SHORT COMMUNICATIONS

Hole Drift Mobility in Dimer Model Compounds of Poly(*N*-vinylcarbazole) Dispersed in a Polymer Binder

Masaaki YOKOYAMA, Koji AKIYAMA, Naoki YAMAMORI,
Hiroshi MIKAWA, and Shigekazu KUSABAYASHI

*Chemical Process Engineering, Faculty of Engineering,
Osaka University, Yamadaoka, Suita,
Osaka 565, Japan*

In the present short communication, the hole drift mobilities of three dimer model compounds of poly(*N*-vinylcarbazole) (PVK) dispersed in a polymer binder are reported to provide a direct evidence of the correlation between the charge carrier trap and excimer forming site as an inherent structural defect in amorphous photoconductive polymers.

The charge carrier transport in amorphous photoconductive polymers such as PVK has been considered to be thermally-activated hopping conduction from trap to trap, in which charge carriers stay for a time.[1-5] Due to these traps, very low drift mobilities of the order of 10^{-7} cm^2 V^{-1} s^{-1} have been generally observed in PVK,[4] its trap-free drift mobility being much higher of the order of 10^{-3} cm^2 V^{-1} s^{-1}.[5-7] Once we know the nature or origin of the carrier traps characteristic of such amorphous polymers, it would open a way to develop better materials required in the practical application of such amorphous photoconductive polymers.

A structural defect as named "excimer forming site" in which the planes of two adjacent pendant chromophores attached to the backbone chain are arranged parallel to each other, has been nominated as one of the possibilities

for the traps.[8] This concept comes from the idea that the hole carrier, for example, on such an excimer forming site would be in a dimer radical cation which is expected to be more stable than the radical cation on a single chromophore, *i.e.*, an isolated hole carrier. Actually, the existence of such excimer forming sites in a solid polymer film has been confirmed from the observation of the excimer fluorescence.[9-11]

Among the present three dimer models shown in Figure 1, *meso*-BCzPen (*meso*-2,4-bis(*N*-carbazolyl)pentane)[12,13] is a model compound which takes the intramolecular excimer-type conformation much easier than others, *i.e.*, BCzPr (1,3-bis(*N*-carbazoyl)propane) and BCzBu (1,4-bis(*N*-carbazolyl)-butane).[14] Figure 2(a) shows a comparison of the fluorescence spectra in a solution (10^{-4} mol l^{-1}) of these compounds at room temperature. BCzBu is well-known as a compound which does not show the excimer fluorescence missing the "$n = 3$" rule,[15] but BCzPr matching to this rule, shows a weak excimer fluorescence as a long tail to lower energy region following to structured monomer-type fluorescence at about 350 nm. Contrary to these spectra, *meso*-BCzPen clearly exhibits a strong
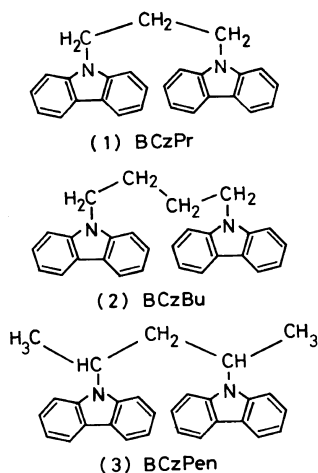
Figure 1. Dimer model compounds of PVK. (1), 1,3-bis(N-carbazolyl)propane (BCzPr); (2), 1,4-bis(N-carbazolyl)butane (BCzBu); (3), meso-2,4-bis(N-carbazolyl)pentane (BCzPen).
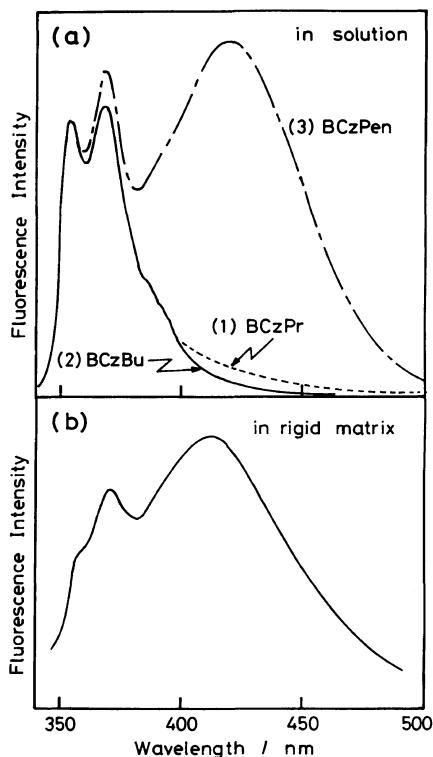

Figure 2. (a) Fluorescence spectra of dimer model compounds in tetrahydrofuran solution (10^{-4} mol/l). (1), BCzPr; (2), BCzBu; (3), BCzPen; 300 K, $\lambda_{ex} = 340$ nm. (b) Fluorescence spectrum of BCzPen in a rigid polymer matrix (30 wt%): 300 K, $\lambda_{ex} = 330$ nm.

structureless excimer fluorescence with its maximum at 415 nm in solution. Interestingly, we have found that meso-BCzPen shows a strong excimer emission even in a polymer rigid matrix (dispersed 30 wt% of meso-BCzPen) as shown in Figure 2(b). This fact indicates that the excimer-type conformation of the dimer model compound, which generally has higher conformational energy, is frozen in a cast polymer film with some population.[10,11] In the case of two other model compounds, BCzBu and BCzPr, however, such pronounced excimer fluorescence could not be observed in the identical condition. In this sense, a comparison between the drift mobilities of these dimer model compounds dispersed in a polymer binder is an attractive subject concerning the problem of carrier traps.

The film samples were prepared by the wire-bar coating technique on a Cu substrate from a dichloromethane solution of polycarbonate resin (Panlite L1250, Teijin Co.) including a given amount (30 wt%) of the dimer model compounds. In this doping concentration, no microcrystal separation of the dopants could be recognized by an optical microscope. After dried, a transparent Au electrode was deposited by vacuum evaporation on the free film surface to form a sandwich-typed cell assembly (sample thickness: 8 μm). The hole drift mobility in these systems was measured by the usual time-of-flight technique with incident light pulse of N_2 gas laser (337 nm, 3 ns duration) through the positively biased Au electrode. Details of the measurements have been described in our previous paper.[5]

The shape of the transient photocurrent generally consisted of an initial spike followed by a sloping plateau and a long tail approaching the dark current level in each system. Transit time was determined from the logarithmic current-versus-time plots.

Figure 3 summarizes hole drift mobilities of these three dimer models as a function of temperature at a field of 5×10^5 V cm^{-1}. The
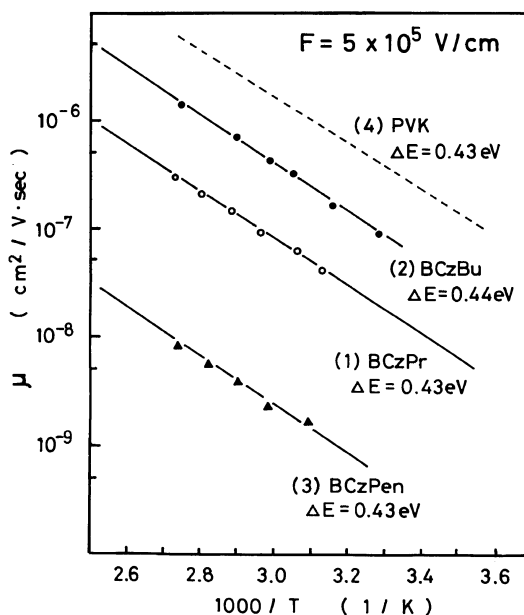
Figure 3. Hole drift mobility of three dimer model compounds, (1) BCzPr, (2) BCzBu, and (3) BCzPen as a function of temperature; measured at 5×10^5 V cm^{-1}. ΔE, activation energy. (4) PVK at the same field strength, for comparison.

most significant observation can be exemplified in the value of the drift mobility. At 333 K, for example, the mobility of *meso*-BCzPen, 1.5×10^{-9} cm^2 V^{-1} s^{-1}, is by almost two orders of magnitude smaller than that of BCzBu, 2.6×10^{-7} cm^2 V^{-1} s^{-1}, and BCzPr gives an intermediate value of 5.3×10^{-8} cm^2 V^{-1} s^{-1}. Interestingly, the decreasing order in the drift mobility, BCzBu > BCzPr > *meso*-BCzPen, is in increasing order in excimer fluorescence yield of model compounds as shown in Figure 2, that is, the lowest drift mobility is obtained in *meso*-BCzPen which exhibits a strong excimer fluorescence even in a dispersion sample. The fact that the activation energy (about 0.4 eV) obtained in each dimer system is almost the same as the value obtained in PVK, may indicate that the carrier trap in the dispersed dimer model systems is of the same origin to the carrier trap in PVK.[16] It should be noted here that the value of 0.4 eV obtained for activation energy corresponds to

the trap depth of about 0.68 eV observed in PVK at zero field, since the Poole–Frenkel type barrier lowering occurs in high fields. The higher drift mobility in PVK as compared with these dispersion systems is also noted to be due to the high density of carbazole moieties in PVK participating to the hole carrier transport.[17]

Thus we are convinced that we now have obtained a strong evidence for the identity of the excimer forming site and the carrier trap site in amorphous photoconductive polymers. Recently, Wada *et al.*[18] reported that the addition of BCzPr capable of excimer formation reduced the hole drift mobility in a solid polymer solution of 1,2-*trans*-bis(*N*-carbazolyl)cyclobutane, a dimer compound incapable of the sandwich pair configuration. Their result also provided another evidence for this problem.

As we have already reported that the drift mobility of PVK under trap-free condition is much larger, *i.e.*, the order of 10^{-3} cm^2 V^{-1} s^{-1}, than the overall drift mobility.[5] Therefore, the present result suggests that there would be a possibility to improve further the drift mobility of amorphous photoconductive polymers by an appropriate molecular design to avoid the excimer forming site, *i.e.*, more generally, by avoiding such a specific dimeric site in which dimer redical ion species can be formed.

REFERENCES

1. J. Mort and A. I. Lakatos, *J. Non-cryst. Solids*, **4**, 117 (1970).
2. W. D. Gill, *J. Appl. Phys.*, **43**, 5033 (1972).
3. G. Pfister and C. H. Griffiths, *Phys. Rev. Lett.*, **40**, 659 (1978).
4. W. D. Gill, "Photoconductivity and Related Phenomena," J. Mort and D. M. Pai, Ed., Elsevier Pub. Co., Amsterdam/New York, 1976, p 303.
5. M. Fujino, H. Mikawa and M. Yokoyama, *Polym. J.*, **14**, 18 (1982); *Photogr. Sci. Eng.*, **26**, 84 (1982); *J. Non-cryst. Solids*, **14**, 163 (1984).
6. B. Reimer and H. Bässler, *Phys. Stat. Sol. (A)*, **51**, 445 (1979).
7. J. Hirsh, *J. Phys. C, Solid State Phys.*, **12**, 321 (1979).

8. M. Fujino, Y. Kanazawa, H. Mikawa, S. Kusabayashi, and M. Yokoyama, *Solid State Commun.*, **49**, 575 (1984).
9. W. Klöpffer, *J. Chem. Phys.*, **50**, 2337 (1969).
10. C. W. Frank and L. A. Harrah, *J. Chem. Phys.*, **61**, 1526 (1974).
11. M. Yokoyama, T. Yano, and H. Mikawa, *Rep. Prog. Polym. Phys. Jpn.*, **20**, 485 (1977).
12. F. C. DeSchryver, L. Moens, M. Van der Auwerear, N. Boens, L. Monnerie, and L. Bokobza, *Macro-molecules*, **15**, 64 (1982).
13. F. Evers, K. Kobs, R. Memming, and D. R. Terrel, *J. Am. Chem. Soc.*, **105**, 5988 (1983).
14. W. Klöpffer, *Chem. Phys. Lett.*, **4**, 193 (1965).
15. F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965).
16. K. Akiyama, S. Teramatsu, S. Kusabayashi, and M. Yokoyama, *Polym. Prepr. Jpn.*, **33**, 2547 (1984).
17. G. Pfister, *Phys. Rev. B*, **16**, 3676 (1977).
18. T. Wada and R. Oshima, *Kobunshi Ronbunshu*, **41**, 383 (1984).