High Mobility Oligomeric Charge Transport Materials

János Veres, John D. Morgan, Stephen W. Leeming and Joanne V. Allen
AVECIA
Manchester, United Kingdom

Abstract

We report on transport properties of very fast oligomeric charge transport materials (CTM). Hole mobilities in excess of 10^{-4} cm^{2}V^{-1}s^{-1} have been observed at the “conven-tional” doping level of 40 wt% in polycarbonate. This mobility is higher than in any molecularly doped polycar-bonate system known to us. The interesting features of field and concentration dependence of carrier hopping are also presented.

Introduction

Oligomeric transport materials have been studied by several workers in the past[1-4]. In most cases the target was to increase the thermal resistance of transport layers. However, carrier mobilities in molecularly doped oligomer/ binder polymer systems were only modest[4]. Young and Rule[5] have shown that “aggregation” of donor units into covalently bound blocks is undesirable and lowers the hopping mobility. Lower mobilities have also been observed when polymeric materials were compared to equivalent small molecule materials and also when bulkier star-shaped molecules were formed from CTM units.

We have found that by suitably controlled synthesis one can indeed prepare very high speed oligomers. The resulting CTM provides excellent mobilities even at low doping concentrations, good stability and high durability in organic photoreceptors.

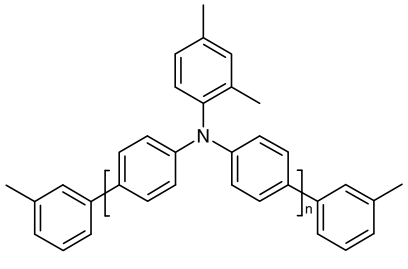

Figure 1. The model oligomeric CTM studied

In this paper we show an example of such a triarylamine based CTM and describe its physical properties such as hole mobility, photosensitivity and durability. The field and concentration dependence of hopping transport in polymers molecularly doped with oligomeric CTM exhibit very interesting behaviour.

Experimental

Our paper concentrates on the properties of the CTM illustrated on Fig.1. Details of the controlled synthesis and purification techniques will be described elsewhere.

The oligomeric CTM (OCTM) was doped into bisphenol-Z polycarbonate (PCZ, Panlite TS2020) at different concentrations in a THF solution. Approximately 25 µ thick charge transport layers (CTL) were formed by dip- or wire bar coating. The CTL was coated onto submicron TiOPc charge generation layer (CGL). The coatings were dried at 100 °C for 90 minutes.

Mobilities were measured by the time-of-flight (TOF) technique. For this purpose small samples were coated with or without CGL onto an aluminised mylar film. A 6 mm diameter semitransparent 20-40 nm thick top metal electrode was formed by vacuum evaporation. This sandwich structure was mounted in a sample holder with the bottom electrode connected to a current feedback ampli-fier. This system combines low impedance with very high speed and sensitivity. The bias was connected to the top electrode. A xenon flash source of 1 µs duration was used for the photoexcitation of the CGL the light being filtered by a 780 nm bandpass filter. For the direct photoexcitation of CTL layers a Model 437 Nanopulser lamp (Xenon Co.) was used with 10 ns duration. The light in this case was filtered to wavelengths around 360 nm. Transients were recorded using a Tektronix TDS430A oscilloscope. In most cases the experiment was carried out in the small signal regime, injecting only a few percent of the surface charge (CV). In order to be certain of this condition we monitored the amount of injected charge in every transient. The transit time was determined as the asymptotes to the plateau and the tail of the transients.

Electrophotographic properties were investigated on a PDT 2000 test apparatus (QEA, Burlington, MA). The photoreceptor film was attached to an aluminium drum substrate. Photosensitivity was measured by charging the OPC to -800 V and discharging with a 780 nm light source controlled by a mechanical shutter. The exposure energy was varied between 0-3 μJcm^{-2}. All experiments were performed in air, at 22 ^{o}C.

Hole Transport

The field dependence of the mobility of the oligomeric CTM is shown in Fig.2 at different concentrations in PCZ. At 40 wt% and 50 wt% the mobility follows the conventional quasi Pool-Frenkel behaviour. At these concentrations the mobility is above 10^{-4} cm^{2}V^{-1}s^{-1}, which is a remarkably high figure for a polycarbonate based system. At lower concentrations the mobility is decreasing at very high fields. At the concentration of 25 wt% the lowered mobility means that the drift velocity is becoming saturated. This is well illustrated in Fig.3 where TOF transients are compared at this limit. While the transit time does not change significantly, the signals become more dispersive at higher fields. At the lower concentration of 15 wt% the drift velocity also starts decreasing under high fields.

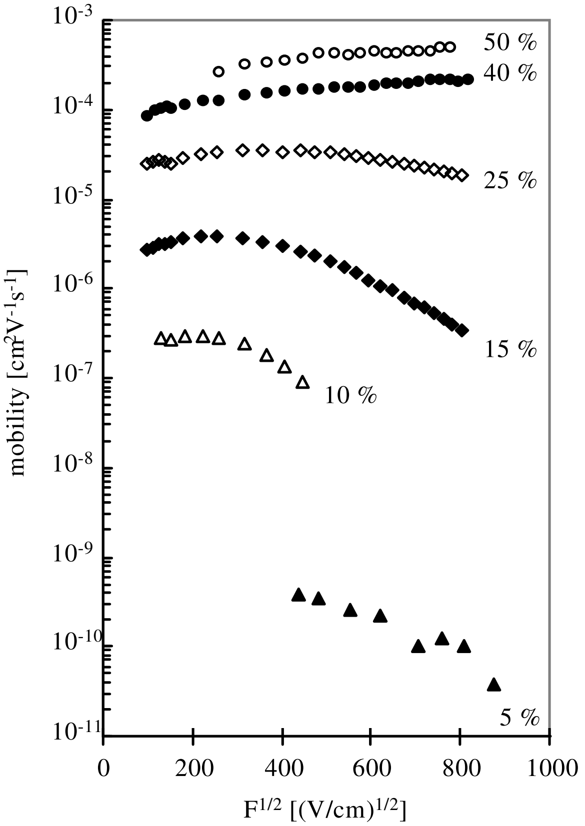

Figure 2. The field dependence of the mobility at different CTM concentrations in PCZ

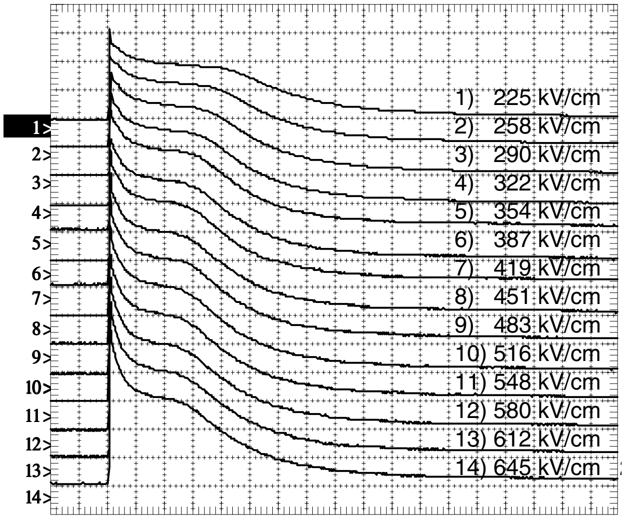

Figure 3. TOF signals at the limit of the saturation of the drift velocity in 25% CTM doped PCZ. The horizontal scale is 100μs/division.

The saturation and sometimes even reduction of the drift velocity at high fields has been observed before[5-8]. It normally appears at lower doping concentrations, i.e. large intersite distances. The carriers hopping in an energetically and spatially random field often have to hop backwards to find a faster path. High fields prohibit this and the carrier may end up at an unfavorable cul-de-sac site. At low CTM concentrations carriers have less and less choice to optimise their path and nearest neighbour hopping is expected. Similarly, high fields force nearest neighbour hopping in the forward direction. Young and Rule[5] have shown that clustering of transport moieties leads to a similar effect.

The combination of the decreasing mobility under high fields with increasing carrier dispersion suggest that high fields lead to increased spatial disorder. Particularly that these effects are more likely to occur at low concentrations.

The dispersive features indicate that some rate limiting residence times on a few field induced traps become more and more comparable to the transit time. It can be pictured as the the field increasing the spread of waiting time distributions. The number of difficult transitions may not be more than 20-30 for a 25 μ thick molecularly doped layer.

Novo et al.[8] reported on a similar transition to decreasing drift velocities at low concentrations of a large molecule, EFTP.

The following observations are recurring regarding the negative field dependence. The field F^*, above which the slope of the mobility curve is negative depends on concentration, temperature and the shape/size of CTM molecules. F^* moves towards lower fields when

- CTM concentration is lower[5,8,9] ,
- CTM molecules are larger or aggregated[5,8,9]
- the temperature is higher[8,9]

In all these cases the relative importance of spatial disorder becomes more significant compared to energetic disorder. It is quite possible that at sufficiently high fields most CTM would change their quasi Pool-Frenkel field dependence to a negative slope even at room temperature. Unfortunately the required fields are so high that in practice such conditions are experimentally inaccessible due to electrical breakdown.

The concentration dependence of the mobiltity is quite interesting. For most hopping models the hopping probability will be proportional to

$$\mu\, R^2 \exp\,(-2R/R_0) \qquad (1)$$

Where R_0 is the wavefunction decay constant. This expression, first used by Gill[10], assumes s-type wavefunctions of HOMO orbitals. If hopping is between p orbitals the transition probability is rather[11]

$$\mu\, R^4 \exp\,(-2R/R_0) \qquad (2)$$

Whichever expression is taken, if one examines the mobility at fields below the saturation regime, R_0=3.7 Å and R_0= 3.4 Å are obtained respectively. These are very high figures for decay constants compared to the usual range of 0.8-1.5 Å reported in the literature. Admittedly, this analysis is very simplistic because of the size/shape of our molecules. However, it illustrates that the site concentration in the current system has a very strong influence on mobility.

Note that mobilities at 5 wt% loading were obtained by the transient space charge limited current (TSCLC) method[12]. The mobility in this system was sufficiently low that charge generating layers became ohmic electrodes capable of supplying mobility limited dark currents to the bulk. (Further illumination did not enhance this current significantly.) Transient points were clearly detectable. PtPd alloy electrodes were similarly useful for this technique, whereas aluminium was a good blocking contact for TOF experients.

Electrophotographic Performance

Despite the negative field dependence, we find that the mobility is higher than in our reference, a well known dimer triarylamine, N,N'-diphenyl-N,N'-bis(3-methyl-phenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD). This is true at all field values at equivalent concentrations. Fig.4 compares transit times for 15, 25 and 40 wt% doped TPD and OCTM respectively. For xerographic fields the transit times for a 15 wt% doped OCTM are equivalent to that of TPD at 40 wt%. Due to this high mobility, films doped with at low concentrations were excellent in double layer photoreceptor structures.

The double layer films were prepared using the oligomeric CTM in the transport layer or TPD as a reference. Fig.5 compares the photosensitivity (PIDC) curves for two types of OPC layers. It can be seen that the high mobility oligomer gives similar photoresponse at 20 wt% doping to that of a 40 wt% TPD doped PCZ layer. Indeed at this concentration the oligomer yields higher hole mobility than TPD at 40 wt%.

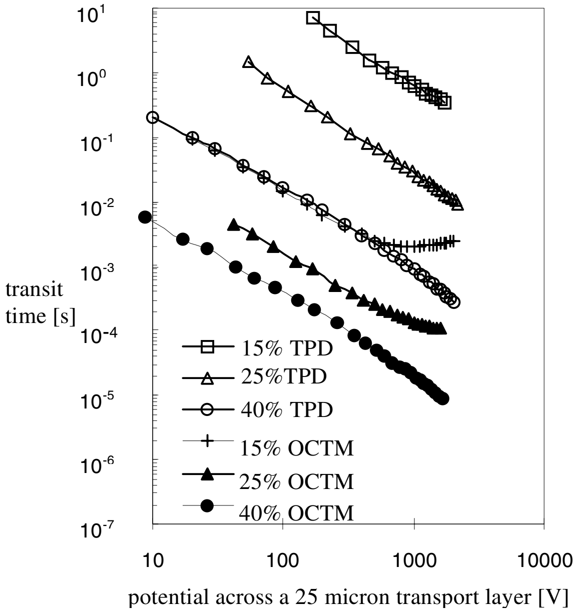

Figure 4. CTL transit times for different transport layers as a function of surface potential

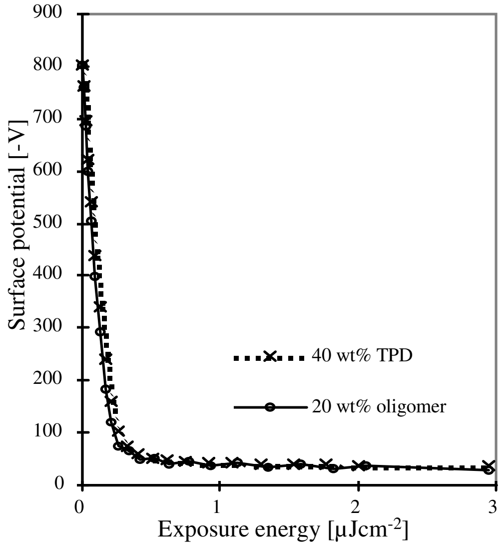

Figure 5. PIDC curves for OPC layers prepared with 40% TPD or 20% OCTM as transport layers

We found that very low residual potentials were achieved even at low oligomeric CTM concentrations. The high mobility, particularly at low fields, allows fast and complete discharge of the OPC. The low field mobility is important since the transit time of the trailing edge of carriers is a limiting factor in the decay of the surface potential. It can be seen from Fig.4 that at 40% OCTM loading the trailing carriers can be swept out nearly two orders of magnitude faster for a 10 V residual than in a 40% TPD system.

Such high mobility materials can be utilised several ways in electrophotographic systems. Lower CTM concentration in the CTL makes the layer more durable and resistant to wear. High photosensitivity is possible with thinner transport layers which is crucial in for targeting higher image resolution. The high mobility/speed also enables the design of faster engines based on small diameter OPC without departing from the use of versatile organic layers. Polar binders such as some polyesters reduce mobility unacceptably for conventional CTM. Some of the high mobility of these compounds can be sacrificed for introducing a more convenient binder polymer.

Conclusions

A model oligomeric compound was prepared to yield high hole mobility and excellent electrophotographic characteristics.

We speculate that high mobility is achieved due to establishing efficient percolation paths via linear, conjugated doner functionalities. These paths are more favorable than “aggregation” in the case of starburst or dendrimer type of linking of CTM units. Furthermore, conjugated linear segments will be more efficient that those that may be linear but contain essentially isolated doner groups. Mobilities of non-conjugated linearly linked triaylamines or those attached to a main polymer chain have been found to be low.5,12 We believe that conjugated oligomers also have a larger perimeter (or rather surface area) than equivalent volume large spherical molecules and this also leads to improved overlap of HOMO wavefunctions. One should not overlook the further effect of binder/CTM morphology – this is currently under study in our laboratory.

The extent of conjugation (i.e. chain length) does not necessarily need to be very long. The way the transporting oligomer or polymer chains coil up may well require interchain hops after visiting a certain number of monomer units due to the externally applied field.

References

1. H. Tanaka, S. Tokito, Y. Taga and A. Okada, *Chem. Commun.*, 2175 (1996).
2. S. Tokito, H. Tanaka, A. Okada and Y. Taga, *Appl. Phys. Lett.*, **69,** 878 (1996).
3. I.K. Yakushchenko, M.G. Kaplunov, O.N. Efimiv, M. Yu. Belov and N. Shamaev, *Phys. Chem. Phys*., **1,** 1783 (1999).
4. O.K. Kocheleva, S.A. Lebedev, B.V. Kotov, E.S. Petrov, A.R. Tameev, A.A. Kozlov and A.V. Vannikov, *Proc. of IS&T's 14th NIP Conference,* IS&T, Springfield, VA, 1998, pg. 528.
5. Ralph H. Young and N. Geoffrey Rule, *Phys. Rev. Lett.,* **72,** 388 (1994).
6. G. Verbeek, M. Van der Auweraer, F.C. De Schryver, C. Geelen, D. Terrel and S. De. Meuter, *Chem. Phys. Lett*., **188,** 85 (1992).
7. M. Van der Auweraer, F.C. De Schryver, P.M. Borsenberger and J. J. Fitzgerald, *J. Phys. Chem*. **97,** 8808 (1993).
8. M. Novo, M. Van der Auweraer, F.C. Schryver, P.M Borsenberger and H. Bassler, *Phys. Stat. Solidi* (b), **177,** 223 (1993).
9. B. Harnestein, H. Bassler, S. Heun, P. Borsenberger, M. Van der Auweraer and F.C. De Schryver, *Chem. Phys*., **191,** 321 (1995).
10. W.D. Gill, *J. Appl. Phys*., **43,** 5033 (1972).
11. J. Hirsch, *J. Phys*. C., **12,** 321 (1979).
12. M. Abkowitz, J.S. Facci and M. Stolka, *Chem. Phys*., **177,** 783 (1993).

Biography

Janos Veres received his MSc from the Faculty of Electrophysics of Lviv University in 1990. He earned his PhD from Imperial College, London in 1995 in solid state electronics studying Organic Photoreceptors (OPC). He worked in R&D and manufacturing of photoconductors for three years at Gestetner Byfleet Ltd. (GBL). Since 1998 he has been a Senior Scientist at Avecia (formerly Zeneca Specialties) leading the Physics and Characterisation of OPC chemicals and organic electronic materials. janos.veres@avecia.com