fit to figure 4 should go through the origin. However, the finite intercept with the x-axis at T_o (470K) (and therefore the loss of field dependence) suggests that the laboratory temperature should be modified to an effective temperature according to $1/T_{eff} = 1/T - 1/T_o$ and hence $\mu = \mu_{o1}$ at $T = T_o$. It is to be stressed that there is no physical basis to this data manipulation. Mobility activation energies determined from the data of figure 3 are found to decrease with F (inset figure 3) as predicted in equation (1) yielding $\delta_o = 0.82$eV, in agreement with that obtained from the activation energy of the zero field mobilities μ_o(inset figure 2). Further the β_{PF} value obtained from the slope of the inset to figure 3 agrees with that of figure 4 and the data exhibit a loss of field dependence at 470K also in agreement with figure 4.

The picture presented above allows analysis of the experimental data in terms of β_{PF}, T_o, δ_o and μ_{o1} (table 1). However, for the range of materials for which data are presented, significant variations in these parameters would not be expected. In particular, δ_o should represent the energetic position of the trapping centres relative to the transport active states. Given the different conditions under which the materials are prepared, it is thought unlikely that these trapping centres are impurity based. Therefore, the trapping centres must be associated with the carbazole groups, in which case the observed spread in activation energies is surprising.

The trap free hopping approach adopted by Bassler[5] and co-workers predicts that

$$\mu = \mu_{o2} \exp [2\hat{\sigma}/3)^2 \exp (\Gamma F^{1/2}) \quad (2)$$

$$\Gamma = C(\hat{\sigma}^2 - \Sigma^2) \quad \Sigma > 1.5 \quad (3)$$

$$\Gamma = C(\hat{\sigma}^2 - 2.25) \quad \Sigma \leqq 1.5$$

where μ_{o2} is the mobility in the disorder free case, $\hat{\sigma} = \sigma/kT$, and $C = 2.9 \times 10^{-4}$ $V^{-1/2}$ $cm^{1/2}$. The experimental data is plotted according to equations 2 and 3 in figures 5 and 6. The slopes of the data sets in figure 5 yield a field dependent T_o value which when plotted against $F^{1/2}$, yields a zero field value of 1135K. This corresponds to a gaussian distribution of states of half width 0.15eV. Analysis of figure 6 yields a Σ value of 2.5 and a C value of 2.3×10^{-4} $V^{-1/2}$ $cm^{1/2}$.

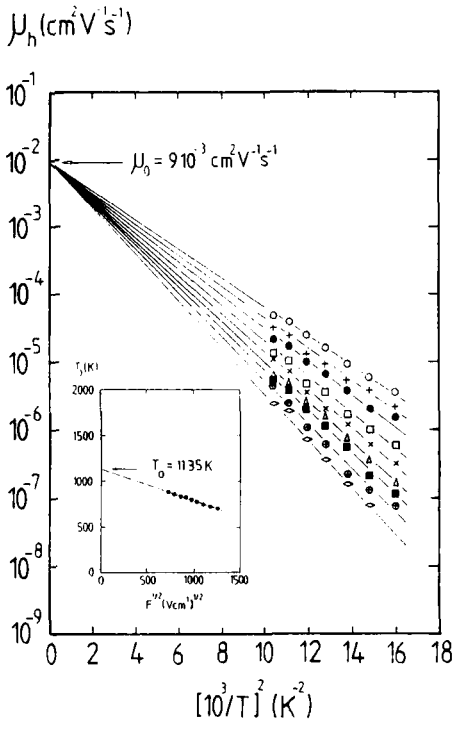

FIGURE 5 Logarithm of μ_h vs $1/T^2$ for CMPs (n=35). Inset shows the variation of T_o with $F^{1/2}$.

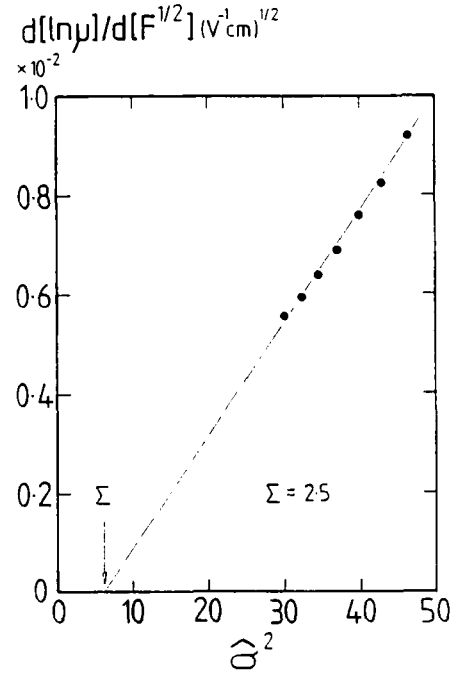

FIGURE 6 Slopes of curves in figure 1 as a function of $\hat{\sigma}^2$.

A comparison of μ_{o2}, σ and Σ parameters obtained from this model for the same specimens as the TL picture is shown in table 1. Compared to the TL case, there is a greater consistency for the TF case. The σ values which represent the half-width of the Gaussian distribution are the same to within $\pm$ 0.01eV. The physical separation of the transport active states might be expected to be larger in CMPs due to the presence of the methylene spacer units and the lower density of carbazole groups. This would be expected to influence μ_{o2}, leading to lower values in CMPs. However, within experimental error, there is no observable trend. Σ is dependent upon the relative degree of change in inter-site coupling and as such would be expected to be larger in a more disordered system. The CMPs materials under study contain relatively short chains and a greater degree of structural flexibility than PVK and therefore would be expected to possess higher Σ parameters. While for the limited data presented here Σ is larger for

Material	β [meV/(Vcm)$^{1/2}$]	T_o (K)	δ_o (eV)	μ_{o1} (cm^2/Vs)	σ (eV)	Σ	μ_{o2} (cm^2/Vs)
PVK[7]	0.24	540	0.64	0.020	0.132	1.5	0.028
PVK[6]	0.27	660	0.65	0.020	0.140	-	0.012
CMP[8]	0.17	∞	0.59	670	0.135		0.014
CMP(a)	0.42	470	0.82	0.025	0.147	2.5	0.009
CMP(b)	0.36	555	0.76	0.021	0.152	1.7	0.030
CMP(c)	0.35	537	0.73	0.008	0.145	1.8	0.010

TABLE 1 Comparison of mobility parameters extracted using the TL and TF approaches. PVK data from references quoted. CMPs results for m=3 and (a) n = 35 (b) n = 56 (c) n = 80. CMPs[8], n = 56

CMPs, it is difficult to envisage why there should be such a variation of values for CMPs with different backbone lengths. Results on molecularly doped carbazole systems yield Σ values approaching 3. Therefore, although there is a large spread in the obtained Σ values, this may disguise an underlying trend in which Σ decreases with increasing backbone length.

Acknowledgement: The authors wish to express their gratitude to the UK Science and Engineering Research Council for financial support under grant GR/F 51906.

REFERENCES

1. J.M. Maud, T.W. Booth, A.R. Hepburn and J.M. Marshall, New Physical Problems in Electronic Materials, (World Scientific Press 1991), p. 294.
2. P. Strohriegl, Makromol. Chem., Rapid Commun., 7, (1986), 771
3. G. Pfister, S. Grammatica and J. Mort, Phys. Rev. Lett., 37, (1976), 1360
4. W.G. Gill, Journal of Applied Physics 43, (1972), 5033.
5. P.M. Borsenberger, L. Pautmeier and H. Bassler, Journal of Chemical Physics 94, (1991), 5447.
6. J. Mort and G. Pfister, Electronic Properties of Polymers, (Wiley 1982), Chapter 6.
7. E. Muller-Horsche, D. Haarer and H. Scher, Physical Review B 35, (1987), 1273.
8. H.Domes, R. Fischer,D. Haarer and P. Strohriegl, Makromol Chem 190, (1989), 165.
9. D.M. Goldie, unpublished results.