(11) Wiegel, F. W. *Introduction to Path-Integral Methods in Physics and Polymer Science*; World Scientific: Singapore, 1986.
(12) Milner, S. T.; Wittn, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610.
(13) Brout, R. *Phys. Rev.* **1959**, *115*, 824.
(14) Milner, S. T.; Wang, Z.-G.; Witten, T. A. *Macromolecules* **1989**, *22*, 489.
(15) Viovy, J. L.; Gelbart, W. M.; Ben-Shaul, A. *J. Chem. Phys.* **1987**, *87*, 4114.
(16) The quantity $R_A/Z_A^{1/2}$ in Helfand and Wasserman's paper corresponds to $(2T)^{-1/2}(D_A/N_A^{1/2})$ in our notation.
(17) Witten, T. A.; Leibler, L.; Pincus, P. A., preprint.
(18) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864.
(19) Kohn, W.; Sham, J. *Phys. Rev.* **1965**, *140*, A1133.
(20) Schweizer, K. S.; Curro, J. G. *Macromolecules* **1988**, *21*, 3070, 3082 and the earlier references quoted therein.

Stabilization of Carbazole Radical Cation Formed in Poly(*N*-vinylcarbazole) by Charge Delocalization

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ABSTRACT: The transient absorption spectra (charge-resonance (CR) band) of poly(*N*-vinylcarbazole) (PVCz) and the copolymers of *N*-vinylcarbazole (VCz) with methyl methacrylate and vinyl acetate were measured by laser photolysis to investigate the charge delocalization in the polymers. For the copolymers in which the fraction of VCz (f_{VCz}) is less than 0.4, the CR band appeared at ca. 1800 nm. In the case of $f_{VCz} > 0.5$, the CR band was shifted to longer wavelengths with increasing f_{VCz} and the copolymer with $f_{VCz} = 0.83$ showed the same transient absorption spectrum as PVCz. By considering the sequential distribution of the copolymers, the charge formed in PVCz was found to be delocalized among more than two chromophores. For the copolymer ($f_{VCz} = 0.07$) having no neighboring chromophore interaction, the radical-cation transfer to a series of amines was measured to investigate the free energy change (ΔG) dependence of an electron-transfer rate constant (k_e). The result shows that there is a linear relationship between log k_e and ΔG. By using this relationship, the stabilization energy of the carbazole radical cation in PVCz was estimated to be 0.5 ± 0.1 eV. This value is larger than that of the carbazole dimer radical cation, i.e., the stabilization by the charge delocalization among more than two chromophores is stronger than that of the dimer radical cation.

Introduction

The stabilization of a radical cation by the interaction with neutral chromophores is one of the most important properties in an electron-transfer reaction of a polymer having a pendant chromophore,[1-5] and the electronic properties of the dimer radical cation have been investigated for intramolecular systems[6-9] and for intermolecular systems[10-15] by ESR, γ-ray-irradiated rigid matrix method, pulse radiolysis, and laser photolysis.

Masuhara et al. showed that the dimeric model compounds, *meso*- and *rac*-2,4-di-*N*-carbazolylpentane (*meso*-and *rac*-DCzPe), form the sandwich dimer radical cation having the fully overlapped conformation of carbazole chromophore and the second dimer radical cation having the partially overlapped one, respectively.[7] Furthermore, they measured the transient absorption spectrum of a carbazole (Cz) radical cation in poly(*N*-vinylcarbazole) (PVCz) in a visible region and concluded that the measured spectrum for PVCz is a superposition of absorption bands of three kinds of dimer radical cations by the comparison with the absorption spectra for dimeric model compounds.[16]

We have studied the stability of the Cz radical cation of PVCz and its dimeric model compounds in a solution by the radical-cation-transfer method[2,17] and by the charge-resonance band measurement[3,8] to understand the neighboring chromophore interaction on a radical cation. Consequently, we found that the stabilization energy is ca. 0.3 eV for the sandwich dimer radical cation and ca. 0.1 eV for the second dimer radical cation by the radical-cation-transfer method[2] and reported that a Cz radical cation formed in PVCz is more stabilized than the dimer radical cations.[1,2]

In the present study, we measured transient absorption spectra (charge-resonance band) of a Cz radical cation formed in PVCz and the copolymers of *N*-vinylcarbazole (VCz) with methyl methacrylate (MMA) and vinyl acetate (VAc) by laser photolysis. In the copolymers, the neighboring chromophore interaction of $Cz^{\bullet+}$ is interrupted by the inert comonomer, MMA, and VAc. The relation between the charge-resonance (CR) band and the fraction of VCz in the copolymer shows that the Cz radical cation in PVCz is stabilized by the charge delocalization among more than two chromophores. By the radical-cation-transfer method, the stabilization energy of the Cz radical cation in PVCz was estimated to be 0.5 ± 0.1 eV.

Experimental Section

A. Materials. 1. Electron Donors (D_1). *N*-Vinylcarbazole (VCz; Tokyo Kasei Kogyo Co.) was recrystallized from methanol and hexane several times. Poly(*N*-vinylcarbazole) (PVCz) was prepared by a radical polymerization initiated by AIBN in degassed benzene at 60 °C. The molecular weight ($\bar{M}_w$) was determined to be 8 × 10^5 by GPC (Toyo Soda HLC 802 UR)

Table I
Monomer Feed Ratio (F), $\bar{M}_w$, the Fraction of VCz (f_{VCz}), and Sequential Distributions of VCz (F_1, F_2, F_3; See the Text) for the Copolymers of VCz with MMA (A Series) and of VCz with VAc (B Series)

copolymer	F^a	$\bar{M}_w/10^5$	f_{VCz}	F_1	F_2	F_3
A1	0.18	1.3	0.07	0.93	0.06	0.01
A2	0.69	1.6	0.22	0.77	0.19	0.04
A3	1.6	3.0	0.37	0.58	0.28	0.14
B1	0.11	0.45	0.38	0.59	0.27	0.14
B2	0.25	0.56	0.62	0.36	0.29	0.35
B3	0.67	1.2	0.79	0.13	0.17	0.70
B4	1.5	2.4	0.83	0.04	0.06	0.90

[a] F = [VCz]/[comonomer].

with G4000H and GMH columns. Methyl methacrylate (MMA; Wako Pure Chem. Ind., Ltd.) was washed with aqueous Na_2SO_3, aqueous NaOH, and aqueous NaCl and then dried on Na_2SO_4 and finally distilled under reduced pressure. Vinyl acetate (VAc; Wako Pure Chem. Ind., Ltd.) was purified by distillation. The copolymers of VCz with MMA and of VCz with VAc were obtained by a radical copolymerization initiated by AIBN in degassed benzene at 60 °C and were purified by precipitation three times.[18,19] The conversion of the copolymerization was suppressed to below 30 mol %. The molecular weight ($\bar{M}_w$) was measured by GPC, and the fraction (f_{VCz}) of the VCz unit in the copolymer was determined by UV absorption spectra in dichloromethane with a Shimadzu UV-200S spectrophotometer. Three samples of the copolymer of VCz with MMA and four samples of the copolymer of VCz with VAc were prepared. These copolymers were designated as A1, A2, and A3 for the former and B1, B2, B3, and B4 for the latter in the order of increasing f_{VCz}. The molecular weight ($\bar{M}_w$) and the fraction (f_{VCz}) are summarized in Table I with the sequential distribution (F_1, F_2, F_3) calculated from the monomer reactivity ratios, r_1 and r_2, according to the terminal model.[20] F_1 is the fraction of isolated VCz. F_2 is the probability that a VCz unit is found in a diad sequence of VCz. F_3 is the probability that a VCz unit is found in the sequence whose sequential length is more than two. *N*-Ethylcarbazole (EtCz) was synthesized by the reaction of sodium carbazole with ethyl bromide and purified by recrystallization.

2. Electron Acceptor (A). 1,4-Dicyanobenzene (DCNB; Wako Pure Chem. Ind., Ltd.) was purified by recrystallization from ethanol three times.

3. Radical-Cation Acceptors (D_2). *N,N,N′,N′*-Tetramethyl-1,4-phenylenediamine (TMPD; Tokyo Kasei Kogyo Co.), 2,5-dimethoxyaniline (DMOA; Wako Pure Chem. Ind., Ltd.), diphenylamine (DPA; Tokyo Kasei Kogyo Co.), triphenylamine (TPA; Tokyo Kasei Kogyo Co.), and 1,2-dimethylindole (DMI; Wako Pure Chem. Ind., Ltd.) were purified by recrystallization. *N,N*-Dimethyl-1,4-toluidine (DMT; Wako Pure Chem. Ind., Ltd.) and *N,N*-dimethylaniline (DMA; Wako Pure Chem. Ind., Ltd.) were purified by distillation under reduced pressure.

4. Solvents. Spectroscopic grades of *N,N*-dimethylformamide (DMF; Dotite Spectrosol) and dichloromethane (Dotite Spectrosol) were used without further purification. Acetonitrile (MeCN; Wako Pure Chem. Ind., Ltd.) was fractionally distilled after reflux over P_2O_5.

B. Measurements of Transient Absorption Spectra. The electron-donating chromophore, carbazole (Cz), was selectively photoexcited in the presence of an electron acceptor, DCNB, and the transient absorption spectrum of the carbazole radical cation ($Cz^{\bullet+}$) was measured by laser photolysis. The photoexcitation was made by a 308-nm laser pulse of a XeCl excimer laser (Lambda Physik EMG101MSC; pulse energy ca. 100 mJ; fwhm ca. 17 ns). The pulse intensity was attenuated properly by filters. As the monitoring system for the measurements of transient absorption spectra, a photovoltaic indium arsenide (InAs) diode detector (Hamamatsu P838) was used, and this detection system has a rise time of ca. 500 ns.[8,21] For the measurements of transient absorption spectra, the absorbance of the Cz chromophore at 308 nm was adjusted to be ca. 1.8, and DCNB (8.0×10^{-2} M) was added to the system. The measurements were carried out in a 1-cm quartz cell in DMF solvent at 298 K. The samples were degassed by the freeze–pump–thaw method.

C. Radical-Cation-Transfer Measurements.[2,17] The photoinduced electron transfer from an electron donor (D_1) to an electron acceptor (A) produces a radical cation, $D_1^{\bullet+}$ and a radical anion, $A^{\bullet-}$. When the second electron donor (D_2, radical-cation acceptor) having a lower oxidation potential than D_1 is added to this D_1–A system, a radical-cation transfer from $D_1^{\bullet+}$ to D_2 (electron transfer from D_2 to $D_1^{\bullet+}$) occurs and a radical cation, $D_2^{\bullet+}$, is produced. This process competes with the recombination of $D_1^{\bullet+}$ with $A^{\bullet-}$. That is, $D_1^{\bullet+}$ decays through two competitive processes, the radical-cation transfer and the recombination. As for the decay rate of $D_1^{\bullet+}$, the following rate equation is derived

$$d[D_1^{\bullet+}]/dt = -k_{tr}[D_1^{\bullet+}][D_2] - k_r[D_1^{\bullet+}][A^{\bullet-}] \qquad (1)$$

where k_{tr} is the rate constant of the radical-cation transfer to D_2 and k_r is the rate constant of the recombination with $A^{\bullet-}$.

We can make the rate of the radical-cation transfer much faster than that of the recombination by adjusting the concentration of D_2. Thus, if $k_{tr}[D_1^{\bullet+}][D_2] \gg k_r[D_1^{\bullet+}][A^{\bullet-}]$, eq 1 gives the equation

$$\ln [A(D_1^{\bullet+})] = -k_{tr}[D_2]t + C \qquad (2)$$

where $A(D_1^{\bullet+})$ is the absorbance of $D_1^{\bullet+}$ measured by laser photolysis and C is a constant. Then, k_{tr} can be determined by the slope of the $\ln [A(D_1^{\bullet+})]$ vs time plot.

In this study, we measured the radical-cation transfer to amine compounds (D_2) from $EtCz^{\bullet+}$ and $Cz^{\bullet+}$ in the copolymer A1 and in PVCz. For the radical-cation-transfer measurements, the detection system equipped with a photomultiplier tube (Hamamatsu R928) was used since it has a fast response time of ca. 5 ns.[8] To avoid excitation of D_2, the Cz chromophore was photoexcited by an attenuated 351-nm laser pulse of XeF excimer laser (pulse energy ca. 60 mJ; fwhm ca. 17 ns). For the radical-cation-transfer measurements, the absorbance of Cz the chromophore at 351 nm was adjusted to ca. 0.7 for the A1 system and ca. 1 for the EtCz and PVCz systems. D_2 was added to the EtCz and A1 systems in the following concentration: [TMPD] = 2.0×10^{-4} M, [DMOA] = 6.0×10^{-4} M, [DMT] = 7.0×10^{-4} M, [DMA] = 7.0×10^{-4} M, [DPA] = 7.0×10^{-4} M, [TPA] = 7.0×10^{-4} M, and [DMI] = 1.0×10^{-3} M. The concentration of D_2 (DMOA, DMA, and DPA) in the PVCz system was adjusted to 1.0×10^{-2} M. The samples contain 6.4×10^{-2} M DCNB as the electron acceptor. The measurements were made in degassed DMF solvent at 298 K.

D. Electrochemical Measurements. The oxidation potentials of EtCz and D_2 were measured by cyclic voltammetry using Ag/0.01 N Ag^+ in MeCN as a reference electrode. The potentials were converted to the ones relative to SCE ($E_{1/2}$): $E_{1/2}$ = 1.18 V for EtCz, 1.06 V for DMI, 0.99 V for TPA, 0.95 V for DPA, 0.77 V for DMA, 0.72 V for DMT, 0.64 V for DMOA, and 0.14 V for TMPD.

Results and Discussion

A. Charge Delocalization of Radical Cation in PVCz.

Figure 1 shows the transient absorption spectrum of the PVCz–DCNB system at 2 μs after excitation. The absorption band observed at ca. 430 nm was assigned to the radical anion, $DCNB^{\bullet-}$. The Cz radical cation gives two absorption bands; one is the visible band at ca. 750 nm,[22,23] which is very broad compared with that of the monomer radical cation, $EtCz^{\bullet+}$, and the other is the CR band at a wavelength longer than 1900 nm. This CR band is shifted to longer wavelengths than that of the dimer radical cation; the sandwich dimer radical cation for *meso*-DCzPe and the second dimer radical cation for *rac*-DCzPe show the CR bands at ca. 1600 nm and at ca. 1800 nm, respectively.[8] The CR band is a characteristic absorption band induced by a charge delocalization among chromophores and is considered a measure of neighboring chromophore interaction.[13a,24,25] According to the Hückel MO theory, the CR band of the dimer radical cation is shifted to shorter wavelengths with the increasing

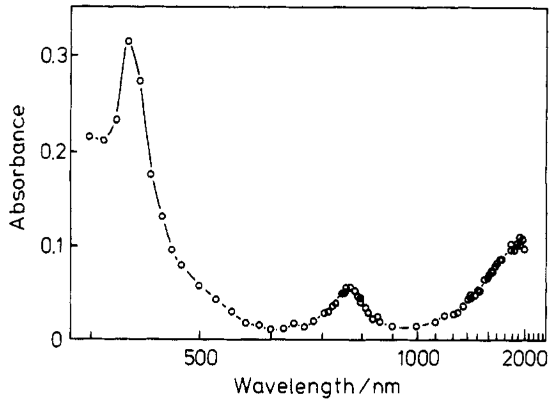

Figure 1. Transient absorption spectrum of the PVCz-DCNB (8.0×10^{-2} M) system in DMF at 298 K at 2 μs after excitation. The concentration of carbazole chromophore was adjusted to be 3.0×10^{-3} M.

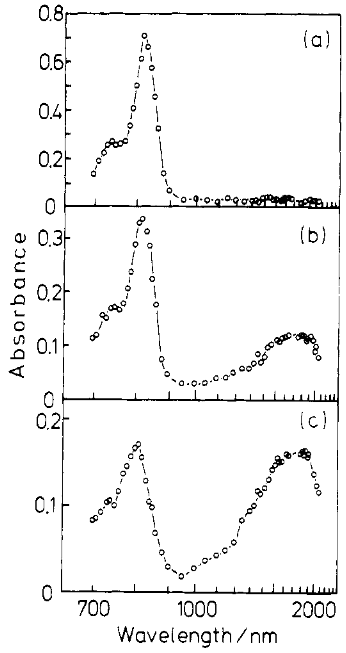

Figure 2. Transient absorption spectra of a carbazole radical cation for the copolymers of VCz with MMA in DMF at 298 K at 2 μs after excitation: (a) A1; (b) A2; (c) A3. The absorbance of carbazole chromophore at 308 nm was adjusted to ca. 1.8. All the samples contain 8.0×10^{-2} M DCNB.

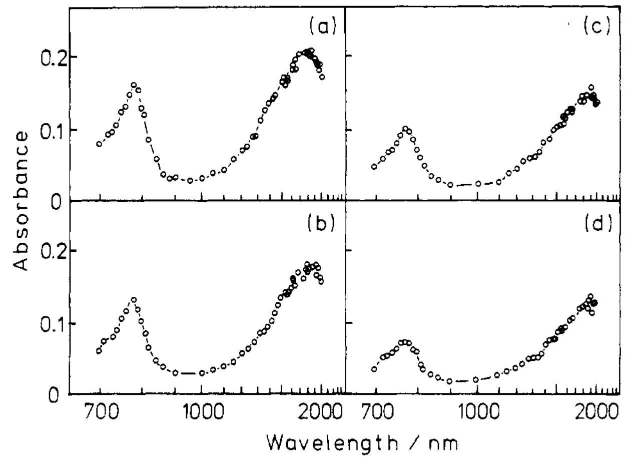

Figure 3. Transient absorption spectra of a carbazole radical cation for the copolymers of VCz with VAc in DMF at 298 K at 2 μs after excitation: (a) B1; (b) B2; (c) B3; (d) B4. The absorbance of carbazole chromophore at 308 nm was adjusted to ca. 1.8. All the samples contain 8.0×10^{-2} M DCNB.

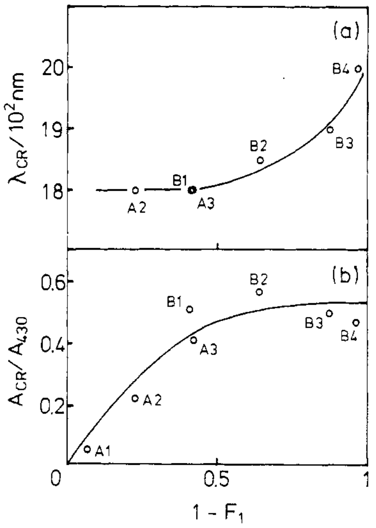

Figure 4. Peak wavelength of the CR band (λ_{CR}) and its relative absorbance to that at 430 nm (A_{CR}/A_{430}) plotted against $1 - F_1$.

interaction, in other words, the increasing stability of the dimer radical cation. Furthermore, the CR band of a radical cation should be shifted to longer wavelengths with increasing charge delocalization such as dimer, trimer, and tetramer.[14,26]

We measured the transient absorption spectra for the copolymers to investigate the neighboring chromophore interaction on the radical cation. Figures 2 and 3 show the transient absorption spectra of $Cz^{\bullet+}$ in the copolymers of VCz with MMA (A1-A3) and of VCz with VAc (B1-B4) at 2 μs after excitation, respectively. As shown in Figure 2a, $Cz^{\bullet+}$ of A1 gave only the visible band at ca. 820 nm, which was similar in shape to that of the monomer radical cation, $EtCz^{\bullet+}$, and the CR band in the near-infrared region was not observed. This means that A1 forms only the monomer radical cation and that the neighboring chromophore interaction is interrupted by the inert comonomer, MMA. This is expected by the fact that the fraction (F_1) of isolated VCz in the comonomer, MMA, is 0.93. This suggests that there is almost no interaction of $Cz^{\bullet+}$ with remote Cz chromophores in a polymer chain. The other copolymers showed the CR band in the near-infrared region along with the visible band. In Figure 4, the peak wavelength (λ_{CR}) of the CR band and the ratio of the absorbance of the CR band to that of the anion radical, $DCNB^{\bullet-}$ (430 nm) (A_{CR}/A_{430}), were plotted against the probability of the Cz chromophore not to be isolated, $1 - F_1$. For the copolymer with $1 - F_1 < 0.4$, the CR bands appear at ca. 1800 nm and the relative absorbance of the CR band increases with increasing $1 - F_1$. Since the probability (F_3) that $Cz^{\bullet+}$ is formed in the sequence having more than two VCz units is very small in the region $1 - F_1 < 0.4$, the CR band is due to the dimer radical cation formed in the diad sequence of VCz. With the increase of $1 - F_1$, the fraction of $Cz^{\bullet+}$ formed in the diad sequence to the monomer radical cation increases and the absorption intensity of the CR band is enhanced. For the copolymer with $1 - F_1 > 0.5$, the CR band is shifted to longer wavelengths with the increase of $1 - F_1$. Absorption of the solvent prevents measurement of a transient absorption spectrum in the wavelength region longer than 2100 nm. Therefore, we roughly evaluated the shape and the half-width of the CR band. The CR band seems to become broader with longer wavelength shifts. At least, the CR bands for B4 and PVCz are obviously broader than those for A2 and A3, which are considered to form mainly the dimer radical cation. The longer wavelength shift and broadening of the CR band for PVCz are not due to a

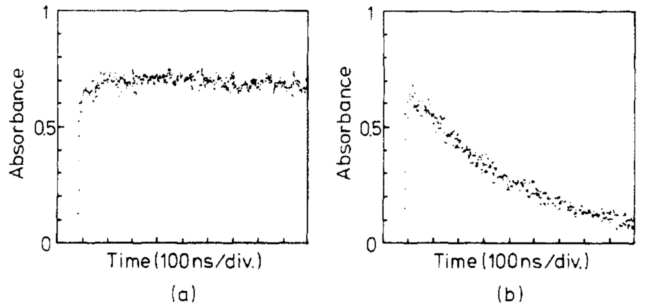

Figure 5. Transient absorption decays at 790 nm of an EtCz radical cation in DMF at 298 K in the presence of DCNB (6.4 × 10^{-2} M): (a) without DPA; (b) with DPA (7.0 × 10^{-4} M).

Table II
Free Energy Change (ΔG) and Rate Constants (k_{tr}, k_e) of Radical-Cation Transfer to D_2 for EtCz and A1 Systems

		EtCz		A1	
D_2	$-\Delta G$/eV	$k_{tr}/10^9$ M^{-1} s^{-1}	$k_e/10^9$ M^{-1} s^{-1}	$k_{tr}/10^9$ M^{-1} s^{-1}	$k_e/10^9$ M^{-1} s^{-1}
TMPD	1.04	6.25		3.07	
DMOA	0.54	5.02	25	2.42	11
DMT	0.46	4.86	21	2.66	
DMA	0.41	4.35	14	2.30	9.17
DPA	0.23	3.22	6.64	1.55	3.13
TPA	0.19	2.92	5.48	1.44	2.71
DMI	0.12	2.73	4.85	1.39	2.54

perturbed dimer radical cation but to increasing contribution of Cz radical cation delocalized among more than two chromophores. In fact, the shift of the CR band begins at $1 - F_1 = 0.5$, where the fraction of $Cz^{\bullet+}$ formed in the VCz sequence having more than two units is larger than that of $Cz^{\bullet+}$ formed in the diad sequence. Furthermore, B4 with $F_3 = 0.9$ gave the same transient absorption spectrum as PVCz (Figure 3d). Thus, the shift and broadening of the CR band correspond to the increase of F_3. This suggests that the Cz radical cation in the polymer, PVCz, is stabilized by the charge delocalization among more than two chromophores.

B. Stabilization Energy of Radical Cation in PVCz. At first we investigated the free energy change (ΔG) dependence of the rate constant (k_{tr}) of the radical-cation-transfer reaction. We measured the radical-cation transfer to amine compounds D_2 (TMPD, DMOA, DMT, DMA, DPA, TPA, and DMI) for EtCz and the copolymer A1. The free energy change (ΔG) in eq 3 was estimated by the

$$\Delta G = E_{1/2}(D_2) - E_{1/2}(\text{EtCz}) \qquad (3)$$

difference between the oxidation potential of EtCz and that of D_2. Since $Cz^{\bullet+}$ in A1 is not stabilized by neighboring chromophore interaction, the oxidation potential of Cz in A1 is assumed to be equal to that of EtCz. The decay curves of $Cz^{\bullet+}$ were measured at 790 nm for EtCz and at 820 nm for A1. As an example, the decay curve of $EtCz^{\bullet+}$ for the EtCz–DPA–DCNB system is shown in Figure 5. In the absence of DPA, $EtCz^{\bullet+}$ recombines with $DCNB^{\bullet-}$ but the absorption scarcely decays in this time region (Figure 5a). The addition of DPA accelerated the decay of $EtCz^{\bullet+}$ by the radical-cation transfer to DPA (Figure 5b). That is, the rate of the radical-cation transfer is much faster than that of the recombination: $k_{tr}[D_1^{\bullet+}][D_2] \gg k_r[D_1^{\bullet+}][A^{\bullet-}]$. Then, the plot of ln A against t (eq 2) gives a slope of $k_{tr}[D_2]$, and k_{tr} is determined. Figure 5b gives $k_{tr} = 3.22 \times 10^9$ M^{-1} s^{-1}. For the other systems, k_{tr} was determined in the same way by addition of a proper concentration of D_2. Table II shows the results. The second and the fourth columns are k_{tr}'s for EtCz and for A1, respectively. In each system, k_{tr} for A1 is smaller than that for EtCz. However, these values cannot be simply compared with each other, since the radical-cation transfer in this intermolecular system contains the diffusion process and the electron-transfer process. For the radical-cation transfer to occur, first of all, $Cz^{\bullet+}$ and D_2 must be brought close together. Therefore, the radical-cation-transfer reaction can be considered to be a consecutive reaction in which the electron-transfer process follows the diffusion process. In the radical-cation-transfer systems studied in this experiment, the electron-transfer process is a rate-limiting step except for the case of TMPD. Then, the rate constant of the radical-cation transfer is given by the equation[27]

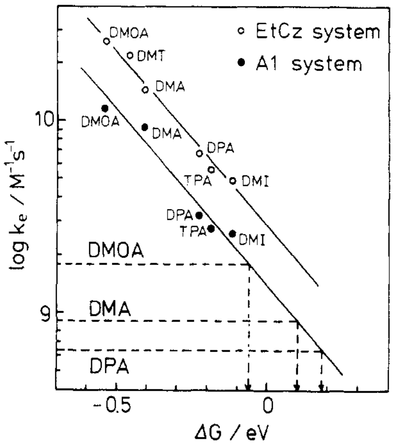

Figure 6. Relationship between k_e and ΔG in the radical-cation transfer to D_2 for EtCz and A1 systems. Open and closed circles indicate EtCz and A1 systems, respectively. D_2 is shown by the abbreviation in the figure. For PVCz, ΔG of the radical-cation transfer to DMOA, DMA, and DPA was estimated from k_e as shown by the dashed lines.

$$k_{tr}^{-1} = k_d^{-1} + k_e^{-1} \qquad (4)$$

where k_d and k_e are rate constants of the diffusion and the electron-transfer processes, respectively. It is considered that the radical-cation transfer to TMPD is exothermic ($\Delta G = -1.04$ eV) enough to be diffusion-controlled. Therefore, the rate constant of the radical-cation transfer to TMPD was taken as k_d: $k_d = 6.25 \times 10^9$ M^{-1} s^{-1} for EtCz systems and $k_d = 3.07 \times 10^9$ M^{-1} s^{-1} for A1 systems. This is supported by the fact that the Einstein–Smoluchowski equation, $k_d = 8RT/3000\eta$, gives 6.50 × 10^9 M^{-1} s^{-1}, where η is the viscosity of a solvent, DMF. The diffusion-rate constant, k_d, for A1 is almost half of that for EtCz. This is justified by the fact that the diffusion of the copolymer, A1, is negligibly small compared with that of the low molecular weight compound. The rate constants, k_e, for EtCz and for A1 are listed in the third and the fifth columns in Table II, respectively. In Figure 6, k_e's for EtCz and for A1 are plotted against ΔG. Each system gave a linear relationship between the logarithm of k_e and ΔG. The linear relationship between the logarithm of the rate constant k_e and ΔG was also observed for the electron-transfer quenching of an excited state of aromatic molecules by anion.[28] The relation was discussed by the Polanyi equation.[29] In the present study, the following experimental equations were obtained:

$$\log k_e = -1.83\Delta G + 9.44 \quad \text{for EtCz system} \qquad (5)$$

$$\log k_e = -1.83\Delta G + 9.14 \quad \text{for A1 system} \qquad (6)$$

Each system has a similar slope in the semilogarithmic plot of k_e as a function of ΔG, but the intercept for A1 is smaller than that for EtCz; that is, k_e for A1 is nearly equal to half

Table III
Apparent Transfer Rate Constant (k_{tr}), Electron-Transfer Rate Constant (k_e), Free Energy Change (ΔG), and Stabilization Energy ($-\Delta H$) for the PVCz System

D_2	$k_{tr}/10^8$ M^{-1} s^{-1}	$k_e/10^8$ M^{-1} s^{-1}	ΔG/eV	$-\Delta H$/eV
DMOA	11.3	17.9	−0.06	0.48
DMA	6.98	9.03	0.10	0.51
DPA	5.28	6.38	0.19	0.42

the value of that for EtCz. As described previously, the chromophore interaction in A1 is interrupted by the inert comonomer and $Cz^{\bullet+}$ in A1 is not stabilized. Therefore, a smaller value of k_e for A1 is considered to be due to the steric hindrance of the polymer chain to the access of D_2; that is, the polymer chain sterically restricts the direction for D_2 to approach $Cz^{\bullet+}$ in the polymer chain, or electron transfer in the polymer system may occur at a longer distance due to the steric hindrance of polymer chain.

As for the Cz radical cation formed in PVCz, the radical-cation transfer to DMOA, DMA, and DPA was measured. The concentration of DMOA, DMA, and DPA was 1.0×10^{-2} M. The rate constant, k_{tr}, was determined by the slope of the semilogarithmic plot of the transient absorption decay of Cz radical cation at 750 nm according to eq 2. Table III shows the results. The rate constant, k_e, was evaluated by eq 4 assuming that k_d is 3.07×10^9 M^{-1} s^{-1}. In the radical-cation transfer from Cz radical cation in PVCz to amines, not only the stabilization by charge delocalization but also polymer effects such as a steric hindrance of a main chain may affect the transfer rate constant. In fact, k_e for A1 having no neighboring chromophore interaction was smaller than that for EtCz. Therefore, by using the linear relationship between log k_e and ΔG for A1, we can determine the increment of ΔG by the stabilization through charge delocalization of Cz radical cation in PVCz. In practice, the ΔG of the radical-cation transfer from Cz radical cation in PVCz to the radical-cation acceptor was estimated from k_e as shown by the dashed line in Figure 6. ΔG's for DMOA, DMA, and DPA are −0.06, 0.10, and 0.19 eV, respectively. In the radical-cation transfer to DMOA, DMA, and DPA, the ΔG for PVCz is larger than that for A1 (−0.54 eV for DMOA, −0.41 eV for DMA, and −0.23 eV for DPA). This is due to the stabilization of Cz radical cation in PVCz by the neighboring chromophore interaction, and the difference between ΔG's estimated for PVCz and for A1 corresponds to the stabilization energy ($-\Delta H$) as discussed in the previous paper.[2] The evaluated stabilization energies ($-\Delta H$) are listed in Table III: ca. 0.48 eV with DMOA, ca. 0.51 eV with DMA, and ca. 0.42 eV with DPA. In this way, the stabilization energy of Cz radical cation in PVCz was estimated to be 0.5 ± 0.1 eV on the average. In this method, the effect of the steric hindrance of the polymer chain is excluded by using the relationship between k_e and ΔG for the copolymer A1 as described above, and this value is the net stabilization energy by the neighboring chromophore interaction. The stabilization energy of Cz radical cation in PVCz is larger than that of the dimer radical cations (ca. 0.1 eV for the second dimer radical cation of *rac*-DCzPe and ca. 0.3 eV for the sandwich dimer radical cation of *meso*-DCzPe).[2] This is consistent with the result of the CR band for the copolymer systems. We found that the Cz radical cation in the polymer is delocalized among more than two neighboring chromophores and that it is more stable than the dimer radical cation.

Conclusion

By investigating the relationship between the CR band of the copolymers of VCz and the sequential distribution of Cz chromophore, we found that the Cz radical cation formed in PVCz is stabilized by charge delocalization among more than two neighboring chromophores. The CR band of the Cz radical cation in PVCz was shifted to longer wavelengths than that of the dimer radical cations. This result is qualitatively consistent with the theoretical MO prediction. The stabilization energy by the charge delocalization was estimated to be 0.5 ± 0.1 eV for PVCz by the radical-cation-transfer method. This stabilization energy is larger than that of the dimer radical cation (ca. 0.1 eV for the second dimer radical cation and ca. 0.3 eV for the sandwich dimer radical cation). This means that the stability of the Cz radical cation increases with the charge delocalization such as a trimer radical cation.

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References and Notes

(1) Washio, M.; Tagawa, S.; Tabata, Y. *Polm. J.* **1981**, *13*, 935.
(2) Tsujii, Y.; Tsuchida, A.; Yamamoto, M.; Nishijima, Y. *Macromolecules* **1988**, *21*, 665.
(3) Tsujii, Y.; Takami, K.; Tsuchida, A.; Ito, S.; Yamamoto, M. *Polym. J.* **1990**, *22*, 319.
(4) (a) Irie, S.; Horii, H.; Irie, M. *Macromolecules* **1980**, *13*, 1355. (b) Irie, S.; Irie, M. *Ibid.* **1986**, *19*, 2182.
(5) Tsujii, Y.; Tsuchida, A.; Ito, S.; Yamamoto, M., submitted for publication in *J. Phys. Chem.*
(6) Yoshimi, H.; Kuwata, K. *Mol. Phys.* **1972**, *23*, 297.
(7) Masuhara, H.; Tamai, N.; Mataga, N.; De Schryver, F. C.; Vandendriessche, J. *J. Am. Chem. Soc.* **1983**, *105*, 7256.
(8) Yamamoto, M.; Tsujii, Y.; Tsuchida, A. *Chem. Phys. Lett.* **1989**, *154*, 559.
(9) Tsuchida, A.; Tsujii, Y.; Ito, S.; Yamamoto, M.; Wada, Y. *J. Phys. Chem.* **1989**, *93*, 1244.
(10) Lewis, I. C.; Singer, L. S. *J. Chem. Phys.* **1965**, *43*, 2712.
(11) Chiang, T. C.; Reddoch, A. H. *J. Chem. Phys.* **1970**, *52*, 1371.
(12) Bühler, R. E.; Funk, W. *J. Phys. Chem.* **1975**, *79*, 2098.
(13) (a) Badger, B.; Brocklehurst, B.; Russell, R. D. *Chem. Phys. Lett.* **1967**, *1*, 122. (b) Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1969**, *65*, 2576. (c) Badger, B.; Brocklehurst, B. *Ibid.* **1969**, *65*, 2582. (d) Badger, B.; Brocklehurst, B. *Ibid.* **1969**, *65*, 2588.
(14) (a) Kira, A.; Arai, S.; Imamura, M. *J. Chem. Phys.* **1971**, *54*, 4890. (b) Kira, A.; Arai, S.; Imamura, M. *J. Phys. Chem.* **1972**, *76*, 1119. (c) Kira, A.; Imamura, M. *Ibid.* **1979**, *83*, 2267.
(15) Grover, J. R.; Walters, E. A.; Hui, E. T. *J. Phys. Chem.* **1987**, *91*, 3233.
(16) (a) Masuhara, H.; Yamamoto, K.; Tamai, N.; Inoue, K.; Mataga, N. *J. Phys. Chem.* **1984**, *88*, 3971. (b) Masuhara, H. *Makromol. Chem., Suppl.* **1985**, *13*, 75.
(17) Tsuchida, A.; Yamamoto, M.; Nishijima, Y. *J. Phys. Chem.* **1984**, *88*, 5062.
(18) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*; Wiley-Interscience: New York, 1974.
(19) Alfrey, T., Jr.; Kapur, S. L. *J. Polym. Sci.* **1949**, *4*, 215.
(20) Ham, G. E. In Copolymerization. *High Polymers*; Ham, G. E., Ed.; Wiley-Interscience: New York, 1964; Vol. XVIII, Chapter 1.
(21) Dorfman, L. M. In *Investigation of Rates and Mechanisms of Reactions*; Hammes, G. G., Ed.; Wiley-Interscience: New York, 1974; Chapter 11.
(22) (a) Lachish, U.; Williams, D. J.; Anderson, R. W. *Chem. Phys. Lett.* **1979**, *65*, 574. (b) Lachish, U.; Anderson, R. W.; Williams, D. J. *Macromolecules* **1980**, *13*, 1143.
(23) Masuhara, H.; Ohwada, S.; Mataga, N.; Itaya, A.; Okamoto, K.; Kusabayashi, S. *J. Phys. Chem.* **1980**, *84*, 2363.
(24) Ishitani, A.; Nagakura, S. *Mol. Phys.* **1967**, *12*, 1.
(25) Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1970**, *66*, 2939.
(26) Badger, B.; Brocklehurst, B. *Nature* **1968**, *219*, 263.
(27) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 3477.
(28) (a) Shizuka, H.; Nakamura, M.; Morita, T. *J. Phys. Chem.* **1980**, *84*, 989. (b) Shizuka, H.; Obuchi, H. *J. Phys. Chem.* **1982**, *86*, 1297.
(29) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1938**, *34*, 11.