Enhanced Hole Drift Mobility in Organopolysilane Doped with Low-molecular-weight Charge Carrier Transport Compounds

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The 'transport-active' organopolysilanes doped molecularly with low-molecular-weight charge carrier transport compounds exhibited the highest hole drift mobility, 10^{-3} cm^2 V^{-1} s^{-1}, for amorphous polymeric solids.

There has been a lot of interest in the industrial uses of organic charge carrier transport materials, especially in the field of electrophotography. Much research on high mobility materials has been directed at developing low-molecular-weight charge transport compounds (CTs) such as arylamine and hydrazone derivatives, which are dispersed molecularly in 'transport-inactive' binder polymers such as polyester or polycarbonate resin, from the practical viewpoint of film-forming.[1—3] In these dispersion systems, the drift mobility strongly depends on the concentration of CTs because there is no charge transport contribution from the binder polymers, but a high concentration of CTs gives rise to microcrystals. However, provided that these 'transport-inactive' polymers are replaced by 'transport-active' binder polymers, it would be possible to develop a new type of high mobility material. There have been recent reports of organopolysilanes with a high hole drift mobility of 10^{-4} cm^2 V^{-1} s^{-1} through the σ-conjugated Si backbone and good film-forming ability;[4—9] these could serve as the 'transport-active' binder polymers.

We report herein an enhanced hole drift mobility in

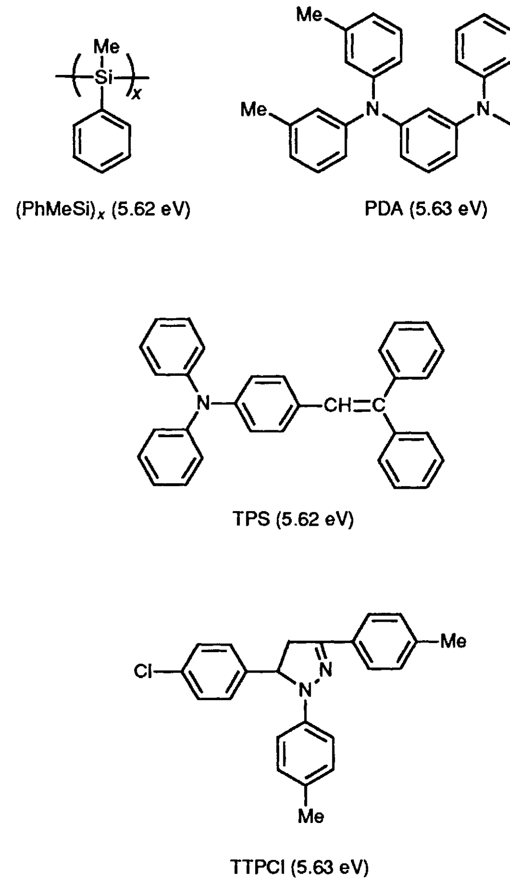

Figure 1. Poly(phenylmethylsilane) as 'transport-active' polymer binder and low-molecular-weight charge transport compounds (CT) as dopants.

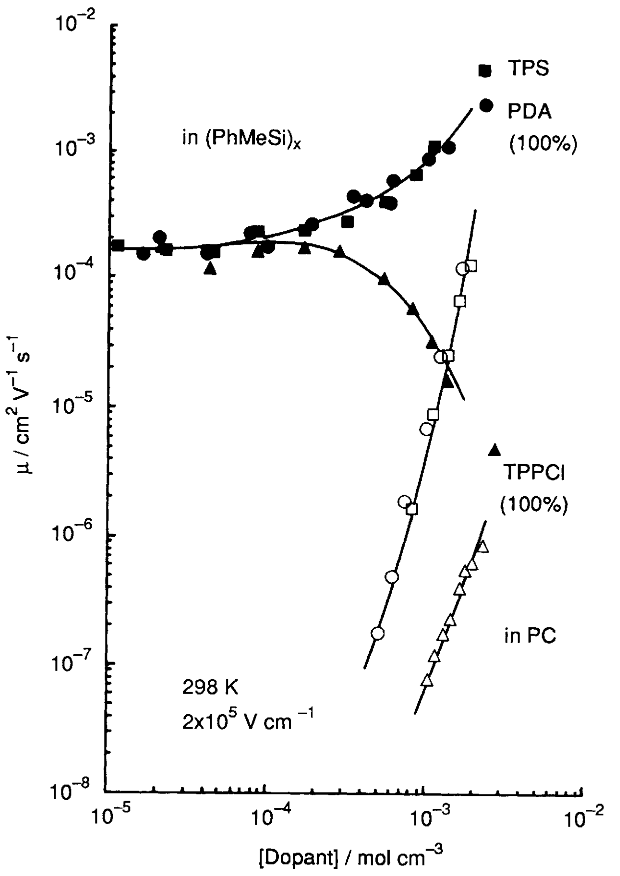

Figure 2. Dopant concentration dependence of hole drift mobility in $(PhMeSi)_x$ (closed) and PC (opened). (●, ○) PDA, (■, □) TPS, (▲, △) TPPCl. *Conditions*: 298 K, 2×10^5 V cm^{-1}.

organopolysilanes doped with low-molecular-weight CTs having the same ionization potential as the host polymers; the highest mobility, 10^{-3} cm^2 V^{-1} s^{-1}, was attained for amorphous polymeric materials.

Poly(phenylmethylsilane), $(PhMeSi)_x$, a typical organopolysilane, was used as the 'transport-active' binder polymer for these studies (hole drift mobility, 10^{-4} cm^2 V^{-1} s^{-1} at room temperature; ionization potential, 5.62 eV, measured by atmospheric photoelectron emission spectroscopy as described elsewhere[10]). The chemical structures of three kinds of CTs used in this study are shown in Figure 1 with their ionization potentials, I_p measured by the same technique. Three of these have a similar I_p to that of the $(PhMeSi)_x$ host polymer; it is possible that the dopants with a lower I_p than $(PhMeSi)_x$ act as hole traps and inversely the dopants with the larger I_p behave as inert binder polymers.[11,12] The neat amorphous films of these CTs exhibit a high mobility of 2.5×10^{-3} cm^2 V^{-1} s^{-1} for tetrakis-(3-methylphenyl)-*N*,*N*,*N'*,*N'*-2,5-phenylenediamine (PDA)[2] and 4.6×10^{-3} cm^2 V^{-1} s^{-1} for α-phenyl-4-*N*,*N*-diphenylaminostylbene (TPS),[3] but only 5.0×10^{-6} cm^2 V^{-1} s^{-1} for 1,3-di(4-methylphenyl)-5-(4-chlorophenyl)-2-pyrazoline (TPPCl) at room temperature. The doping of $(PhMeSi)_x$ or the polycarbonate (PC) host polymer with CTs was done at the concentration where no microcrystals were formed. The doping concentration is given in terms of the number of molecules, *i.e.*, mol cm^{-3}, assuming a density of 1 g cm^{-3} for $(PhMeSi)_x$ and 1.2 g cm^{-3} for PC, instead of a wt% expression because of the different molecular weight of each CT. The details of the drift mobility measurements are described elsewhere.[9]

Figure 2 compares the concentration dependence of the hole drift mobilities in PC and $(PhMeSi)_x$ doped with these CTs (field 2×10^5 V cm^{-1}, room temp.). The hole drift mobilities of CTs in the PC dispersions varied in the range 10^{-7}—10^{-4} cm^2 V^{-1} s^{-1} depending on the charge hopping distance between the localized sites provided with CT molecules in the polymer binder. The exponential increase of the mobility with increasing concentration of CTs clearly indicates that the carrier transport in these systems is dominated by the tunnelling process through the inert binder.[13] The upper value of the mobility, $\sim 10^{-4}$ cm^2 V^{-1} s^{-1}, is limited by the compatibility of CTs with the binder polymer to form homogeneous films, but an extrapolation tends to the value of the amorphous neat solids of each CT. Thus, mobility over 10^{-4} cm^2 V^{-1} s^{-1} is unexpected in using 'transport-inactive' binder polymers.

On the other hand, the drift mobilities in $(PhMeSi)_x$ doped with PDA or TPS began to increase beyond the dopant concentration of $\sim 10^{-4}$ mol cm^{-3} (*ca.* 5 wt%), and interestingly reached $\sim 10^{-3}$ cm^2 V^{-1} s^{-1} at 1×10^{-3} mol cm^{-3} (*ca.* 50 wt%), which is almost one order of magnitude higher than that of the $(PhMeSi)_x$ host itself. To our knowledge, this is the highest value obtained under ordinary conditions for carrier transport polymeric materials. The comparison of the high mobility of 10^{-3} cm^2 V^{-1} s^{-1} with those of PC dispersion systems at the same concentration, which are lower by about one order of magnitude, reasonably excludes the possibility of charge hopping only through CT molecules, and indicates that $(PhMeSi)_x$ operates as a 'transport-active' matrix. The activation energies in these doped $(PhMeSi)_x$ systems, which are determined from the temperature dependence of the mobility, were found to be almost the same as that of the $(PhMeSi)_x$ host irrespective of dopant concentration, indicating that CTs do not work as hole traps as expected from their ionization potentials.

The explicit reason for the enhancement of the mobility remains unestablished, but it is noteworthy that the mobility in doped $(PhMeSi)_x$ systems maintained the value of $(PhMeSi)_x$ up to a doping concentration of 1×10^{-4} mol cm^{-3}, and tended to converge to the values of the amorphous neat films of PDA and TPS, respectively. These facts indicate that at lower concentrations the CTs incorporated in the interstitials of the host polymer chains do not affect the hopping transport in $(PhMeSi)_x$, while at higher concentrations the CTs, which have excellent hole transport ability, provide additional hopping sites with the same ionization potential, enhancing the hole mobility by favouring charge hopping between CT and localized states of $(PhMeSi)_x$. The increase in mobility in the doped $(PhMeSi)_x$ systems, however, is attributed to the high mobility of the CTs. This is supported by the addition of TTPCl with a poorer hole mobility than that of the $(PhMeSi)_x$ host, which resulted in a decrease in mobility, although TTPCl has a similar ionization potential (5.63 eV). Therefore, the use of 'transport-active' binder polymers can be said successfully to bring out the high mobility of CTs themselves.

The mobility reported here, 10^{-3} cm^2 V^{-1} s^{-1}, is the highest value for insulating amorphous polymeric materials reported to date. This result provides a new approach to developing composite materials of high mobility, using 'transport-active' binder polymers instead of inactive ones.

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References

1 M. Stolka, J. F. Yanus, and D. M. Pai, *J. Phys. Chem.*, 1984, **88**, 4707.

2 M. Yokoyama, 'Advanced Printing of Paper Summaries of the Japan Hardcopy '88,' The Society of Electrophotography, Tokyo, 1988, 51.

3 K. Ohta, *Electrophotography*, 1986, **25**, 303.

4 R. G. Kepler, J. M. Zeigler, L. A. Harrah, and S. R. Kurtz, *Phys. Rev. B*, 1987, **35**, 2818.

5 M. Stolka, H.-J. Yuh, K. McGrane, and D. M. Pai, *J. Polym. Sci. Polym. Chem. Ed.*, 1987, **25**, 823.

6 M. Abkowitz, F. E. Knier, H.-J. Yuh, R. J. Weagley, and M. Stolka, *Solid State Commun.*, 1987, **62**, 547.

7 M. Stolka and M. Abkowitz, *J. Non-Cryst. Solids*, 1987, **97/98**, 1111.

8 M. Abkowitz and M. Stolka, *Philos. Mag. Lett.*, 1988, **58**, 239.

9 K. Yokoyama and M. Yokoyama, *Philos. Mag. B*, 1990, **61**, 59.

10 K. Yokoyama and M. Yokoyama, *Solid State Commun.*, 1989, **70**, 241.

11 D. M. Pai, J. F. Yanus, and M. Stolka, *J. Phys. Chem.*, 1984, **88**, 4717.

12 K. Yokoyama and M. Yokoyama, *Solid State Commun.*, 1990, **73**, 199.

13 J. Mort and G. Pfister, 'Electronic Properties of Polymers,' Wiley, New York, 1982, p. 215.