

4P075 フェムト秒過渡二色性測定によるポリ(N-ビニルカルbazol)系におけるホール非局在化過程溶媒効果

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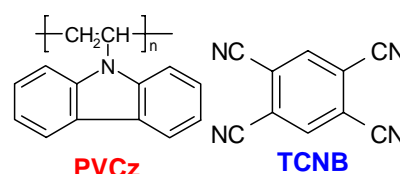
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Introduction

Aromatic vinyl polymers have been the focus of considerable research and development during past several decades especially on their application for the hole transport materials in organic photoconductor, OLED etc. On the hole transfer (HT) process in poly(N-vinylcarbazole) (PVCz) and other aromatic vinyl polymers, we have studied its dynamics and mechanisms by means of picosecond transient absorption spectroscopy and dichroism measurement^{1,2}. The HT dynamics in PVCz was well described by one-dimensional random walk model along the polymer chain with the HT rate constant, k_{HT} , of $2.0 \times 10^9 \text{ s}^{-1}$ in 1,2-dichloroethane solution. It can be mentioned that the hole transfer reaction is endothermic, since the increase in the inter-ionic distance reduces the Coulombic attractive interaction in the ion pair. The activation energy predicted for the model reaction of the initial hole escape reaction, $A^+D_0^+D_1 \rightarrow A^+D_0D_1^+$, by the standard theory of ET reaction is $\gg 10k_B T$ and the corresponding rate constant of HT in the order of $10^5 \sim 10^6 \text{ s}^{-1}$ even in rather polar solution of 1,2-dichloroethane. Therefore, experimentally observed such a large hole migration rate constant in the order of 10^9 s^{-1} could not be accounted for within the framework of usual ET theories assuming very weak interaction in the reactants. It has been suggested that the delocalization³ of the cationic state takes an important role in such rapid hole transfer (HT) process. Delocalization process decreases the Coulombic attraction in the ion pair and suggested to be dependent on the polarity of the solvent. To clearly elucidate this delocalization process and its solvent polarity dependence, we have studied femtosecond dichroism dynamics of PVCz-TCNB (electron acceptor) in solution phase. On the basis of the present results and previous investigation in picosecond time region, the molecular motion leading to the rapid HT and delocalization will be discussed.

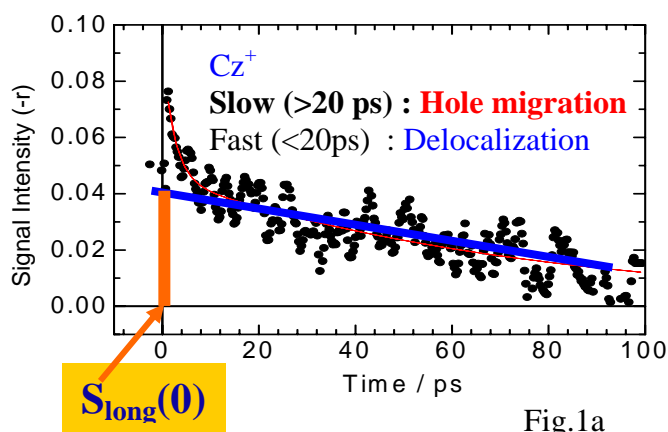
Experimental

Dual OPA femtosecond Ti:Sapphire laser at 490 nm with 150 fs fwhm and ca. 5 μJ output power was used for the excitation of the weak charge transfer (CT) complex between Cz and TCNB. All the measurements were carried out at $20 \pm 1^\circ \text{C}$.



Results and Discussion

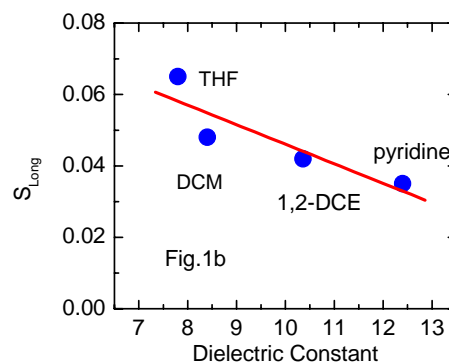
Fig.1a shows the anisotropy decay of Cz^+ (at 800 nm: solid circles) of PVCz-TCNB system in 1,2-dichloroethane solution. The anisotropy decay of the cation shows fast decay within 10~20 ps followed by a slow decay process. The fast decay of the Cz^+ can be



attributed to the delocalization process of the cationic state of Cz^+ over several Cz moieties. The bold solid line is the curve based on the HT scheme obtained in the ps measurement. The extrapolated value of the bold line at $t=0$ in Fig.1b can be termed as absolute anisotropy value, which was used to estimate the delocalization size as $S_{long}(0)$. It is important to mention here that such fast decay of the anisotropy was not observed for monomer and dimer model system.

The $S_{long}(0)$ value was used to estimate the delocalization size in the following manner. In the monomer model, ethylcarbazole-TCNB system this value is -0.14 i.e., hole is localized in one carbazole unit. In the dimer model, di-carbazolylcyclobutane-TCNB system, this value is -0.11 i.e., hole is delocalized almost within 1.3 Cz moieties. On the other hand, in the polymer system, this value is -0.07 ($t=0$) and -0.04 ($t=20ps$) respectively. This means that hole is delocalized over 3-4 Cz moieties in the polymer system.

As mentioned earlier section that the delocalization process decreases the Coulombic attraction in the ion pair and suggested to be dependent on the polarity of the solvent. In fact, the $S_{long}(0)$ value increases with the decrease of the solvent polarity according to the relationship as delocalization size $1/S_{long}(t=0)$, which is shown in the Fig.1b.



The energy required, for the separation of hole from distance r_1 ($A^-D_1^+D_2^+...$) to r_2 ($A^-...D_1^+...D_i^+...$) can be termed as

$$W = \int_{r_1}^{r_2} \frac{e^2}{4\pi\epsilon_0\epsilon} \frac{1}{r^2} dr \quad \text{So as to,} \quad W = \frac{e^2}{4\pi\epsilon_0\epsilon} \left[\frac{1}{r_1} - \frac{1}{r_2} \right]$$

This energy, W is independent of the solvent polarity, however $S_{long}(t=0)$ is dependent as r_1 $1/S_{long}(t=0)$. Therefore, the following relation can be satisfied,

$$S_{long}(0) = S_{total}(0) - \frac{4\pi\epsilon_0\epsilon W}{e^2} \times k$$

From this relation, the calculated energy can be obtained in the range of 0.2 ~ 0.3 eV and this value is comparable with the stabilization enthalpy of cation radical in the polymer system. Actually, the delocalization of the cationic state prepares the conditions for the fast HT to take place; decrease in the Coulombic attraction between the anion and the cation via the increase in the inter-ionic distance and the reduction of the outer reorganization energy. The anisotropy values in several solvents after the fast decay of Cz^+ shows smaller value for the system with larger HT rate constant. This result indicates that the degree of the delocalization is dependent on the solvent polarity. On the basis of these results and previous one, we will discuss the HT dynamics at the conference site.

- (1) H. Miyasaka, T. Moriyama, and A. Itaya, *J. Phys. Chem.* **1996**, *100*, 12609.
- (2) H. Miyasaka, T. Moriyama, S. R. Khan, A. Itaya, in “*Femtochemistry*”, Ed. by F.C. De Schryver, Wiley-VCH, **2001**, pp335-344.
- (3) H. Miyasaka, S. R. Khan and A. Itaya, *J. Phys. Chem. A* **2002**, *106*, 2192.