Steric Effect on Dimer Radical Cation Formation of Poly(3,6-di-*tert*-butyl-9-vinylcarbazole) and Its Dimeric Model Compounds Studied by Laser Photolysis

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ABSTRACT: The steric effect of bulky *tert*-butyl group on the formation of a dimer radical cation was investigated. Transient absorption spectra for poly(3,6-di-*tert*-butyl-9-vinylcarbazole) (PBVCz) and its dimeric model compounds were measured by laser photolysis. Though the interaction was weak compared with the case of carbazole chromophores, all these compounds formed the dimer radical cation and gave the dimer band in a visible region and the charge-resonance (CR) band around *ca.* 2000 nm. This is quite in contrast to the result that the meso isomer of 2,4-bis(3,6-di-*tert*-butyl-9-carbazolyl)pentane and 1,3-bis(3,6-di-*tert*-butyl-9-carbazolyl)propane do not form an intramolecular excimer. In these compounds, two chromophores cannot come close together and the dimer radical cation has a rather loose conformation. This means that the conformational requirement for the formation of the dimer radical cation is rather loose and that the stabilization energy is larger than that of the excimer. In PBVCz, interactions among more than two chromophores are hindered and the partially-overlapped dimer radical cation is formed in contrast to the case of poly(*N*-vinylcarbazole).

KEY WORDS Steric Hindrance / Neighboring Chromophore Interaction /
Dimer Radical Cation / Laser Photolysis / Charge-Resonance Band /
Poly(3,6-di-*tert*-butyl-9-vinylcarbazole) /

Numerous investigations have been made on the photophysical and photochemical properties of polymers having pendant aromatic chromophores.^{1–5} An important characteristic of such polymers is that the local concentration is very high even in a dilute solution. Therefore, an excited state of a chromophore is expected to be stabilized to form an excimer by interaction with the neighboring chromophore. One of such polymers, poly(*N*-vinylcarbazole) (PVCz) is known to form at least two kinds of excimers, the sandwich excimer with a fully-overlapped conformation and the second

excimer with a partially-overlapped conformation.^{6–14} These excimers were identified by comparison with dimeric model compounds: meso- and rac-di(*N*-carbazolyl)pentanes (m- and r-CzPe) form the sandwich excimer and the second excimer, respectively.^{13,15}

Radical cations of aromatic chromophores are also stabilized by interactions with neighboring chromophore. The stabilization of the radical cation leads to the formation of a dimer radical cation, which has been investigated in intramolecular^{16–21} and inter-

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molecular systems.^{22–27} Concerning the dimer radical cation of a carbazole (Cz) chromophore, two kinds of dimer radical cations have been reported for *m*- and *r*-CzPe,¹⁸ where the overlapping of two Cz chromophores is different. That is, the meso isomer forms the sandwich dimer radical cation with the same fully-overlapped conformation as the sandwich excimer, and the racemic isomer forms the second dimer radical cation with the same partially-overlapped conformation as the second excimer. In the previous paper,¹⁹ we investigated the stability of these dimer radical cations and the Cz radical cation (Cz^+) formed in PVCz by the radical ion transfer method,²⁸ and concluded that the sandwich dimer radical cation is more stabilized than the second one and that Cz^+ formed in PVCz is the most stable.²⁹ This was supported by measurement of the charge-resonance (CR) band whose absorption was observed in a near-infrared wavelength region.²⁰ The sandwich and the second dimer radical cations showed the CR band around 1600 nm and 1800 nm, respectively. The CR band reflects the strength of the neighboring interaction in the dimer radical cation; the CR band is shifted to shorter wavelengths with the increasing interaction with the neighboring chromophore.

The fluorescent behavior of poly(3,6-di-*tert*-

butyl-9-vinylcarbazole) (PBVCz) and its dimeric model compounds, 2,4-bis(3,6-di-*tert*-butyl-9-carbazolyl)pentanes (BCzPe) was studied at our laboratory.³⁰ Figure 1 shows the molecular structure of 3,6-di-*tert*-butylcarbazole. *tert*-Butyl groups are very bulky as shown in the shaded parts, and their steric hindrance is considered to be very large. Consequently, the neighboring interaction in the excited state is suppressed by the steric hindrance of bulky *tert*-butyl groups introduced in the Cz chromophore. PBVCz gives only one kind of unstable excimer whose stability is smaller than the second excimer. The meso isomer of BCzPe forms no excimer at all owing to the steric hindrance and in the case of the racemic isomer of BCzPe, the fraction of the excimer is very small compared with that of *r*-CzPe.

In the present study, we carried out transient absorption measurements of radical cations of these compounds having bulky *tert*-butyl groups in Cz chromophore, and investigated the effect of steric hindrance on the radical cation interaction.

EXPERIMENTAL

Materials

The preparation of poly(3,6-di-*tert*-butyl-9-vinylcarbazole) (PBVCz), 2,4-bis(3,6-di-*tert*-butyl-9-carbazolyl)pentane (BCzPe), and 3,6-di-*tert*-butyl-9-ethylcarbazole (BEtCz) was described in detail previously.³⁰ PBVCz with a molecular weight of *ca.* 1×10^6 was obtained by a cationic polymerization of its vinyl monomer, 3,6-di-*tert*-butyl-9-vinylcarbazole. As for BCzPe, the racemic and the meso isomers (*r*- and *m*-BCzPe) were separated by liquid chromatography and were used as models for syndiotactic and isotactic dyads in PBVCz, respectively. 1,3-Bis(3,6-di-*tert*-butyl-9-carbazolyl)propane (BCzPr) was synthesized from 3,6-di-*tert*-butylcarbazolylsodium and 1,3-dibromopropane (Wako Pure Chem. Ind., Ltd.) and was purified by silica-gel column chromatography and recrystallization.

Figure 1. Molecular structure of 3,6-di-*tert*-butylcarbazole. Shaded parts show *tert*-butyl groups.

An electron acceptor, dimethyl terephthalate (DMTP, Wako Pure Chem. Ind., Ltd.) was purified several times by recrystallization.

Acetonitrile (MeCN, Wako Pure Chem. Ind., Ltd.) was distilled over P_2O_5 several times. Tetrahydrofuran (THF, Dotite Spectrosol) was used without further purification.

Measurements

Transient absorption measurements were made by nanosecond laser photolysis. A 351-nm laser pulse of XeF excimer laser (Lambda Physik EMG101 MSC) was used for excitation. The laser pulse had a pulse energy of *ca.* 60 mJ and a fwhm of *ca.* 17 ns. Two kinds of detection systems were used; one equipped with a photomultiplier tube (Hamamatsu, R928) as a detector^{20,21,28} and the other equipped with a photovoltaic indium arsenide (InAs) diode (Hamamatsu, P838).^{20,31} The former photomultiplier-system is well suited for measurement in the visible region (350–850 nm) and its rise time is *ca.* 5 ns. The latter photodiode-system was used for measurement in the visible and the near-infrared regions (350–2200 nm) and has a response time of *ca.* 500 ns.

An electron donating chromophore, 3,6-*tert*-butylcarbazole (BCz), was excited selectively by the laser pulse in the presence of an electron acceptor, DMTP (0.05 M), and the transient absorption decays and spectra of radical ions formed by a photoinduced electron transfer reaction were measured. The pulse intensity was attenuated properly by filters. The concentration of BCz chromophore was adjusted to about unity in the absorbance at 351 nm. THF solvent was used for PBVCz system. The other systems were measured in MeCN. All samples were degassed by the freeze-pump-thaw method in a 1-cm quartz cell.

RESULTS

Figure 2 shows the transient absorption

Figure 2. Transient absorption spectrum of BEtCz–DMTP (0.05 M) system in MeCN at 25°C at 1 μ s after excitation. The absorbance of BEtCz at 351 nm is about unity.

spectrum of the BEtCz–DMTP system in MeCN at 25°C at 1 μ s after excitation. The absorption band of a radical cation of BEtCz (BEtCz^+) appears at *ca.* 795 nm along with that of a radical anion of DMTP (DMTP^-) observed at *ca.* 530 nm.^{28,32} No absorption was observed in the near-infrared region (1000–2000 nm). The monomer band of BEtCz^+ is similar in shape and peak wavelength to that of the radical cation of 9-ethylcarbazole (EtCz^+).^{19,28} Therefore, the *tert*-butyl group is considered to have little effect on a radical cationic state of Cz chromophore.

Figure 3 shows the transient absorption spectra of the dimeric model compound–DMTP systems in MeCN at 25°C at 1 μ s after excitation. Each system gives two absorption bands of the radical cation of BCz chromophore; one is the visible dimer band and the other is the band around *ca.* 2000 nm. The former band shifts to shorter wavelengths and is broader than that of BEtCz^+ ; the peak wavelength is at 760 nm for *m*-BCzPe (Figure 3A), at 750 nm for BCzPr (Figure 3B), and at 700 nm for *r*-BCzPe (Figure 3C). The latter is the CR band of the dimer radical cation formed intramolecularly. The CR band shifts to the shorter wavelengths in the order: >2100 nm for *m*-BCzPe (Figure 3A), 2100 nm for BCzPr

Figure 3. Transient absorption spectra of the dimeric model compound-DMTP (0.05 M) systems in MeCN at 25°C at 1 μ s after excitation. A, m-BCzPe; B, BCzPr; C, r-BCzPe. The absorbance of BCz chromophore at 351 nm is about unity.

(Figure 3B), and 2000 nm for r-BCzPe (Figure 3C). For all dimeric model compounds, there was no obvious absorption peak of the monomer radical cation (*ca.* 795 nm), though the molar extinction coefficient (ϵ) of the monomer radical cation is larger than that of the dimer radical cation as described later. This suggests that the contribution of the monomer radical cation can be neglected. The molar extinction coefficient (ϵ) of dimer radical cation was estimated on the basis of that of DMTP $^{\cdot+}$ at 530 nm ($\epsilon=12300$)²⁸ by assuming that the concentration of the dimer radical cation is equal to that of DMTP $^{\cdot+}$, since almost all the

Table I. Peak wavelength ($\lambda_{\max}$) and molar extinction coefficient (ϵ) of the visible dimer band and those of the CR band for dimeric model compounds

	$\lambda_{\max}/\text{nm}$	ϵ	$\lambda_{\max}/\text{nm}$	ϵ
BEtCz ^a	795	10500	—	—
m-BCzPe	760	6400	> 2100	3700
BCzPr	750	4600	2100	3000
r-BCzPe	700	3900	2000	5400

^a The values for BEtCz are for the monomer radical cation.

Figure 4. Temperature dependence of the visible dimer band of BCzPe-DMTP (0.05 M) systems in MeCN at 1 μ s after excitation. A, m-BCzPe; B, r-BCzPe. Closed and open circles indicate the spectra measured at 25°C and 72°C, respectively, and these spectra are normalized by the absorbance of DMTP $^{\cdot+}$ at 530 nm.

radical cations form the dimer radical cation. Table I gives the peak wavelength ($\lambda_{\max}$) and the molar extinction coefficient (ϵ) of the visible dimer band, and those of the CR band.

The transient absorption spectra of the visible dimer band were measured at 25°C and 72°C to observe the dissociation of the dimer

Figure 5. Transient absorption spectrum of PBVCz-DMTP (0.05 M) system in THF at 25°C at 1 μ s after excitation. The absorbance of BCz chromophore is about unity.

radical cation to the monomer radical cation. These spectra were normalized by the absorbance of DMTP $^+$ at 530 nm. Figure 4A and B are for m-BCzPe and r-BCzPe, respectively. The visible dimer band did not change obviously with increase in temperature in any system, though the visible dimer band for m-BCzPe showed a little longer-wavelength shift at 72°C. In this way, the dimer radical cation could scarcely dissociate into the monomer radical cation at 72°C.

Figure 5 shows the transient absorption spectrum of the PBVCz-DMTP system in THF at 25°C at 1 μ s after excitation. The radical cation formed in PBVCz was found to have two absorption bands; one is a very broad band around 700 nm and the other is the CR band around 2000 nm. This spectrum is similar to that of the r-BCzPe-DMTP system. The absorbance of the spectrum was very small compared with that of the monomeric and dimeric model compounds. This is partly due to the low quantum efficiency of ionization in low dielectric constant of THF and partly due to S-S annihilation along the polymer chain.

DISCUSSION

Figure 6 shows the energy level diagram of

Figure 6. Schematic diagram of the CR band of dimer radical cation.

the dimer radical cation. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of a chromophore are split into two levels by the interaction with the neighboring chromophore. The CR band corresponds to the transition between two levels of split HOMO. With increasing interaction, the width of the splitting increases and the CR band shifts to shorter wavelengths. As for the dimeric model compounds having Cz chromophores without *tert*-butyl groups, the sandwich and second dimer radical cations give the CR band around 1600 nm and 1800 nm, respectively.²⁰ The CR bands of the dimer radical cations of BCz chromophore (*ca.* 2000 nm) shift to longer wavelengths than those of the Cz chromophore. This means that the interaction in the dimer radical cation is weakened by steric hindrance of *tert*-butyl groups. That is, the stabilization energy is less than 2 kcal mol $^{-1}$, which we estimated for the second dimer radical cation of r-CzPe.¹⁹

However, the monomer radical cation was not detected and dissociation of the dimer radical cation to the monomer radical cation was not observed at 72°C (Figure 4). This suggests that the stabilization energy of the dimer radical cation is sufficiently large compared with the thermal energy.

The neighboring interaction in the dimer radical cation is very different from that in the excimer, especially in m-BCzPe and BCzPr. In contrast to the fact that m-BCzPe and BCzPr

do not form the excimer,³⁰ they form the dimer radical cation easily. In m-BCzPe and BCzPr, two BCz chromophores cannot come close together due to steric hindrance of *tert*-butyl groups and the dimer radical cation has a loose conformation. This means that the conformational requirement for the formation of the dimer radical cation is loose as compared with that of the excimer, and that the stabilization energy of the dimer radical cation is larger than that of the excimer.

The shift of the CR bands suggests that interaction increases in the order: m-BCzPe⁺ < BCzPr⁺ < r-BCzPe⁺. This increase is accompanied by shorter-wavelength shift and broadening (the decreasing ϵ) of the visible dimer band and by increasing ϵ of the CR band. The differences in interactions among the dimeric model compounds are due to configurational differences. In the racemic isomer of the pentane model, TT conformation is stable, having interaction between two chromophores. Then, r-BCzPe forms the dimer radical cation in the partially-overlapped conformation near the TT one. This is the most stable among the three dimeric model compounds. On the other hand, m-BCzPe cannot form the dimer radical cation in TT conformation (fully-overlapped conformation) owing to steric hindrance of the *tert*-butyl groups in BCz chromophore. This means that m-BCzPe also forms the partially-overlapped dimer radical cation. To form the partially-overlapped dimer radical cation, m-BCzPe must take the distorted conformation and the dimer radical cation is unstable as compared with that of r-BCzPe. Thus, all dimeric model compounds form the dimer radical cation with the partially-overlapped conformation and the stability of the dimer radical cation is affected by slight change in the dimer structure induced by configurational differences.

As for the radical cation formed in PBVCz, the transient absorption spectrum is similar to that of r-BCzPe⁺. This suggests that PBVCz forms the partially-overlapped dimer radical

cation in the syndiotactic dyad, which corresponds to the racemic isomer of the pentane model. The situation is very different from the case of PVCz. The radical cation formed in PVCz is considered to interact with more than two neighboring chromophores and to be more stabilized than the dimer radical cation.¹⁹ By introduction of *tert*-butyl groups to the BCz chromophore, interactions of more than two chromophores are hindered and the dimer radical cation is formed in a polymer chain.

CONCLUSION

Dimeric model compounds having BCz chromophores form the dimer radical cation in spite of the steric hindrance of *tert*-butyl groups, though the interaction is weakened compared with the dimer radical cation of Cz chromophore. The neighboring chromophore interaction is increased in the order: m-BCzPe⁺ < BCzPr⁺ < r-BCzPe⁺. The difference in the stability of the dimer radical cation is due to the little change in the dimer structure induced by the configurational difference. It is noteworthy that formation of the dimer radical cation was observed even in m-BCzPe and BCzPr which cannot form excimers. This suggests that the conformational requirement for the formation of the dimer radical cation is loose as compared with that of the excimer, and that the stabilization energy of the dimer radical cation is larger than that of the excimer. As for PBVCz, interactions among more than two chromophores are hindered by steric hindrance in contrast to the case of PVCz and the formation of the same partially-overlapped dimer radical cation as r-BCzPe was observed.

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