Hole Resonance among More Than Two Carbazole Chromophores in Poly(*N*-vinylcarbazole)

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ABSTRACT: Hole resonance among more than two chromophores for the radical cationic carbazole (CZ) group of poly(*N*-vinylcarbazole) (PVCZ) in solution was shown by the radical ion transfer method and charge resonance (CR) band measurements. The sample was PVCZ with its oligomers (degree of polymerization (DP) = 2–100). The hole transfer rate from the radical cationic CZ of the oligomers to a 2,5-dimethoxyaniline, which has a lower ionization potential than the CZ chromophore, decreased with an increase in the oligomer molecular weight due to the hole resonance among neighboring chromophores. Thus, the stabilization energy of *N*-vinylcarbazole oligomers increases with increase in DP. The peak position of the CR band can be a good measure of the degree of charge resonance. The peak wavelength of the CR band was red-shifted for the larger molecular weight oligomers. This shift also suggested the existence of charge resonance in PVCZ among more than two CZ chromophores.

Introduction

The charge resonance among two aromatic chromophores for a dimer radical ion was reported by Lewis and Singer.[1] This dimer radical ion has a charge resonance (CR) band in the near-IR region.[2] The peak position of this CR band has been used as a good measure of the stabilization energy of the dimer.[3–8] In spite of extensive studies on the dimer radical ions, radical ions composed of more than two chromophores, such as trimers and tetramers, have been rarely studied. Kira and Imamura studied the dimer radical cation formation of aromatic hydrocarbons by warming the γ-irradiated glassy solutions and suggested the possibility of the trimer radical cation formation.[8] The CR band of the trimer radical cation was shifted to a lower energy due to the hole delocalization among three chromophores.

We have studied the properties of radical ions formed in polymer systems.[3,9–12] In the course of these studies, the radical cationic carbazole (CZ) group of poly(*N*-vinylcarbazole) (PVCZ) was found to be stabilized by the charge resonance among more than two neighboring chromophores. This multichromophore interaction has been proved by measurements of radical ion transfer[9] and the CR band.[10]

In this article, we will show the hole resonance among more than two CZ chromophores for the oligomers of *N*-vinylcarbazole (VCZ) obtained by a living cationic polymerization. Aromatic vinyl polymer is one of the best systems to show the existence of the charge resonance among more than two chromophores because the successive aromatic groups are connected close together by the methylene main chain. The measurements of radical cation transfer rates and the CR band positions will indicate the hole resonance among several CZ chromophores.

Experimental Section

Materials. VCZ (Nacalai Tesque, Inc.) was purified by recrystallization twice from hexane and twice from methanol and subsequently dried in vacuo. 1,4-Dicyanobenzene (DCNB; Tokyo Kasei Kogyo, Co., Ltd.), as an electron acceptor, was purified by recrystallization from ethanol three times. *N,N,N',N'*-Tetramethyl-1,4-phenylenediamine (TMPD; Aldrich Chemical Co., Inc.) and 2,5-dimethoxyaniline (DMOA; Wako Pure Chem. Ind., Ltd.), as radical cation acceptors for the radical ion transfer measurements, were purified by recrystallization three times from petroleum ether and hexane, respectively. *N,N*-Dimethylformamide (DMF; Dotite Spectrosol) and *N,N*-dimethylformamide-d_7 (DMF-d_7; Wako Pure Chem. Ind., Ltd.), for the spectroscopic measurements, were used without further purification. Dichloromethane and toluene, for oligomerization solvents, were dried by CaH_2 and purified by distillation just before use.

VCZ oligomer samples were prepared by the living cationic oligomerization, whose procedure has already been published in detail.[13,14] The oligomerization was carried out in dry dichloromethane or toluene at low temperatures (195 or 233 K). Polarographic grade tetrabutylammonium iodide (in hexane) was used as a common ion salt in dichloromethane solvent. HI (in hexane) as an initiator was prepared as already reported.[13,14] After a certain period from the initiation, the oligomerization was terminated by a ammoniacal methanol, and therefore, the obtained oligomers have an OCH_3 group in their chain end. The oligomerization was performed in five batches of different monomer-to-initiator feed ratios. The applied VCZ monomer-to-HI initiator feed ratios were 3, 7, 10, 20, and 100 mol/mol. After precipitation from the mixture of water and methanol several times and drying in vacuo, the oligomers were then separated in fractions by degree of polymerization (DP), where DP = 3 (CZ3), 4 (CZ4), 5 (CZ5), 10 (CZ10), 20 (CZ20), and 100 (CZ100), by a GPC (Tosoh HLC802R, THF solvent, polystyrene standard) equipped with an autosampler (Tosoh AS8071) and a fraction collector (Tosoh FC8010). Two combinations of GPC columns (Tosoh, G1000H8 + G2000H8 or G4000H8 × 2) were used for the oligomer fractionation. Oligomers thus separated by GPC were finally purified by precipitation and dried in vacuo. There remained a slight molecular weight dispersion for the fraction of DP = 10, 20, and 100 oligomers (M_w/M_n = 1.14, 1.15, and 1.05, respectively).

For the oligomer fraction of DP = 3, we further separated the stereoisomers by HPLC (Jasco, TRI ROTAR-V, Megapak SIL columns). In this case, trimers with a CH_3 group in the chain end were also prepared by the oligomerization procedure terminated by CH_3MgBr (Aldrich). The molecular structure of these stereoisomeric trimers was unambiguously determined by two-dimensional ^1H COSY NMR spectroscopy. Thus far, isotactic trimer (CZ3*mm*) and heterotactic trimer (CZ3*mr*) with CH_3 termination and syndiotactic trimer (CZ3*rr*) with OCH_3 termination have already been obtained. The details of the separation and assignments have been reported elsewhere.[15]

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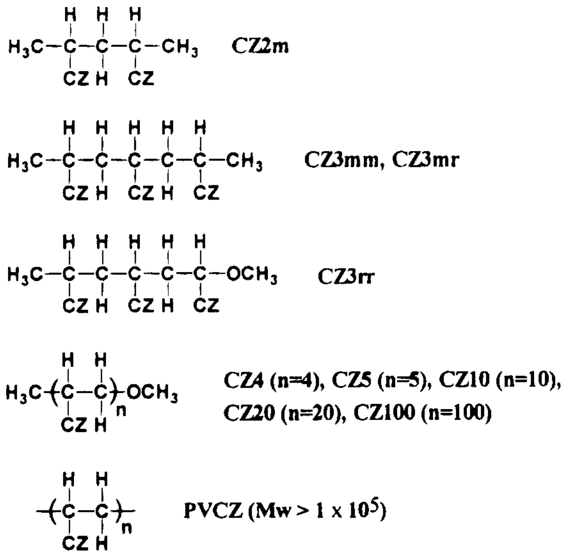

Figure 1. Structural formulas of VCZ oligomers used in this work with their abbreviations. CZ2*m* is the mesotactic dimer. CZ3*mm*, CZ3*mr*, and CZ3*rr* are the iso-, hetero-, and syndiotactic trimers, respectively.

Poly(*N*-vinylcarbazole) (PVCZ; Tokyo Kasei Kogyo, Co., Ltd., $M_w > 1 \times 10^5$) was purified by precipitation from a benzene solution into methanol several times. meso-2,4-Di(*N*-carbazolyl)pentane (CZ2*m*) was synthesized from 2,4-pentanediol as already reported.[9]

Spectroscopic Measurements. Fluorescence spectra of VCZ oligomers were measured by a Hitachi 850 fluorescence spectrophotometer. Transient absorption spectra and decays were measured by a laser photolysis system reported before.[16] The excitation pulse from a Lambda Physik EMG101MSC excimer laser has ~20 ns fwhm at 351 nm (XeF gas). A pulsed 150-W xenon lamp (Ushio) or photoflash lamp (Matsushita) was used as a monitor light source. Transient absorption spectra were collected by an optical multichannel analyzer (Unisoku USP-500) equipped with an image intensifier (Hamamatsu C2925, C4078). Transient absorption decays were observed by a Hamamatsu R1477 photomultiplier (τ_r < 5 ns)[17] for the UV and visible regions and by a Hamamatsu P838 InAs photodiode (τ_r < 500 ns)[18] for the near-IR region. The decay signal was recorded by a Hewlett Packard 54510A digital oscilloscope (250 MHz) and transferred to a personal computer.

Samples for the spectroscopic measurements were dissolved in DMF (for UV and visible) or DMF-d_7 (for near-IR) and degassed by the freeze–pump–thaw method (samples for the fluorescence and transient absorption spectra measurements) or freed from oxygen by argon bubbling for 15 min (samples for the radical ion transfer measurements). The sample absorbance at the 352-nm peak was adjusted to 0.3 for the fluorescence measurements and that for laser photolysis measurements at 351 nm was 1.5. These sample concentrations were low enough to prevent intermolecular interaction or inhomogeneous excitation for the laser photolysis. DCNB (8.0×10^{-2} mol/L) was added to the laser photolysis samples as an electron acceptor for VCZ oligomers. Appropriate concentrations of TMPD (5.0×10^{-4} mol/L) or DMOA (1.0×10^{-3} mol/L for CZ3 and CZ4, 2.5×10^{-3} mol/L for CZ10 and CZ20, and 5.0×10^{-3} mol/L for CZ100) were added to the samples for the radical ion transfer measurements as radical cation acceptors. All measurements were done in a 1-cm quartz cell at 298 K.

Results and Discussion

Figure 1 shows the structural formulas of the CZ compounds with their abbreviations used in this work. Stereoisomers were separated for CZ dimer (CZ2) and trimer (CZ3), whereas other oligomers of DP ≥ 4 were measured without separation of the isomers.

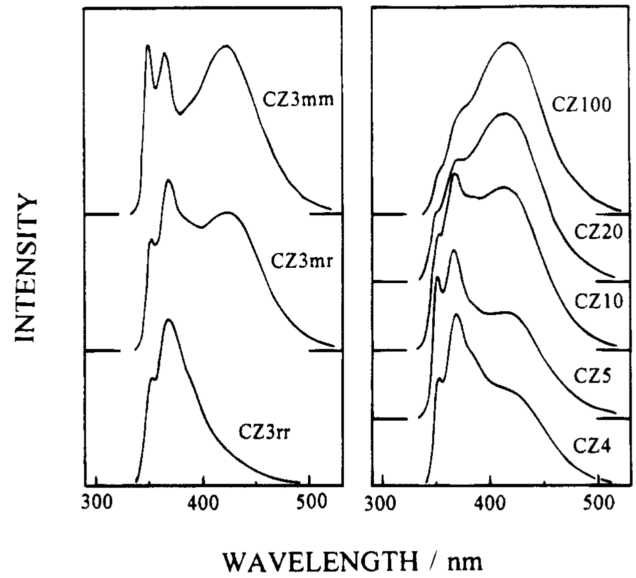

Figure 2. Fluorescence spectra of VCZ oligomers measured in degassed DMF solvent at 298 K.

Figure 2 shows the fluorescence spectra of the VCZ oligomers. The CZ chromophore is known to give a partial-overlap (so called second) and a full-overlap (normal) excimer emission at 370 and 420 nm, respectively.[19-21] *rac*-2,4-Di(*N*-carbazolyl)pentane (CZ2r) prefers to form the partial-overlap excimer because the ground state TT conformation is very close to this excimer conformtion. On the other hand the meso dimer CZ2*m*, whose ground state conformation is TG/GT, forms the full-overlap excimer in the TT conformation due to the larger stabilization energy of this type of excimer.[6] As shown in the left spectra of Figure 2 for the trimers, CZ3*rr* and CZ3*mm* formed almost selectively the partial- and full-overlap excimers, respectively, whereas CZ3*mr* gave both excimer emissions. The details of the excimer formation and decay kinetics of these trimers will be reported separately. For the oligomers of DP ≥ 4, the full-overlap excimer emission became major with the increase of DP due to the participation of intramolecular energy migration and the preferable isodiad formation in the living cationic oligomerization.[13,14,19]

Radical Cation Transfer Measurements. The details of the radical ion transfer method have already been published,[3,9-11] and here only the main points of the method will be explained by taking CZ3*mm* as an example.

Photoexcitation of a CZ chromophore of CZ3*mm* in a polar DMF solvent with DCNB produced a radical cation of CZ3*mm* (CZ3$mm^{\bullet+}$) and a radical anion of DCNB (DCNB$^{\bullet-}$). This ionization process was completed within 10 ns after laser pulse excitation by the addition of a sufficient concentration (8.0×10^{-2} mol/L) of DCNB electron acceptor. These radical ions of CZ3$mm^{\bullet+}$ and DCNB$^{\bullet-}$ were deactivated by the charge recombination reaction with the rate constant of k_r. Figure 3a shows the decay of CZ3$mm^{\bullet+}$ measured by laser photolysis at a 780 nm band peak. The value of the k_r obtained by the long time-scale measurements was mostly diffusion-controlled. However, the decay shown by Figure 3a is negligible in this time scale due to the low concentrations of CZ3$mm^{\bullet+}$ and DCNB$^{\bullet-}$.

When a second electron donor TMPD (as a radical cation acceptor), which has a lower oxidation potential than CZ chromophore, was added to the system, a hole

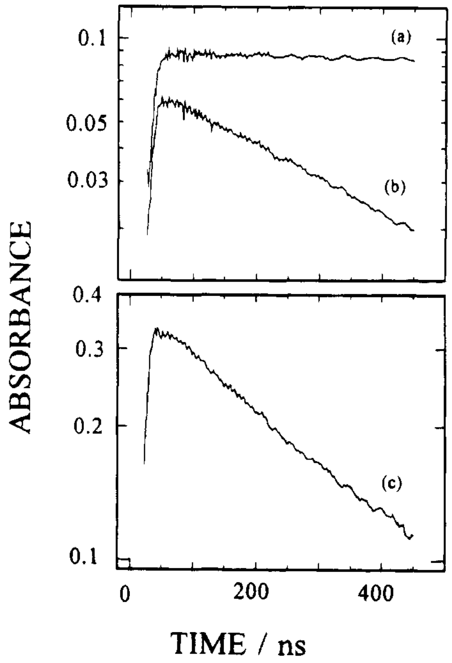

Figure 3. Transient absorption decays of CZ3*mm* radical cation (CZ3$mm^{\bullet+}$) at 780 nm measured in argon-bubbled DMF solvent at 298 K: (a) CZ3*mm* with [DCNB] = 8.0×10^{-2} mol/L as an electron acceptor; (b) CZ3*mm* with [DCNB] = 8.0×10^{-2} mol/L and [TMPD] = 5.0×10^{-4} mol/L; (c) CZ3*mm* with [DCNB] = 8.0×10^{-2} mol/L and [DMOA] = 2.5×10^{-3} mol/L.

Table 1. Radical Cation Transfer Rate Constant from VCZ Oligomers to TMPD and to DMOA (k_d and k_tr, Respectively), and Electron Transfer Rate Constant (k_e)

oligomer	$k_\mathrm{d}/10^9$ M^{-1} s^{-1}	$k_\mathrm{tr}/10^9$ M^{-1} s^{-1}	$k_\mathrm{e}/10^9$ M^{-1} s^{-1}
CZ2*m*	8.5	4.2	8.4
CZ3*mm*	7.9	2.9	4.5
CZ3*mr*	7.9	3.0	4.7
CZ3*rr*	7.9	2.9	4.5
CZ4	7.4	2.3	3.4
CZ5	6.8	2.1	3.0
CZ10	6.3	1.8	2.6
CZ20	5.6	1.6	2.2
CZ100	4.5	1.0	1.3

of CZ3$mm^{\bullet+}$ was transferred to TMPD to form TMPD$^{\bullet+}$, and the decay of the CZ3$mm^{\bullet+}$ was accelerated. Figure 3b shows this enhanced decay of CZ3$mm^{\bullet+}$ at 780 nm, where TMPD$^{\bullet+}$ has no absorption. The oxidation potential of TMPD is low enough to give a diffusion-controlled hole transfer rate constant k_d.[10] The decay rate of CZ3$mm^{\bullet+}$ is represented by the following rate equation:

$$\mathrm{d}[\mathrm{CZ3}mm^{\bullet+}]/\mathrm{d}t = -k_\mathrm{d}[\mathrm{CZ3}mm^{\bullet+}][\mathrm{TMPD}] - k_\mathrm{r}[\mathrm{CZ3}mm^{\bullet+}][\mathrm{DCNB}^{\bullet-}] \tag{1}$$

In the time scale of Figure 3 and under the TMPD concentration, the condition of

$$k_\mathrm{d}[\mathrm{CZ3}mm^{\bullet+}][\mathrm{TMPD}] \gg k_\mathrm{r}[\mathrm{CZ3}mm^{\bullet+}][\mathrm{DCNB}^{\bullet-}] \tag{2}$$

is satisfied. In this case, eq 1 is reduced to

$$\ln[\mathrm{Abs}(\mathrm{CZ3}mm^{\bullet+})] = -k_\mathrm{d}[\mathrm{TMPD}]t + C \tag{3}$$

where Abs(CZ3$mm^{\bullet+}$) is the absorbance of CZ3$mm^{\bullet+}$ at 780 nm measured by laser photolysis and C is a constant. From this equation it is possible to obtain k_d by plotting ln[Abs(CZ3$mm^{\bullet+}$)] *vs* time as shown in Figure 3b.

Table 1 shows a summary of the k_d values for CZ oligomers. This k_d value is considered to depend strongly on the diffusion constant of CZ oligomers, and therefore, it is quite reasonable that the k_d value for CZ2*mm* is about twice that for CZ100. The possibility that the steric effects in the longer coiled chains prevent the close approach of the low molecular TMPD to the CZ$^{\bullet+}$ center is also excluded by this fact.

DMOA is another radical cation acceptor whose ionization potential is lower than that of the CZ chromophore. However, the ionization potential is not as low as that of TMPD. The oxidation potential $E_{1/2}$ *vs* SCE for ethylcarbazole, DMOA, and TMPD were measured as 1.06, 0.64, and 0.14 V, respectively.[10] This potential difference of 1.06 and 0.64 V is not enough to cause a diffusion-controlled hole transfer from CZ chromophore to DMOA. In this case, the hole transfer rate constant k_tr measured by the radical cation transfer method consists of the diffusion-controlled rate constant k_d and the rate-limiting electron transfer rate constant k_e as shown in eq 4. In other words, to obtain the pure electron transfer rate constant k_e, k_tr must be corrected by k_d, under the assumption that the diffusion coefficients of TMPD and DMOA are the same. This k_e, which can be calculated from eq 4, will be a measure of the hole resonance in VCZ oligomers.[10]

$$k_\mathrm{e}^{-1} = k_\mathrm{tr}^{-1} - k_\mathrm{d}^{-1} \tag{4}$$

Figure 3c shows the CZ3$mm^{\bullet+}$ decay accelerated by the addition of DMOA to the system. From this decay slope it is possible to obtain k_tr values.

Table 1 summarizes the measured k_tr values with those of k_e calculated by eq 4. Table 1 shows that the electron transfer rate constant k_e decreased with the increase of DP. The slow diffusion rates of the large DP oligomers have already been corrected by eq 4. Therefore, this decrease of k_e is due to the increase of the charge resonance among CZ chromophores. Trimer CZ3*mm* showed a smaller k_e value than the dimer CZ2*m*. This means that the hole stabilization by three CZ chromophores is stronger than that by two CZ chromophores. The k_e value of CZ100 was almost the same as that of PVCZ, and therefore, the radical cation stabilization in PVCZ is considered to be mostly attained with this DP = 100;[10] however, this does not necessarily mean the existence of the charge resonance among 100 CZ chromophores (see discussion below).

Charge Resonance (CR) Band Measurements. The existence of charge resonance among more than two CZ chromophores can also be shown by the CR band measurements of the VCZ oligomers. Figure 4 shows a schematic electronic state diagram of the dimer radical ion formation. The charge resonance interaction between two constituent CZ rings of the dimer radical cation causes the splitting of the ground and excited state energy levels.[2] This splitting gives a new charge resonance transition in the near-IR region for the CZ chromophore.[4] ΔH in the figure shows the stabilization energy of the dimer radical cation formation. The radical ion transfer rate from CZ$^{\bullet+}$ to the radical cation acceptor DMOA was reduced by this stabilization as explained in the previous section. If the hole delocalizes among n CZ chromophores, the ground and excited state energy levels will split in n levels. This splitting will lead to the smaller charge resonance transition energy; in other words, the shift of the CR band to the longer wavelength[8] and the larger stabilization energy ΔH.

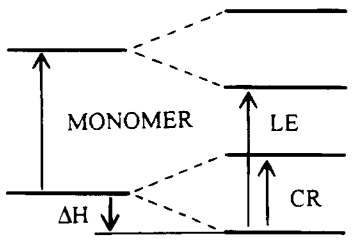

Figure 4. Schematic diagram of the CR band origin of dimer radical cation. LE, CR, and ΔH represent the locally excited transition, charge-resonance transition, and stabilization energy, respectively.

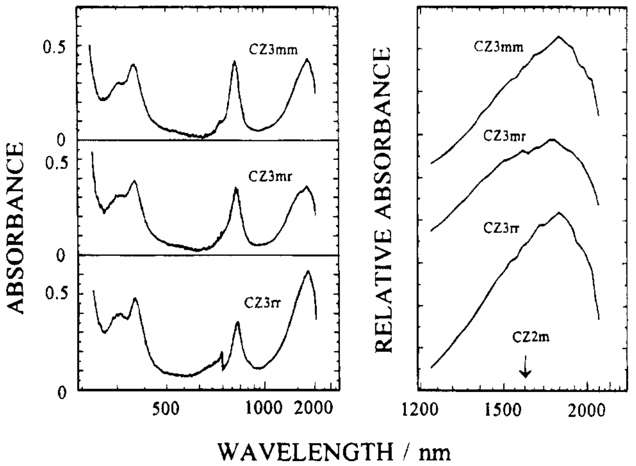

Figure 5. Transient absorption spectra of VCZ trimers of CZ3*rr*, CZ3*mr*, and CZ3*mm* with the enlarged CR bands in the near-IR region in the right panel. Measurements were made in degassed DMF solvent with [DCNB] = 8.0 × 10^{-2} mol/L at 298 K. Peak intensities were normalized by using the $DCNB^{\bullet -}$ peak at 430 nm as a reference. Gate time of the image intensifier was 500−1000 ns after excitation. The offset at 690 nm is due to a grating change.

Figure 5 (left) shows the transient absorption spectra of VCZ trimers measured by laser photolysis. The visible bands at *ca.* 780, 430, and 420 nm are ascribed to $CZ^{\bullet +}$, $DCNB^{\bullet -}$, and $^3CZ^*$, respectively.[22,23] As already observed for the dimer compounds of CZ2*r* and CZ2*m*, the molar extinction coefficient of the partial-overlap-type radical cation LE band was smaller than that of the full-overlap type.[23] The absorption bands in the 1000−2500-nm region are the CR band, whose enlarged shape is shown in the right figure. The CR band peak of all these trimers was located at ~1800 nm, which is obviously a longer wavelength than that of the dimer CZ2*m* at 1600 nm.[4] As mentioned above, the peak position of the CR band can be a measure of the number of chromophores that participate in the charge resonance. Therefore, this peak shift from 1600 to 1800 nm is considered to be caused by the hole resonance among three CZ chromophores of the trimers.

The three VCZ trimers of CZ3*mm*, CZ3*mr*, and CZ3*rr* gave a different excimer emission, as shown in Figure 2. On the other hand, the peak position of the CR bands was almost the same, 1800 nm. This lack of difference in peak position in the radical cationic state may be attributed to the loose conformational requirement of the charge resonance interaction. The excimer emission is sensitive to the conformation of the constituent chromophores, whereas the charge resonance interaction is not so sensitive. The charge resonance interaction could be observed even in the two far-apart CZ chromophores of *trans*-1,2-di(*N*-carbazolyl)cyclobutane.[9] Therefore the position of the CR band peak of VCZ oligomers seems to be determined by the number of CZ chromophores that participate in the charge resonance interaction.

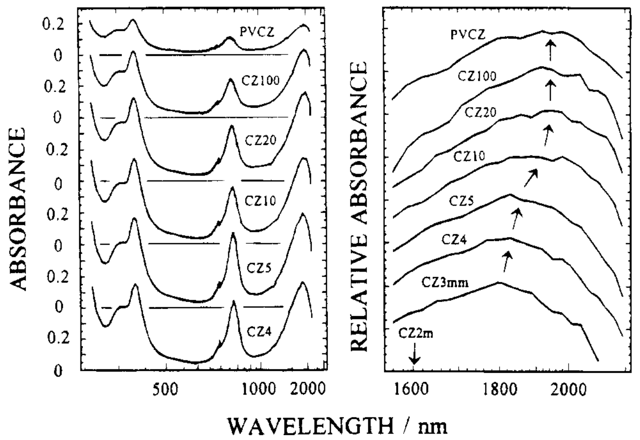

Figure 6. Transient absorption spectra of VCZ oligomers and PVCZ. Measurement conditions were the same as those in Figure 5 except that DMF-d_7 was used as a solvent. Right panel shows the enlarged CR bands.

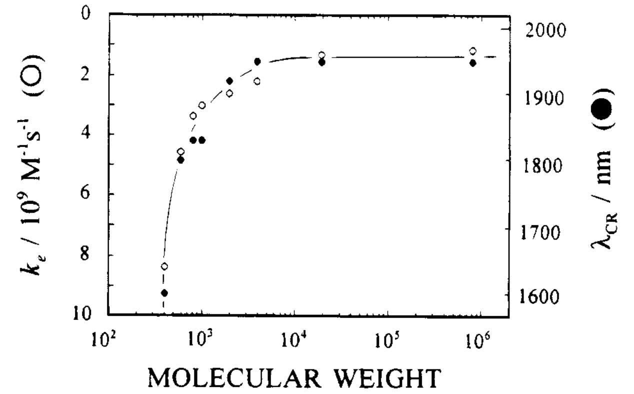

Figure 7. Molecular weight dependence of k_e (open circles) and λ_{CR} (closed circles) of VCZ oligomers.

Figure 6 (left) shows the transient absorption spectra of VCZ oligomers and PVCZ. The ordinates of these spectra are comparable because the measurements were done in the same CZ base chromophore concentration at the same laser excitation intensity. The larger DP oligomers and PVCZ gave a smaller transient species absorbance, probably due to the participation of the efficient intramolecular $^1S^*$−$^1S^*$ annihilation. Figure 6 (right) shows the enlarged CR band of the left spectra. This figure clearly shows the shift of the CR band peak to the longer wavelength for the larger DP oligomers. The peak shift was limited at the DP = ~20 oligomer. This means that the molecular weight effect on the radical ion stabilization by the charge resonance is almost saturated with this DP (see below).

Molecular Weight Dependence of the Charge Resonance Interaction. Figure 7 shows the k_e value and the peak wavelength of the CR band (λ_{CR}) plotted against the molecular weight of the VCZ oligomers. Both the radical ion transfer rate k_e and the wavelength of CR band peak gave a similar tendency. As mentioned before, the values of k_e and λ_{CR} in this figure can be a measure of the intramolecular charge resonance interaction of the VCZ oligomers. Therefore, this figure shows that the charge resonance interaction increases markedly from DP = 2 to 10 due to the participation of some chromophores to the resonance and then is saturated at DP = 20. The existence of a charge resonance among more than two CZ chromophores is clear from this figure. However, this does not necessarily suggest the presence of a charge resonance interaction throughout all 20 CZ chromophores. It is difficult for a flexible polymer chain to maintain a certain conformation for the charge resonance among 20 CZ chromophores against the molecular motion in solution at room temperature. In fact, the expected ratio of the charge resonance transition energy for the dimer and trimer is 1:0.71 by the Hückel MO calculation.[8] However, the ratio from Figure 7 is 1:0.89. This means that the radical cationic state formed among several CZ chromophores is less stabilized than that expected from the theory. It is considered that the balance between the charge resonance stabilization and micro-Brownian motion of the polymer chain determines the degree of charge resonance in equilibrium; in our feeling the maximum persistent length of the hole delocalization may be among several CZ chromophores even in PVCZ. Molecular weight dependence of the charge resonance is considered to be caused by the end-group effect. For small DP oligomers, the conformational changes of all the CZ chromophores are not effectively restricted as that in the middle of the large DP oligomers; this situation causes the efficient motion of CZ groups and makes the charge resonance unstable for small DP oligomers. The presence of this end-group effect has been reported for the intramolecular excimer formation of polystyrene oligomers.[24] Itagaki *et al.* also reported this end-group effect.[25] The charge resonance among CZ chromophores in VCZ oligomers is considered to occur mostly in the midchain, and the molecular motion of the polymer chain interrupts the charge resonance.

Conclusions

The radical cationic state of the VCZ oligomers was measured by laser photolysis to show the existence of charge resonance among more than two CZ chromophores. The radical ion transfer method showed the decrease of hole transfer rates with the increase of stabilization energy for the large DP oligomers. CR band measurements also indicated the increase of stability with increase of DP. This stabilization is caused by the hole resonance among several CZ chromophores in the VCZ oligomers. The balance between the charge resonance stabilization and micro-Brownian motion of the polymer chain determines the degree of charge resonance in equilibrium.

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