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The Photoconductivity of Poly(*N*-vinylcarbazole). VII.[1] The Effect of the Singlet and Triplet Quenchers on the Photoconductivity

Ken-ichi Okamoto, Norikazu Oda, Akira Itaya, and Shigekazu Kusabayashi

Department of Chemical Engineering, Faculty of Engineering, Yamaguchi University, Ube 755

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Synopsis. The singlet quenchers significantly reduce the photocurrents of poly(*N*-vinylcarbazole) and of brominated poly(*N*-vinylcarbazole), but the triplet quenchers do not do so at all regardless of the high efficiency of the polymer-to-quencher triplet energy transfer. This result excludes the possibility of the photocarrier generation from the triplet excited state in these polymers.

The photocarrier generation process in poly(*N*-vinylcarbazole) (PVCz) films, in the case of the singlet π-π^* excitation, has been widely investigated in the last few years.[2–4] It is considered that photocarriers in PVCz films are generated from the singlet excited states *via* either the intrinsic charge transfer exciton state in the case of the higher π-π^* excitation or the extrinsic exciplex state in the case of the lower π-π^* excitation. The exciplex state is considered to be formed efficiently, even if some electron-accepting impurities have very low concentrations, because of the high efficiency of the singlet exciton migration.[5]

On the other hand, the triplet excitation energy also migrates very efficiently in this polymer.[6–8] Furthermore, the triplet excitation energy of PVCz is fairly high (E_T=3.02 eV; *cf.* the singlet excitation energy, E_S= 3.55 eV) as compared with that of other aromatic vinyl polymers, such as poly(1-vinylnaphthalene) (E_T=2.5 eV, E_S=3.8 eV[9]). Therefore, the photocarrier generation from the triplet excited state in the case of the singlet π-π^* excitation may be possible in PVCz, as has been suggested by Yokoyama *et al.*[7] In order to decide on this possibility, we examined the effect of the triplet and singlet quenchers on the photoconductivity of PVCz and brominated poly(*N*-vinylcarbazole) (BPVCz).

Experimental

PVCz was prepared by free-radical polymerization and brominated by using *N*-bromosuccinimide. The BPVCz thus obtained had one bromine atom per 1.1 carbazolyl groups.[10] The copolymer of *N*-vinylcarbazole (VCz) with 1-vinylnaphthalene (VN) was also prepared by free-radical polymerization. These polymers were purified by repeated reprecipitations. Naphthalene and fluorene were used as the triplet quenchers of the carbazolyl chromophore, while anthracene and perylene were used as singlet and triplet quenchers. The scintillation-grade reagents were used after being purified by repeated recrystallizations, vacuum sublimation, and zone melting. The electrical measurements were made by the DC method in a vacuum of 10^{-5} Torr, as has been described previously.[11]

Results and Discussion

BPVCz has photoconductive properties similar to those of PVCz.[11] The magnitude of the photocurrent in BPVCz is twice as large as that in PVCz in the case of the hole current and is a most the same in the case of the electron current.

In both PVCz and BPVCz, the triplet quencher mixed or copolymerized does not affect the photoconductive properties at all. Anthracene and perylene acting as both singlet and triplet quenchers significantly reduce the photocurrent in magnitude, but do not affect the other photoconductive properties, such as the

Table 1. Comparison of magnitudes of the photocurrent

Material			Number of samples	Magnitudes of the photocurrent[a]			
Polymer	Dopant	mol %		Hole current/10^{-10} A cm^{-2}		Electron current/10^{-11} A cm^{-2}	
				350 nm	330 nm	350 nm	330 nm
PVCz	None	0	7	(4.0±0.2)	(3.7±0.3)	(4.3±0.4)	(3.0±0.2)
	Fluorene	1.5	3	1.1±0.1	1.1±0.1	—	—
	Naphthalene	1.5	3	1.1±0.1	1.2±0.3	1.1±0.3	0.93±0.23
	Naphthalene	5.0	3	0.81±0.08	0.99±0.19	—	—
	Copolymerized	VN[b]	2	1.4±0.1	1.5±0.1	1.5±0.3	1.4±0.2
	Anthracene	3.0	2	0.18±0.07	0.23±0.09	0.09±0.01	0.14±0.01
	Perylene	2.0	3	0.20±0.06	0.22±0.09	0.13±0.05	0.25±0.08
VCz–VN (5 mol %) copolymer		0	2	(5.5±0.2)	(5.6±0.1)	(6.3±0.9)	(4.1±0.4)
	Anthracene	3.0	2	0.29±0.01	0.36±0.01	0.29±0.06	0.40±0.07
BPVCz	None	0	3	(7.2±0.2)	(7.0±0.2)	(3.2±0.2)	(2.6±0.1)
	Naphthalene	5.0	3	0.95±0.06	1.1±0.2	0.77±0.21	0.81±0.06
	Anthracene	3.0	2	0.16±0.03	0.19±0.02	0.37±0.03	0.54±0.06

a) The relative photocurrent values in the doped films taking the photocurrent values in the corresponding undoped films as unity. The values in parentheses are the photocurrent values in the undoped films measured under the condition of 35000 V/cm, 1×10^{13} photons/cm^2 s, 20 °C, and 1×10^{-5} Torr. b) VCz–VN (5 mol % in feed) copolymer.

voltage and the temperature dependences of the photocurrent. Table 1 shows a comparison of the magnitude of the photocurrent among the films undoped and doped with triplet or singlet quenchers. From this table, it is clear that, at the quencher concentrations of 1.5—5 mol%, the singlet quenchers reduce the photocurrent by a factor of about 5, while the triplet quenchers do not do so at all.

In both polymers, the triplet quenchers trap the freely-migrating triplet excitons rather than the trapped ones, resulting in both a significant decrease in the host phosphorescence and the appearance of the sensitized guest phosphorescence.[8] The host phosphorescence is completely replaced by the guest one at guest concentrations above 1 mol%.[8] It is, therefore, clear that the concentration of the freely-migrating triplet exciton in the films doped heavily (more than 1 mol%) with the triplet quenchers is remarkably reduced as compared with that in the undoped films. The situation is the same as for the case of the singlet quencher. Therefore, the present effect of the singlet and triplet quenchers on the photoconductivity excludes the possibility of photocarrier generation from the triplet state in these polymers under ordinary experimental conditions.

It is noted that the photocarrier generation from the singlet excited state is predominant even in BPVCz, which has a low efficiency of the singlet exciton migration because of the very short lifetime of the singlet exciton due to the enhanced intersystem crossing.[12] A similar example has been reported of the photoconductivity in tetracene crystals, where the low efficiency of the singlet exciton migation is attributed to the enhanced singlet fission into two triplet excitons.[13] In tetracene crystals, the photocarrier generation from the triplet excited state is possible only in the presence of a strong electron acceptor like *p*-chloranil.

Under the present experimental conditions, the two photon processes are negligible because of the weak light intensity. In the case of the lower singlet π-π^* excitation, the extrinsic photocarrier generation process with the participation of some electron-accepting impurities must be considered, whether the singlet channel or the triplet one is chosen. From the simple energetic calculation, this process is considered to be endothermic in the case of a weak electron acceptor such as some photoxidation products of carbazolyl chromophores, the most conceivable acceptors. In such an endothermic process, the energy difference between the singlet excitation energy and the triplet one (0.5 eV) seems to be determined in the choice between the singlet channel and the triplet one, although it is much smaller than those of other aromatic vinyl polymers. This is the reason for the lack of the photocarrier generation process from the triplet excited state in these polymers.

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