Radical ion pair in carrier generation process of photoconductive organic polymer films

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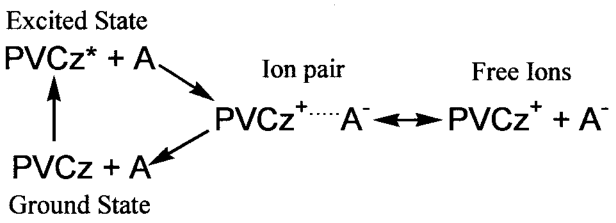
A concept of the ion pair with the interionic distance (r_0) of 2–3 nm in carrier generation process of photoconductive polymer films has been believed for a long time. Recently, however, the experimental and theoretical results denying the distant ion pair born from thermalization have been reported. This brief review describes our paper addressing the controversy over the ion pair in photoconductive polymer films, which proves the presence of distant ion pair of $r_0 = 0.8$–0.9 nm by employing time-resolved electron paramagnetic resonance spectroscopy.

Introduction

Thin-film electronic devices based on molecular and polymeric materials have been proposed for a number of applications such as displays, photodetection and plastic solar cell systems due to potentially lower costs, simpler packaging and compatibility with flexible substrates. Poly(N-vinylcarbazole) (PVCz) has received much attention, since the film of PVCz is one of the best functional materials as organic photoconductor. As increasing the engineering applicability of PVCz film, many basic studies also have been made to clarify the photoconduction mechanism in the organic amorphous film. Based on the fact that doping of the electron acceptor (A) markedly enhances the photoconductivity, a simplified mechanism for the carrier generation prior to the carrier transport is proposed in the case of acceptor-doped films (Scheme 1).



Scheme 1.

The ion pair consisting of PVCz$^+$ and A$^-$ radicals acts as a key intermediate to generate the free ions. The analysis using an Onsager model provides the interionic distance (r_0) of 2-3 nm for the ion pair.1) However, according to Marcus theory, Murata and Tachiya theoretically indicated the overestimation of the initial distance of the photoinduced electron transfer on the Onsager model.2) Also, by means of picosecond optical spectroscopy, Miyasaka *et al.* experimentally showed a negative response to the presence of the hypothetical distant ion pair developed during a cooling process of the contact ion pair.3) This review briefly introduces our recent EPR study on the structure of the transient radical ion pair generated in a 1,2,4,5-tetracyanobenzene (TCNB)-doped PVCz solid film.4)

Time-resolved EPR spectrum

The spin polarized EPR spectrum was observed, when the charge-transfer (CT) complex in the PVCz film was selectively excited (Fig. 1 (a). The spectrum was observed at 500 ns after the laser pulse of 532 nm at room temperature. The spectral phase is enhanced absorption (A) in the low field and emission (E) in the high field. The signals are detected over a relatively wide region of more than 8 mT. For the sake of assignment of the observed transient paramagnetic species, we separately measured the steady state EPR spectra for the TCNB anion and the PVCz cation in rigid glassy solvents (Fig. 1 (b)). The central field of the time-resolved EPR spectrum for the TCNB-doped PVCz film is in agreement with those of the free ions, indicating that the transient species are associated with the TCNB$^-$ and PVCz$^+$ radicals. However, the spectral width of transient signal in the film is much broader than those of the component free ions that are broadened only by the intramolecular interactions such as the anisotropic Zeeman and the hyperfine interactions. The broadness of the time-resolved EPR spectrum indicates that the transient signal is attributed to the ion pair (TCNB$^-$ ... PVCz$^+$) rather than to the free ions, because the intermolecular magnetic interactions of the exchange and dipolar interactions between TCNB$^-$ and PVCz$^+$ can make the EPR spectrum broader.

The intensity of the time-resolved EPR signal linearly increases with the incident power of the laser for the excitation. The linear laser power dependence indicates that the observed ion pair is created through a one-photon process. The time-profiles of the EPR signal always showed an exponential decay with a time constant of about 1.0 μs, even when the laser power was varied. The exponential behavior, meaning the first order kinetics, supports the fact that the observed decay of the ion pair under zero external electric field represents the recombination within a geminate pair rather than free pair, because the free pair recombination should obey second order kinetics.

Since the EPR spectrum is broadened by the large anisotropy due to the spin dipolar interaction as described later, the shape of EPR spectrum may be distorted by the angle selection experiment with linearly polarized light,5) as long as

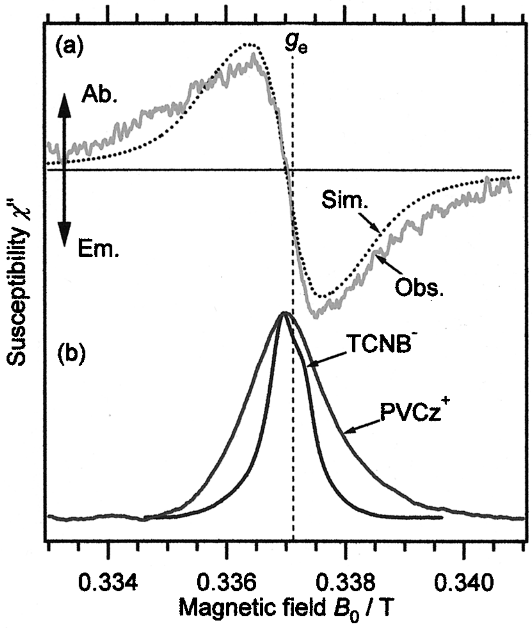


Fig. 1. (a) Time-resolved EPR spectrum of TCNB-doped PVCz film observed at 500 ns after the pulse excitation at the CT band under room temperature. The broken line indicates the simulation spectrum for a singlet-born SCRP consisting of PVCz$^+$ and TCNB$^-$. (b) Cw-EPR spectra of PVCz$^+$ in conc. H_2SO_4 and TCNB$^-$.

the ion pair holds the initial orientation of the CT complex. However, excitation with the polarized light did not give rise to any influences on the spectral shape. No effect of the angle selection experiments is interpreted in term of the loss of memory of the initial orientation in the ion pair due to a charge migration. Therefore, it is suggested that the ion pair giving the spin polarized EPR spectrum is a distant ion pair generated after the hole hopping from the contact ion pair, which occur randomly in direction and within the nanosecond region.[3)]

Spin correlated radical ion pair

The multiplet spin polarization in the ion pair can be understood by the polarization mechanism of spin correlated radical pair (SCRP) in which a coherent spin singlet-triplet interconversion takes place within the ion pair (Fig. 2). The coherent interconversion is induced by the difference between the intramolecular interactions of the ion radicals. The SCRP born from the singlet contact ion pair under a magnetic field has the four spin sublevels split by the large Zeeman and the small exchange interactions. Although the $|2\rangle$ and $|3\rangle$ states that are comprised of the singlet and triplet spin levels are populated through the coherent interconversion, the $|1\rangle$ and $|4\rangle$ states are empty due to their non-singlet character. Consequently two absorptive transitions ($|1\rangle \leftarrow |2\rangle$ and $|1\rangle \leftarrow |3\rangle$) and two emissive transitions ($|4\rangle \leftarrow |2\rangle$ and $|4\rangle \leftarrow |3\rangle$) appear in the EPR spectrum of the SCRP. In addition, each resonance line is uniaxially broadened by the dipolar interaction. The simulation on the SCRP mechanism using the constants around $J_{\mathrm{SS}} = -22 \pm 2\,\mathrm{MHz}$ and $D_{\mathrm{SS}} = -140 \pm 20\,\mathrm{MHz}$ reproduced well the observed spectrum of the distant ion pair between PVCz$^+$ and TCNB$^-$ (Fig. 1 (a)). The obtained D_{SS} value of the distant ion pair is reduced to $r_0 = 0.83 \pm 0.04\,\mathrm{nm}$ within a point dipole approximation.

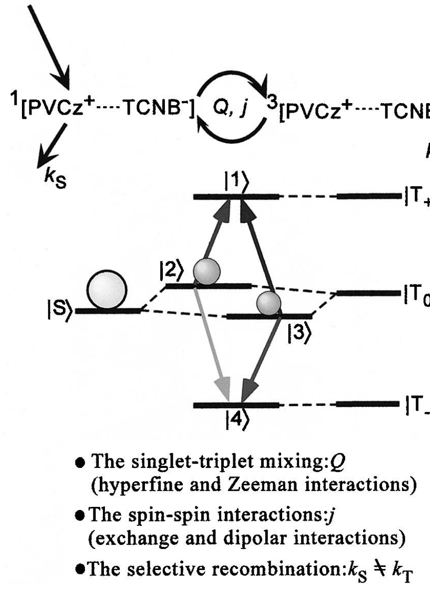


Fig. 2. The energies of spin sublevels and the EPR transitions of the ion pair giving the A/E spin polarization based on a SCRP model. The circles on the sublevels indicate their populations.

The interionic distance is much shorter than the values acquired in the static measurements of the electric field quenching.[1)] The analysis based on the Onsager model,[6)] in which the polymer matrix is regarded as an isotropic dielectric medium and the recombination rapidly takes place within a reaction radius, has been adopted for the electric field quenching experiments. The assumptions of the isotropic continuum and the infinitely fast back electron transfer seem to be not applicable to organic solid system. Taking into account the dichroism memory up to several nanoseconds,[3)] the distant ion pair may be generated by the stepwise hole hopping rather than by an electron jump of *ca.* 0.8–0.9 nm during thermalization of a hot contact ion pair. The decay rate of the distant ion pair seems to be mainly determined by an endothermic activation step in the process back to the contact ion pair rather than by the hole hopping, since the EPR signal decayed without any change in the spectral shape. The slow recombination of the geminate distant ion pair would be related to the trap site structure or low reorganization energy of PVCz$^+$. At present, our studies on the reaction mechanism in amorphous photoconductive organic polymers are in progress by using both the magnetic and electric field effects on the EPR signals and CT-fluorescence.

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