Structure and Stability of Dimer Radical Cations of Poly(vinylnaphthalene)s Studied by Charge-Resonance Band Measurement and Radical-Cation-Transfer Method

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ABSTRACT: The charge-resonance (CR) band of dimer radical cations for three isomers of dinaphthylpropanes and poly(vinylnaphthalene)s was measured by laser photolysis. 1-(1-Naphthyl)-3-(2-naphthyl)-propane forms an intramolecular partially overlapped dimer radical cation and shows a CR band at ca. 1050 nm, which corresponds to that (ca. 1100 nm) of an intermolecular dimer radical cation for naphthalene and 2-ethylnaphthalene. By contrast, 1,3-di-2-naphthylpropane (22DNP) and 1,3-di-1-naphthylpropane (11DNP) form partially overlapped and fully overlapped dimer radical cations intramolecularly. These CR bands were superposed and were observed at ca. 1250 nm for 22DNP and at ca. 1350 nm for 11DNP. Therefore, the CR band of the fully overlapped dimer radical cation is considered to be at a longer wavelength than 1250 nm. This means that the partially overlapped dimer radical cation is more stable than the fully overlapped one. This was confirmed by measuring the rate constant of a radical-cation transfer to triethylamine; owing to the stabilization, the rate constant of the radical-cation transfer for the partially overlapped dimer radical cation is smaller than that for the fully overlapped one. The radical cation in poly(vinylnaphthalene)s gives the same transient absorption spectrum as that of the dimeric model compound. This was assigned to the partially overlapped dimer radical cation. The radical cation was not stabilized by the charge resonance among more than two chromophores.

Introduction

The photophysical properties of excimers and dimer radical cations formed by the interaction between aromatic chromophores are known to be affected by their dimer structure, that is, overlapping of chromophores. The relationship between the degree of the neighboring chromophore interaction and the dimer structure has been investigated by using 1,3-diaryl-substituted propane and 2,4-diaryl-substituted pentane, which are models for a polymer having aromatic pendant chromophores. Valuable information has been obtained on the formation of the excimer[1-11] and the dimer radical cation[12-16] of these dimeric model compounds, which often contains significant information on their structure and properties in the polymer system.

Many studies on the dimer radical cation of naphthalene and its derivatives have been made.[15-25] Lewis and Singer detected the formation of the intermolecular dimer radical cation of naphthalene by ESR,[17] and Badger et al. observed its charge-resonance (CR) band in a glassy matrix at 77 K by warming after γ-irradiation.[19] Badger and Brocklehurst, who carried out the Hückel MO calculations, proposed that the dimer structure of the intermolecular naphthalene dimer radical cation is distorted.[20] Recently, Irie et al. proposed the possibility of fully overlapped and partially overlapped forms for the dimer radical cation of 1,3-di-2-naphthylpropane (22DNP) by the pulse radiolysis experiments.[15] Previously, we measured the transient absorption bands of the naphthalene dimer radical cations by laser photolysis for 22DNP, 1-(1-naphthyl)-3-(2-naphthyl)propane (12DNP), and *rac*- and *meso*-2,4-di-2-naphthylpentanes (r- and m-DNPe). 12DNP showed the transient absorption band due to the dimer radical cation (a visible dimer band) at ca. 585 nm.[16] This band was assigned to a partially overlapped dimer radical cation where two naphthyl groups partially overlap, since 12DNP takes only a partially overlapped conformation as shown in Figure 1a. By contrast, 22DNP, r-DNPe, and m-DNPe take two conformations, a partially overlapped and a fully overlapped one (Figure 1b). These compounds gave two visible dimer bands at ca. 580 and ca. 660 nm. The former band was ascribed to the partially overlapped dimer radical cation from the analogy to that of 12DNP. We proposed that the dimer radical cation having the latter band has a fully overlapped conformation, which we called a fully overlapped dimer radical cation.

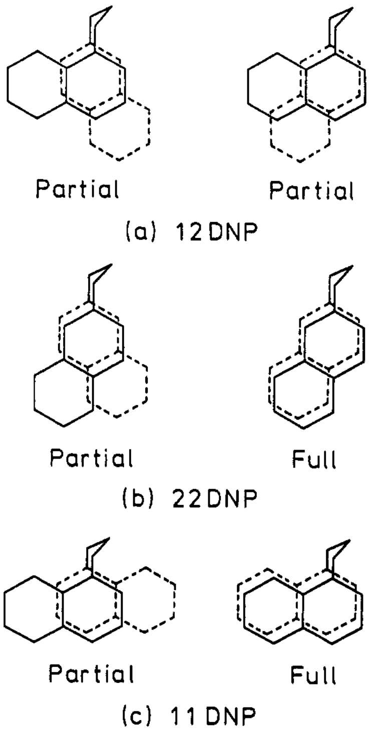


Figure 1. Overlapped conformations of dinaphthylpropanes: (a) 12DNP; (b) 22DNP; (c) 11DNP.

We have measured the CR band observed in the near-infrared region for these dimer radical cations. The CR band is characteristic of the dimer radical cation and reflects the neighboring chromophore interaction in the dimer radical cation directly. The partially overlapped dimer radical cation showed a CR band around 1050 nm. The CR band of the fully overlapped dimer radical cation is shifted to longer wavelengths (>1250 nm). This suggests that the partially overlapped dimer radical cation is more stabilized than the fully overlapped one. This was also confirmed by the radical-cation-transfer method. Herein, we report the stability of the naphthalene dimer radical cation from the standpoint of the dimer structure. On the basis of the results for the dimeric model compounds, we also discuss the naphthalene radical cation formed in poly(1-vinylnaphthalene) (P1VN) and poly(2-vinylnaphthalene) (P2VN).

Experimental Section

A. Materials. Naphthalene (Np; Wako Pure Chem. Ind.) was purified by recrystallizing it from ether three times. 1-Ethylnaphthalene (1-EN; Tokyo Kasei Kogyo Co.) and 2-ethylnaphthalene (2-EN; Tokyo Kasei Kogyo Co.) were purified by distillation under reduced pressure. 11DNP, 22DNP, and 12DNP were synthesized according to the procedure of Chandross and Dempster[5] and purified by silica gel column chromatography and recrystallization. P1VN was prepared by a radical polymerization of 1-vinylnaphthalene initiated by α,α'-azobis(isobutyronitrile) in benzene. P2VN was prepared by an anionic polymerization of 2-vinylnaphthalene initiated by *n*-butyllithium in tetrahydrofuran. These polymers were purified by 3-fold precipitation, and the molecular weight was determined to be 4×10^3 for P1VN and 9×10^3 for P2VN by GPC (Toyo Soda HLC 802UR) with GMH and G4000H columns. 1-Vinylnaphthalene and 2-vinylnaphthalene were synthesized from 1-bromonaphthalene (Wako Pure Chem. Ind.) and 2-acetonaphthone (Wako Pure Chem. Ind.), respectively.

The electron acceptor, 1,2-dicyanobenzene (DCNB; Wako Pure Chem. Ind.) was purified by 3-fold recrystallization. Triethylamine (TEA; Wako Pure Chem. Ind.) was purified by distillation. TEA was used as a radical-cation acceptor in the radical-cation-transfer experiments.

Acetonitrile (MeCN; Wako Pure Chem. Ind.) was purified by refluxing over P_2O_5 and subsequent distillation. Spectroscopic-grade *N,N*-dimethylformamide (DMF; Dotite Spectrosol) was used without further purification.

B. Measurements. Transient absorption was measured on an excimer laser photolysis system equipped with a XeCl excimer laser (Lambda Physik EMG101MSC, 308 nm, pulse energy ca. 100 mJ, fwhm ca. 17 ns). Two detection systems were used;[14] one was a photomultiplier system (rise time ca. 5 ns) for measurements in the visible region, and the other was a photovoltaic indium arsenide (InAs) diode system (rise time ca. 500 ns) for measurements in the visible and near-infrared regions. Naphthyl chromophore was selectively photoexcited by an attenuated laser pulse. The concentration of naphthyl chromophore was so adjusted that it gave about a unit absorbance at 308 nm. An electron acceptor, DCNB (1.0×10^{-1} M), was added to the samples, and the solution was degassed by the freeze–pump–thaw method. DMF was used as a solvent for polymer systems, and MeCN was used for other systems. The measurements were made in a 1-cm quartz cell at 298 K. For the radical-cation-transfer experiments, TEA was added to the above system as a radical-cation acceptor.

The absorption spectra were obtained with a UV-200S spectrophotometer (Shimadzu).

C. Method. 1. CR Band and Stabilization of Dimer Radical Cation. The CR band reflects the neighboring chromophore interaction in the dimer radical cation. Figure 2 shows the energy level diagram of a dimer radical cation. The interaction between a radical cation and a neutral chromophore makes the orbitals split into two energy levels. The CR band corresponds to the transition between two levels of split HOMO. The visible dimer band is due to the absorption from split HOMO to split LUMO as shown by an arrow in Figure 2. The stronger the chromophore interaction, the larger the width of the splitting. This leads to the shorter wavelength shift of the CR band. The stabilization energy (ΔH) of the dimer radical cation is approximately equal to half of the energy gap (ΔE) of the CR band. Thus the CR band is a measure of the strength of the chromophore interaction, i.e., the stability of the dimer radical cation.

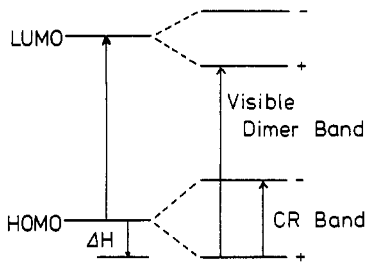
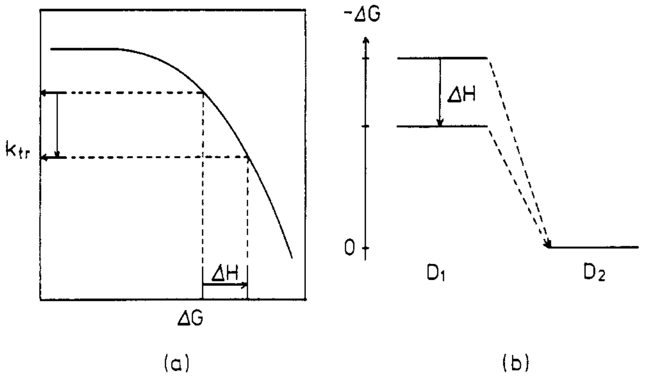


Figure 2. Schematic diagram of energy levels of dimer radical cation.



(a) (b)

Figure 3. Estimate of the stability of dimer radical cation by the radical-cation-transfer method: (a) relation between k_{tr} and ΔG; (b) increased ΔG by stabilization.

2. Radical-Cation-Transfer Method.[13,26] A radical cation ($D_1^{\bullet}$) of an electron donor is produced by photoinduced electron transfer to an electron acceptor (A). The $D_1^{\bullet +}$ can transfer the radical cation to an acceptor (D_2), which is a stronger electron donor than D_1 (eq 1). These radical cations, $D_1^{\bullet +}$ and $D_2^{\bullet +}$

$$D_1^{\bullet +} + D_2 \xrightarrow{k_{tr}} D_1 + D_2^{\bullet +} \tag{1}$$

disappear by recombination with the radical anion, $A^{\bullet -}$ (eq 2 and

$$D_1^{\bullet +} + A^{\bullet -} \xrightarrow{k_{r1}} D_1 + A \tag{2}$$

$$D_2^{\bullet +} + A^{\bullet -} \xrightarrow{k_{r2}} D_2 + A \tag{3}$$

3). These equations (eqs 1–3) lead to the rate equations

$$d[D_1^{\bullet +}]/dt = -k_{tr}[D_1^{\bullet +}][D_2] - k_{r1}[D_1^{\bullet +}][A^{\bullet -}] \tag{4}$$

$$d[D_2^{\bullet +}]/dt = k_{tr}[D_1^{\bullet +}][D_2] - k_{r2}[D_2^{\bullet +}][A^{\bullet -}] \tag{5}$$

$$d[A^{\bullet -}]/dt = -k_{r1}[D_1^{\bullet +}][A^{\bullet -}] - k_{r2}[D_2^{\bullet +}][A^{\bullet -}] \tag{6}$$

where k_{tr} is the rate constant of the radical-cation transfer, and k_{r1} and k_{r2} are the rate constants of the recombination with $A^{\bullet -}$ for $D_1^{\bullet +}$ and $D_2^{\bullet +}$, respectively. The transient absorption decay of $D_1^{\bullet +}$ is measured by laser photolysis, and the rate constant k_{tr} is determined by simulating its decay curve with eqs 4–6.

The stability of the dimer radical cation is estimated by k_{tr} as shown in Figure 3. The rate constant of the electron transfer, k_{tr}, depends on the free energy change (ΔG) as shown in Figure 3a.[13,26] That is, k_{tr} increases with decreasing ΔG (an uphill region) and is diffusion-controlled in a sufficient exothermic region. If the dimer radical cation is stabilized by ΔH as shown in Figure 3b, the exothermic quantity of the radical-cation transfer decreases (ΔG increases). If ΔG is in the uphill region by using a D_2 having a proper oxidation potential, the increase of ΔG by

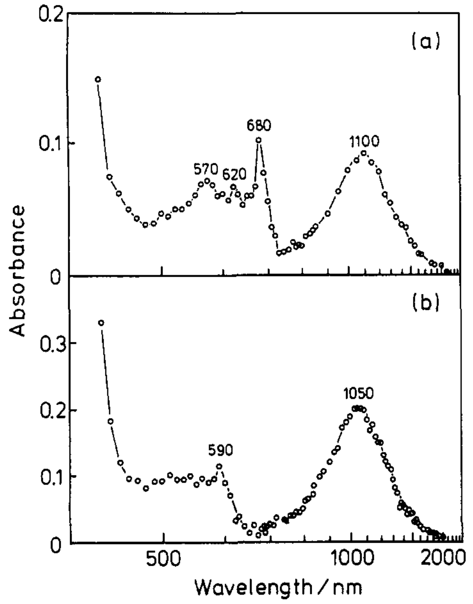


Figure 4. Transient absorption spectra of radical cations with 1,2-dicyanobenzene (0.1 M) at 900 ns after excitation in MeCN at 298 K: (a) naphthalene (5.9×10^{-3} M); (b) 12DNP (1.0×10^{-3} M).

the stabilization causes the decrease of k_{tr}. That is, the stabilization of the dimer radical cation can be estimated by the decreasing k_{tr}.

Results and Discussion

Figure 4a shows the transient absorption spectrum for a Np–DCNB system at 900 ns after excitation. Np forms a dimer radical cation intermolecularly, which is in equilibrium with the monomer radical cation. In the spectrum, a visible dimer band at ca. 570 nm[16] and a CR band at ca. 1100 nm were observed along with the monomer bands at ca. 620 nm and at ca. 680 nm. The absorption below 450 nm is due to the triplet state of Np.[16] The CR band at ca. 1100 nm corresponds to the one at 1030–1040 nm[19,23,24] observed at 77 K by warming the γ-irradiated glassy matrix. The difference in the experimental conditions has caused the small shift of the peak. This means that, by warming the glassy matrix, Np is allowed to diffuse to form a stable dimer radical cation as in solution. A comparison with the transient absorption spectrum for 12DNP as will be described later suggests that this intermolecular dimer radical cation has a partially overlapped structure (the partially overlapped dimer radical cation).[16] This is consistent with the distorted structure proposed by Badger and Brocklehurst.[20]

Figure 4b shows the transient absorption spectrum of the dimer radical cation of 12DNP at 900 ns after excitation. There was no absorption band of the monomer radical cation, but only the dimer radical cation was observed. This suggests that the dimer radical cation is formed intramolecularly.[16] Two dimer bands were observed; one is a visible dimer band at ca. 590 nm,[16] and the other is a CR band at ca. 1050 nm. These bands correspond to the dimer bands at 570 nm and at 1100 nm for the intermolecular dimer radical cation of Np. The RIS model (Figure 1a) suggests that 12DNP can take only the partially overlapped conformation. Therefore, these bands can be assigned to the intramolecular partially overlapped dimer radical cation. This means that Np, which shows the same transient absorption spectrum as 12DNP, also forms a partially overlapped dimer radical cation intermolecularly.

Figure 5a shows the transient absorption spectrum for a 2-EN–DCNB system at 900 ns after excitation. A shoulder around 570 nm, which was observed along with the monomer bands at ca. 620 nm and at ca. 680 nm, was ascribed to the partially overlapped dimer radical cation formed intermolecularly.[16] This is confirmed by the fact that 2-EN gives the same CR band at ca. 1100 nm as Np. There was little effect of the 2-position substitution on transient absorption bands.

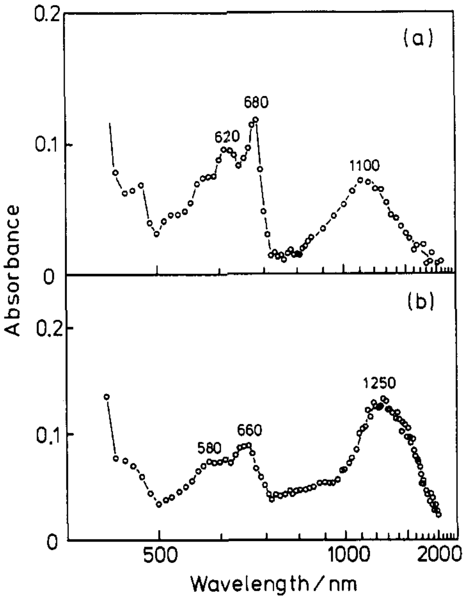


Figure 5. Transient absorption spectra of radical cations with 1,2-dicyanobenzene (0.1 M) at 900 ns after excitation in MeCN at 298 K: (a) 2-ethylnaphthalene (2.9×10^{-3} M); (b) 22DNP (8.3×10^{-4} M).

Figure 5b shows the transient absorption spectrum of the dimer radical cation of 22DNP at 900 ns after excitation. Two visible dimer bands (ca. 580 and ca. 660 nm) appeared.[16] The former is ascribed to the intramolecularly partially overlapped dimer radical cation. 22DNP can take both the partially overlapped and fully overlapped conformations. Therefore, we currently consider that the latter is due to the dimer radical cation having a fully overlapped conformation. That is, 22DNP forms both partially overlapped and fully overlapped dimer radical cations. The superposed CR band of these dimer radical cations was observed at ca. 1250 nm. In the ground state, 22DNP takes the open form in which the two naphthyl groups are far apart from each other, owing to a steric repulsion. If a naphthyl group is photoexcited, a naphthalene radical cation is formed by an electron transfer to DCNB. Though the formation of the intramolecular excimer is generally a competitive process, the electron-transfer quenching is a main process at this high-concentration condition ([DCNB] = 1.0×10^{-2} M).[16] The naphthalene radical cation with the open form, thus produced in 22DNP, interacts with the neighboring chromophore and forms the dimer radical cation. Here, there are two kinds of dimer radical cations depending on the direction of the naphthyl groups approaching each other.

We measured the transient absorption spectra of the radical cation of 22DNP at 25 and 72 °C at 500 ns after excitation. These spectra were almost the same, and no dissociation of the dimer radical cation to the monomer radical cation was observed. This means that the stabilization energy of the dimer radical cation is sufficiently large in comparison with the thermal energy at 72 °C (kT = ca. 0.3 eV). Though the partially overlapped dimer radical cation is expected to be more stabilized than the fully overlapped one, as will be described below, 22DNP

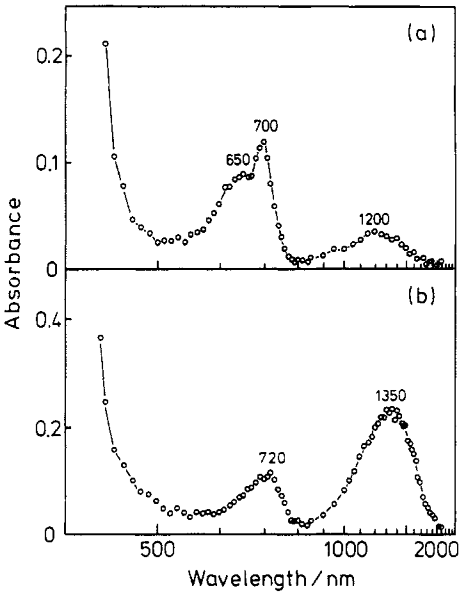


Figure 6. Transient absorption spectra of radical cations with 1,2-dicyanobenzene (0.1 M) at 900 ns after excitation in MeCN at 298 K: (a) 1-ethylnaphthalene (1.6×10^{-3} M); (b) 11DNP (8.4×10^{-4} M).

forms both types of dimer radical cations. This may be because the conformational change between the partially overlapped and fully overlapped dimer radical cations passes through the monomer radical-cation state, but the dimer radical cation scarcely dissociates to the monomer radical cation at 25 °C, owing to the sufficient stabilization energy. Then, the thermodynamic equilibrium between two kinds of dimer radical cations does not hold, and the fraction of these dimer radical cations is determined by the direction of the naphthyl groups at the stage of initial formation.

Figure 6a shows the transient absorption spectrum for a 1-EN–DCNB system at 900 ns after excitation. The monomer bands were observed at ca. 650 nm and at ca. 700 nm, which are shifted to longer wavelengths than those of Np and 2-EN. This is considered to be due to a 1-substituted effect. No observable visible dimer band is detectable, while a CR band is observable at ca. 1200 nm. The CR band is also shifted to longer wavelengths than those of the partially overlapped dimer radical cations for Np and 2-EN. Because 1-EN shows a substituted effect and the intermolecular dimer radical cations for Np and 2-EN are of the partially overlapped type, 1-EN is also considered to form a partially overlapped dimer radical cation intermolecularly.

The transient absorption spectrum of the dimer radical cation of 11DNP at 900 ns after excitation, shown in Figure 6b, suggests that 11DNP preferentially forms an intramolecular dimer radical cation. A visible dimer band and a CR band appear at ca. 720 nm and at ca. 1350 nm, respectively. These bands are shifted to longer wavelengths than those for 22DNP, due to the substitution effect. The CR band is also shifted to longer wavelengths than that of the intermolecular partially overlapped dimer radical cation for 1-EN. Like 22DNP, 11DNP also forms partially overlapped and fully overlapped dimer radical cations.

Table I shows the peak wavelength (λ_{CR}) of the CR band and the stabilization energy (ΔH) estimated from half of the band gap. The monomeric model compounds (Np, 1-EN, and 2-EN) and 12DNP form the partially overlapped dimer radical cation. The CR band of the partially overlapped dimer radical cation except 1-EN appears at

Table I
Peak Wavelength (λ_{CR}) of the CR Band and Stabilization Energy (ΔH) Estimated by Half of the Band Gap

	λ_{CR}/nm	ΔH/eV
Np	1100	0.56
2-EN	1100	0.56
1-EN	1200	0.52
12DNP	1050	0.59
22DNP	1250	0.50
11DNP	1350	0.46

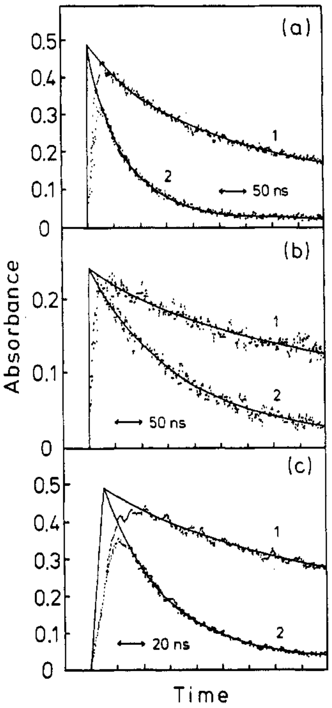


Figure 7. Transient absorption decays of dimer radical cation without triethylamine (curve 1) and with triethylamine (curve 2): (a) the decay curve at 590 nm for 12DNP (1.0×10^{-3} M); (b) the decay curve at 660 nm for 22DNP (8.3×10^{-4} M); (c) the decay curve at 720 nm for 11DNP (8.4×10^{-3} M). As for the concentration of triethylamine, see Table II. The solid line indicates the simulation line for the radical-cation transfer.

1050–1100 nm, and the stabilization energy was estimated to be 0.56–0.59 eV. By contrast, 22DNP and 11DNP gave a CR band shifted to longer wavelengths. The observed CR band is a superposition of the CR bands of the partially overlapped and fully overlapped dimer radical cations. Therefore, the fully overlapped dimer radical cation should have its CR band at longer wavelength than 1250 nm, and the stabilization energy (ΔH) of the fully overlapped dimer radical cation should be less than 0.50 eV. This means that the partially overlapped dimer radical cation is more stable than the fully overlapped one.

To obtain direct information on the stability of the dimer radical cation, we measured the rate constant of the radical-cation transfer. In Figure 7, the measured transient absorption decay of the dimer radical cation in the visible dimer band is shown by the dotted line. Parts a–c of Figure 7 show the absorbances for 12DNP (590 nm), 22DNP (660 nm), and 11DNP (720 nm), respectively. For 22DNP and 11DNP, the contribution of the partially overlapped dimer radical cation is negligible at the measured wavelength, the absorption being predominated by the fully overlapped dimer radical cation. In the absence of TEA, the dimer radical cation decays by recombination with the radical anion, DCNB$^{\bullet-}$, giving a slower decay curve (curve 1). The recombination with DCNB$^{\bullet-}$ is exothermic enough to allow us to assume it to be a diffusion-controlled value, 1.7 ×

Table II
Molar Extinction Coefficient (ϵ) at the Measured Wavelength (λ) and Rate Constant (k_{tr}) of the Radical-Cation Transfer to TEA

	[TEA]/10^{-3} M	λ/nm	ϵ	$k_{tr}/10^9$ M^{-1} s^{-1}
12DNP	6.0	590	2000	1.8
22DNP	1.1	660	1950	3.5
11DNP	6.0	720	1750	2.9

10^{10} M^{-1} s^{-1}, for the rate constant of recombination. When the radical-cation acceptor, TEA, was added, the decay of the dimer radical cation was accelerated by the radical-cation transfer to TEA, as shown by curve 2. These decay curves were simulated by using eqs 4–6, and the rate constant (k_{tr}) of the radical-cation transfer and the molar extinction coefficient (ϵ) at this wavelength were determined. Curve 1 was simulated as $[D_2] = 0$. Although the amount of added TEA was sufficient, the absorbance did not vanish completely, with a small absorption remaining. Because TEA$^{\bullet+}$ has no absorption at this wavelength, this small residual absorption is considered to be due to a byproduct. Because this contribution was minor in any case, we subtracted the absorbance from curve 2 on simulation. The simulation lines are given by the solid curves. Table II shows the relevant parameter values, the concentration of TEA, and the wavelengths of measurements. The rate constant k_{tr} of the partially overlapped dimer radical cation is ca. 1.8×10^9 M^{-1} s^{-1}, while the rate constants k_{tr} of the fully overlapped dimer radical cation are ca. 3.5×10^9 M^{-1} s^{-1} for 22DNP and 2.9×10^9 M^{-1} s^{-1} for 11DNP. Hence, the k_{tr} of the partially overlapped dimer radical cation is smaller than that of the fully overlapped one, the former being more stable than the latter. This is consistent with the stability estimated by the CR band.

Furthermore, this result is supported by the fact that the partially overlapped dimer radical cation is preferentially formed when two chromophores can take either the partially overlapped or the fully overlapped conformation intermolecularly. The instability of the fully overlapped form is due to a large repulsion force. Badger and Brocklehurst predicted that the stable conformation of the Np dimer radical cation has a distorted structure.

We measured the transient absorption spectra of the radical cations formed in P1VN and in P2VN to investigate the neighboring chromophore interaction in the polymer chains. Parts a and b of Figure 8 show the spectra for P2VN and for P1VN in DMF at 900 ns after excitation, respectively. P2VN gave a visible dimer band at ca. 660 nm and a CR band at ca. 1300 nm. The CR band is red-shifted by ca. 50 nm from that of the dimeric model compound, 22DNP, and the ratio of the absorbance of the CR band to that of the visible dimer band is larger than that of 22DNP. As for the trimer radical cation stabilized by the charge resonance among three chromophores, the CR band energy should be $2^{-1/2}$ times that of the dimer radical cation, according to the Hückel MO theory,[19] and thus the CR band for naphthalene should appear at a longer wavelength region than 1500 nm. Therefore, the visible dimer band and the CR band are essentially the same as those for 22DNP. A similar result was obtained for P1VN. P1VN gave a visible dimer band at 700–750 nm and a CR band at ca. 1400 nm. These bands appear at almost the same wavelengths as those for the dimeric model compound, 11DNP. This means that in the polymer chain the dimer radical cation is formed between two neighboring chromophores and that the neighboring chromophore interaction in the polymer chain can be well described by the interaction of dimer model. This is in contrast to the fact that poly(*N*-vinylcarbazole) (PVCz) shows a CR band shifted to longer wavelengths than the dimer radical cation and that the radical cation in PVCz is considered to be stabilized by the neighboring chromophore interaction among more than two chromophores.

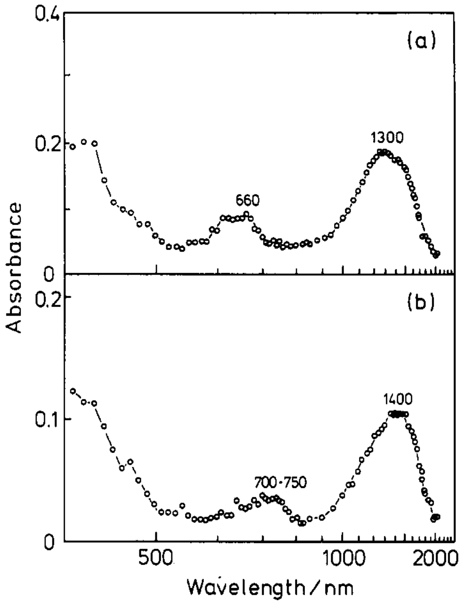


Figure 8. Transient absorption spectra of radical cations with 1,2-dicyanobenzene (0.1 M) at 900 ns after excitation in DMF at 298 K: (a) poly(2-vinylnaphthalene); (b) poly(1-vinylnaphthalene). The concentration of naphthyl chromophore is 3.0×10^{-3} M for poly(2-vinylnaphthalene) and 1.6×10^{-3} M for poly(1-vinylnaphthalene).

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