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Dynamical Formation of Intramolecular Carbazole Dimer Cations in Poly(methyl methacrylate) Solids below the Glass Transition Temperature

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ABSTRACT: Structures and dynamical formation of carbazole (Cz) dimer cations in solid states were investigated by absorption spectroscopy of dicarbazolyl compounds doped in PMMA solids. Charge resonance (CR) bands originating from Cz dimer cations were observed even in PMMA solids at room temperature, which is below the glass transition temperature. Peak wavelengths of the CR bands observed were similar to those previously reported for Cz dimer cations formed in *N*,*N*-dimethylformamide (DMF) solutions at room temperature. This result shows that Cz dimer cations formed in PMMA solids have structures similar to those formed in DMF solutions. These Cz dimer cations were still observed even at 150 K, although the ratios of dimer cations to monomer cations were lower than those at room temperature. The ratios were kept almost constant below 170 K and steeply increased in the temperature range 200−290 K. This observed temperature corresponds to the transition temperature of the β-relaxation in PMMA solids. We conclude that Cz dimer cations are dynamically formed even in PMMA solids, owing to an increase in thermal fluctuation of free volumes induced by the β-relaxation.

1. Introduction

Intramolecular interactions of carbazole (Cz) moieties in poly(*N*-vinylcarbazole) (PVCz) play an important role in various photophysical properties such as photoconductivity.[1−5] The local concentration of Cz moieties in PVCz is so high that neighboring Cz moieties can electronically interact. The interaction leads to transport of hole[1−3] and excitation energy[4,5] among Cz moieties. The hole transport in PVCz solids is regarded as a thermally activated hopping process where the hole migrates from one Cz radical cation to a neutral Cz moiety.[1−3] However, the hole mobility in PVCz solids is extremely low.[1] This is probably because the interaction also leads to formation of Cz dimer cations,[6−8] which is believed to be one of trap sites for migrating holes.[8,9] To elucidate the nature of the hole traps, we need to investigate the structures and formation of Cz dimer cations in polymer solids.

Stabilization energy and structures of dimer cations have been intensively studied by absorption spectroscopy.[10−13] Dimer cations of aromatic molecules have characteristic absorption bands in the visible and near-IR wavelength range.[10] Figure 1 shows a schematic energy diagram of a dimer cation formed in bischromophoric compounds.[11] The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a chromophore are split into two levels by the interaction with the neighboring chromophore. The local excitation (LE) band of the dimer cation corresponds to the transition from the lower split orbital of HOMO to the lower split orbital of LUMO. The charge resonance (CR) band corresponds to the transition between the two split orbitals of HOMO. This CR band reflects the stabilization energy due to the charge delocalization and structures of the dimer cations. Half of the energy required for the CR transition is approximately equal to the stabilization energy of dimer cations,[10,11] which depends on structures, in particular, the degree of overlap of the two aromatic groups in the dimer cation.[12,13]

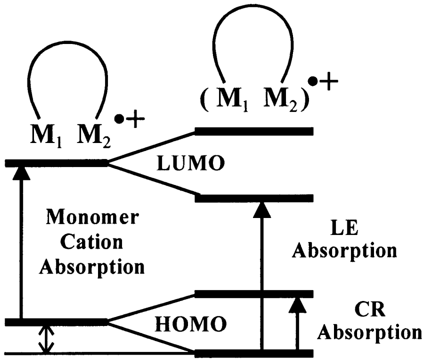

Figure 1. Schematic energy diagram of a radical cation of bischromophoric compounds with a conformation where the two aromatic moieties are close to each other. M_1 and M_2 are the same kind of aromatic molecules. Left: a positive charge is completely localized at M_2. Right: a positive charge is delocalized over M_1 and M_2. E_{CR} denotes the stabilization energy due to the charge resonance.

There have been many structural and kinetic studies on excimers and dimer cations formed in solutions using bischromophoric model compounds.[12−17] Both *meso*- and *racemic*-2,4-di(*N*-carbazolyl)pentane (*m*- and *r*-DCzPe) have been used as model compounds for the isotactic and syndiotactic sequences in PVCz, respectively.[12−15] From the analogy of Cz excimers, Masuhara et al. proposed that *m*- and *r*-DCzPe form the fully and

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partially overlapped dimer cations in DMF solutions, respectively.[15] Our research group has directly observed the CR band due to Cz dimer cations formed in solutions by near-IR transient absorption spectroscopy.[6−8,11−13] Tsujii et al. revealed that the fully overlapped dimer cation is more stable than the partially overlapped dimer cation by the near-IR transient absorption spectroscopy[12,13] and the radical-cation transfer method.[18] They also demonstrated by the matrix-isolation spectroscopy that the Cz dimer cations are dynamically formed by conformational changes after photoionization.[13]

On the other hand, there is little knowledge about structures and formation of dimer cations in polymer solids. In polymer solids, most molecular motions including main chains are highly restricted below the glass transition temperature. Thus, Cz dimer cations in PVCz solids are believed to be formed mainly owing to hole migration to trap sites, e.g., excimer forming site, where two Cz moieties are close enough to delocalize the hole.[2,9] Heretofore, there have been no reports on dynamical formation of dimer cations by conformational changes in polymer solids below the glass transition temperature. The present study not only shows the structures of Cz dimer cations in polymer solids but also provides clear evidence that Cz dimer cations in polymer solids are dynamically formed by conformational changes even below the glass transition temperature. In particular, the latter finding leads to a new concept for the hole transport mechanism in photoconductive polymers.

2. Experimental Part

Materials. The synthesis of *m*-DCzPe and *r*-DCzPe has been described elsewhere.[18] *N*-Ethylcarbazole (EtCz) was synthesized by the reaction of sodium carbazole with ethyl bromide and purified by recrystallization. Methyl methacrylate (MMA) (Nacalai Tesque) was washed with aqueous 5% NaOH solution, dried by Na_2SO_4, and then distilled under reduced pressure. PMMA solids doped with the Cz compounds were prepared in Pyrex cells ($1 \times 1 \times 4$ cm^3) by bulk polymerization of degassed MMA solutions containing ca. 5×10^{-4} mol L^{-1} of the dopants (*m*-DCzPe, *r*-DCzPe, or EtCz) and 5×10^{-4} mol L^{-1} of 2,2′-azobis(isobutyronitrile) as an initiator. The polymerization was done at 60 °C for 12 h, 90 °C for 12 h, and then 120 °C for 12 h. The fraction of residual monomer was estimated to be less than 0.7 mol % by ^{1}H NMR measurement. The glass transition temperature was estimated to be 390−391 K by DSC measurement at a heating rate of 10 K min^{-1}. These results show that plasticization due to the residual monomer is negligible.

Measurements. The dopants in the samples were photoionized at 77 K by irradiation of laser pulses (308 nm, 20 mJ cm^{-2}, fwhm ca. 17 ns, repetition frequency 10 Hz) from a XeCl excimer laser (Lambda Physik, EMG101MSC). Both sides of each sample were irradiated for 250 s. Emission spectra of the samples were measured at room temperature with a fluorescence spectrophotometer (Hitachi, 850). Absorption spectra of the irradiated samples settled in a quartz Dewar were measured with a spectrophotometer (Hitachi, U-3500) at several temperatures from 77 to 290 K. The temperature of the samples was controlled by liquid nitrogen or precooled nitrogen gas. Absorption spectra of ions produced by the irradiation were obtained as the differences of absorption spectra after the irradiation and those before the irradiation at each temperature. The decay of the ions during the spectroscopic measurement was negligible because the ions formed in PMMA solids were so stable that about half of the ions remained 12 h after the photoionization even at room temperature.[19−22]

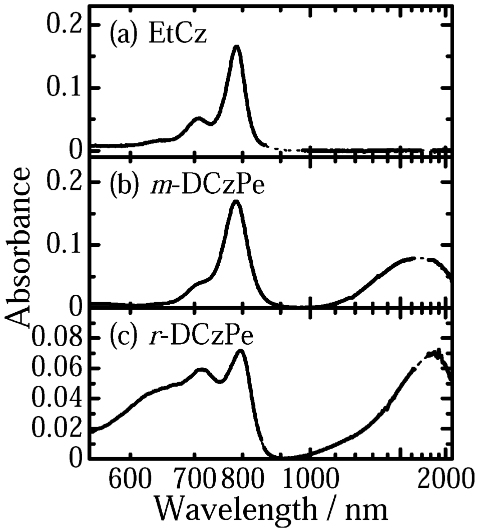

Figure 2. Absorption spectra of Cz cations formed in PMMA solids doped with (a) EtCz, (b) *m*-DCzPe, and (c) *r*-DCzPe after photoionization at room temperature.

3. Results and Discussion

Structures of Cz Dimer Cations Formed in PMMA Solids. First, we discuss the structures of intramolecular dimer cations formed in PMMA solids. Parts a, b, and c of Figure 2 show absorption spectra of EtCz, *m*-DCzPe, and *r*-DCzPe in PMMA solids photoirradiated at room temperature, respectively. The EtCz cation (Figure 2a) in PMMA solids had an absorption peak at 785 nm but no absorption in the near-IR region. On the other hand, the *m*-DCzPe cation in PMMA solids (Figure 2b) had a broad absorption around 1650 nm in addition to an absorption peak at 785 nm, and the *r*-DCzPe cation in PMMA solids (Figure 2c) had a broad absorption band around 1850 nm in addition to absorption peaks at 715 and 795 nm. Tsujii et al. reported transient absorption spectra of the same compounds in DMF solutions and found LE and CR bands characteristic of dimer cations.[12,13] They reported that *m*-DCzPe had LE and CR bands at 780 and around 1600 nm, respectively, and ascribed them to the fully overlapped dimer cation. They also reported that *r*-DCzPe had LE and CR bands at 710 and 1800 nm, respectively, and ascribed them to the partially overlapped dimer cation. The absorption spectra observed for PMMA solids were similar to those for DMF solutions except for the absorption at 795 nm of *r*-DCzPe: this absorption was ascribed to the isolated Cz radical cation. Therefore, these findings show that the structures of Cz dimer cations formed in PMMA solids are similar to those formed in solutions, i.e., the fully overlapped dimer cation for *m*-DCzPe and the partially overlapped dimer cation for *r*-DCzPe.

Formation of Cz Dimer Cations in PMMA Solids. Here, we discuss whether the Cz dimer cations were dynamically formed in PMMA solids or not. Assuming that conformational changes of Cz molecules are completely restricted in PMMA solids below the glass transition temperature, the Cz dimer cations are formed only in specific molecules where the two Cz moieties are occasionally located close enough to electronically interact. These two Cz moieties should form an excimer in the excited state. However, no excimer fluorescence was observed for *m*- or *r*-DCzPe in PMMA solids before

Table 1. Peak Wavelengths and Molar Absorption Coefficients of Cz Cations

	monomer cation	fully overlapped dimer cation		partially overlapped dimer cation	
		LE	CR	LE	CR
λ_{max}/nm	785[a]	780	1650	710	1800
ϵ/M^{-1} cm^{-1}	9400[a]	7800	4600	3100	4800

[a] The values are taken from ref 24.

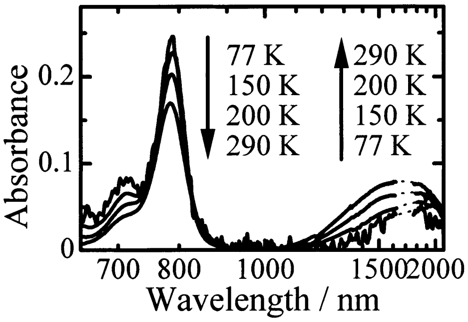

Figure 3. Absorption spectra of Cz cations of *m*-DCzPe in PMMA solids at several temperatures after the photoionization at 77 K.

the photoionization. This finding clearly proves that the two Cz moieties in *m*- and *r*-DCzPe molecules are far apart from each other in the ground and singlet excited states and that there are no aggregations of *m*- or *r*-DCzPe molecules in PMMA solids. To evaluate the molar fractions of the Cz dimer cations to all Cz cations formed in PMMA solids, we estimated the molar absorption coefficients of the LE and CR bands of the fully and partially overlapped Cz dimer cations from the transient absorption spectra of *m*- and *r*-DCzPe molecules in DMF solutions.[23] The estimated values are listed in Table 1.

Molar fractions of the dimer cations for *m*- and *r*-DCzPe in PMMA solids at room temperature were calculated to be ca. 80 and 70%, respectively.[25] This shows that most Cz cations in *m*- and *r*-DCzPe form the dimer cations not the isolated Cz radical cation. Therefore, we conclude that these Cz dimer cations are dynamically formed after the photoionization by conformational changes in PMMA solids even below the glass transition temperature. This finding demonstrates that dynamical formation of hole traps has to be considered for the hole transport in PVCz solids even below the glass transition temperature.

(A) Conformational Change in *m*-DCzPe Dimer Cations in PMMA Solids. Figure 3 shows the absorption spectra of *m*-DCzPe cations in PMMA solids at several temperatures. As the temperature increased from 77 to 290 K, the absorbance of the CR band in the near-IR region increased whereas the absorbance of the isolated Cz radical cation at 785 nm decreased. The compensative changes in the two bands show that isolated Cz radical cation gradually converts to the dimer cations as the temperature increased. In addition to the changes in absorbance, the peak wavelength of the CR band shifted from 1800 to 1650 nm as the temperature increased. This finding shows that most dimer cations have structures similar to the partially overlapped dimer cation at 77 K and convert to the fully overlapped dimer cation with increasing temperature.

To discuss the driving force for the formation of the dimer cations, we examined the reversibility of the formation of the dimer cations with increasing and decreasing temperature. The absorption spectra remained much the same even when the polymer solids were subsequently cooled to 77 K. This result shows that the dimer cations formed cannot reversibly return to the isolated Cz radical cation when the temperature decreases again. Thus, the formation of the dimer cations with increasing temperature is kinetically controlled. Even at room temperature, the formation is still kinetically controlled because 20% of Cz cations did not form the fully overlapped dimer cation in PMMA solids at room temperature whereas all Cz cation formed the fully overlapped dimer cation in DMF solutions at room temperature. The nonequilibrium formation of the dimer cations results from high restriction of molecular motions in polymer solids.

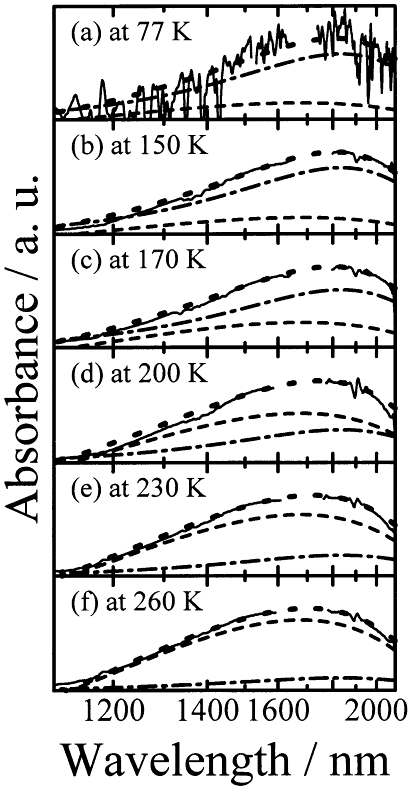

Figure 4. Spectral separations of CR bands at (a) 77, (b) 150, (c) 170, (d) 200, (e) 230, and (f) 260 K. The solid lines represent experimental data. The dotted lines represent the linear combinations of the CR bands of the fully overlapped dimer cation (dashed line) and the partially overlapped dimer cation (dash−dotted line) formed in PMMA solids at room temperature.

Next, we evaluated the temperature dependence of the formation of the dimer cations. The molar fractions of each Cz dimer cation were evaluated from spectral separation of the CR bands. In the previous section, we revealed that most *m*- and *r*-DCzPe molecules form the fully and partially overlapped dimer cations in PMMA solids at room temperature, respectively. Thus, we used the CR band of *m*- and *r*-DCzPe in PMMA solids at room temperature as a template of the fully and partially overlapped dimer cations, respectively. As shown in Figure 4, the CR bands of *m*-DCzPe were well reproduced at each temperature with linear combinations of the two templates. Figure 5 shows the temperature dependence of the molar fraction of the fully overlapped dimer cation to all dimer cations. The molar fraction was almost constant below 170 K and steeply increased around 200−290 K. This sudden increase shows that

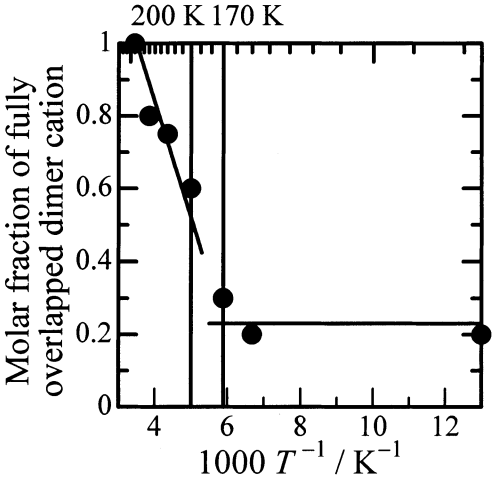

Figure 5. Temperature dependence of the molar fraction of the fully overlapped dimer cation to all dimer cations of *m*-DCzPe in PMMA solids.

the formation of the dimer cations is sensitive to a sub-transition of PMMA.

The temperature observed corresponds to the transition temperature of the β-relaxation in PMMA solids. The transition temperature of β-relaxation in polymer solids heavily depends on the measuring frequency. Spiess et al. reported a plot between the transition temperature of the β-relaxation in PMMA solids and correlation time obtained with the NMR measurement and relaxation time obtained with dielectric and dynamic-mechanical measurements.[26] From extrapolation of the plot to our measuring time range of 10^4−10^5 s, the transition temperature of the β-relaxation in PMMA solids was evaluated to be lower than 200 K. This temperature is in good agreement with the transition temperature observed in Figure 5. Horie et al. reported that the free volume in PMMA solids increases above 170 K because of the β-relaxation by using the positron annihilation lifetime measurement.[27] Therefore, we conclude that the conformational change to form the fully overlapped Cz dimer cation in *m*-DCzPe is allowed by an increase in the free volume due to the β-relaxation in PMMA solids.

Next, we discuss the conformational change in *m*-DCzPe dimer cations in terms of the free volume in PMMA solids. We assumed that the conformation of *m*-DCzPe in PMMA solids before the photoionization is TG/GT conformation, which is reported to be most preferable conformation of *m*-DCzPe in solutions.[14,28] Below 170 K, most of the Cz cations in *m*-DCzPe molecules retained the TG/GT conformation, and less than half (ca. 35% at 150 K, ca. 40% at 170 K) of the Cz cations changed their conformation from TG/GT to the partially overlapped dimer cation.

Figure 6 shows the conformations and the mutual configurations of the two Cz moieties in *m*-DCzPe. The conformational change from TG/GT conformation to the partially overlapped dimer cation requires a small free volume: only 30° rotation around one C−C bond in the pentane chain. Above 200 K, as shown in Figure 6, *m*-DCzPe molecules change their conformations from TG/GT to TT conformation where the fully overlapped dimer cation is formed. This conformational change requires a large free volume sufficient to rotate a Cz moiety 120° around one C−C bond in the pentane chain. This conformational change probably needs an increase in free volume due to the β-relaxation.

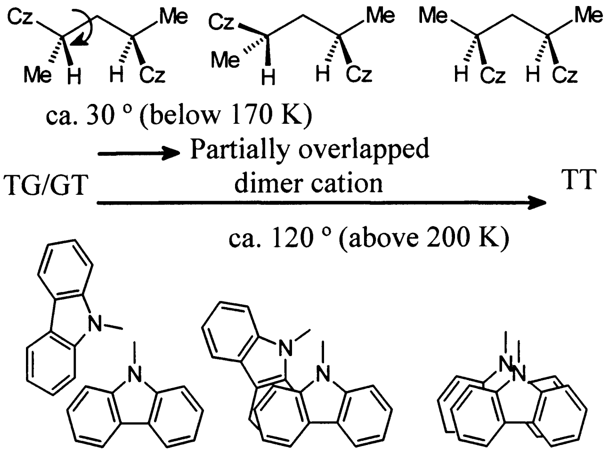

Figure 6. Conformational change of *m*-DCzPe from TT to the conformation of the fully overlapped dimer cation. (upper). Mutual configurations of the two Cz moieties (bottom).

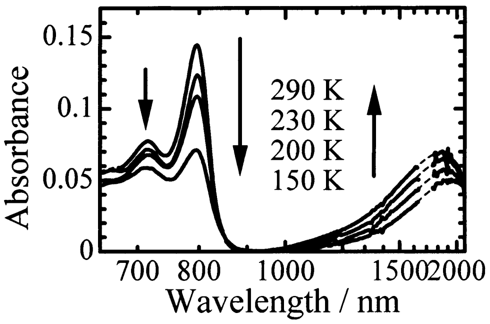

Figure 7. Absorption spectra of Cz cations of *r*-DCzPe in PMMA solids at several temperatures after the photoionization at 77 K.

The volume required for the formation of the fully overlapped dimer cation was roughly estimated to be about 300 Å^3 from the product of the area of a Cz moiety and the path length of the centroid of the Cz moiety. Torkelson et al. reported photoisomerization of 4,4′-diphenylazobenzene in PMMA solids under continuous irradiation at 25 °C and estimated the volume required for the photoisomerization to be 356 Å^3.[29] This value is similar to the volume required for *m*-DCzPe to form the fully overlapped dimer cation. However, the value seems too large as physical voids in polymer solids below the glass transition temperature.[29] Naito et al. proposed that photoisomerization was promoted by the thermal fluctuation of the free volume in polymer solids.[30] In our system, the lifetime of the Cz cation formed in PMMA solids is so long that the free volume thermally fluctuated became large enough to form the fully overlapped dimer cation, whereas the lifetime of the excited Cz is too short to form Cz excimers.

(B) Conformational Change in *r*-DCzPe Dimer Cation in PMMA Solids. Figure 7 shows the absorption spectra of *r*-DCzPe cations formed in PMMA solids at several temperatures. As the temperature increased from 150 to 290 K, the absorbance of the CR band in the near-IR region increased whereas the absorbance of the isolated Cz cation at 795 nm decreased. The isolated Cz cation formed in *r*-DCzPe was gradually converted to the partially overlapped dimer cation as the temperature increased.

Figure 8 shows the temperature dependence of the molar fraction of the partially overlapped dimer cation to all cation. The slope in Figure 8 becomes steeper

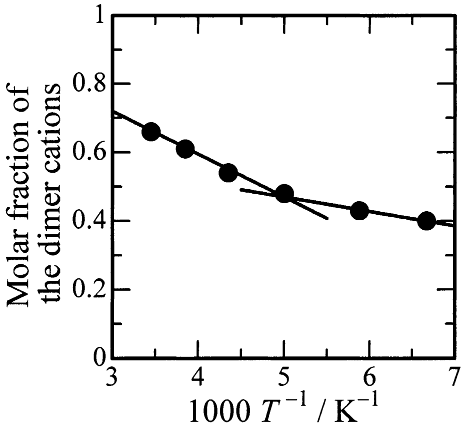

Figure 8. Temperature dependence of the molar fraction of the dimer cations to all cations of *r*-DCzPe in PMMA solids.

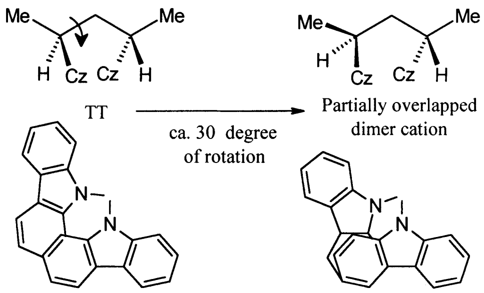

Figure 9. Conformational change of *r*-DCzPe from TT to the conformation of the partially overlapped dimer cation (upper). Mutual configurations of the two Cz moieties (bottom).

above 200 K. This transition temperature was ascribed to the β-relaxation in PMMA solids along the discussion described above for *m*-DCzPe. Thus, the formation of the dimer cation of *r*-DCzPe is essentially similar to that of *m*-DCzPe. The formation of the partially overlapped dimer cation of *r*-DCzPe in PMMA solids is kinetically controlled and is promoted by an increase in the free volume due to the β-relaxation in PMMA solids. The difference in the formation of the dimer cations between *r*-DCzPe and *m*-DCzPe is only the route of the conformational change. As shown in Figure 9, the partially overlapped dimer cation of *r*-DCzPe is formed from TT conformation[14,28] via a ca. 30° of rotation around one C−C bond in the pentane chain.

4. Conclusions

Below the glass transition temperature, *m*- and *r*-DCzPe form the dimer cations in PMMA solids. The structures of the dimer cations in PMMA solids at room temperature are similar to those in DMF solutions, i.e., the fully overlapped dimer cation for *m*-DCzPe and the partially overlapped dimer cation for *r*-DCzPe. These dimer cations are dynamically formed by conformational changes after the photoionization even in PMMA solids below the glass transition temperature. The fully overlapped dimer cation of *m*-DCzPe in PMMA solids is formed by the conformational change from TG/GT to TT conformation. The partially overlapped dimer cation of *r*-DCzPe in PMMA solids is formed by the conformational change from TT conformation. The dynamical formation of dimer cations in polymer solids is allowed by an increase in the thermally fluctuated free volume due to the β-relaxation in PMMA solids. The thermal fluctuation enough to form Cz dimer cations results from the long lifetime of Cz cations formed in PMMA solids. These findings lead to a new concept for the hole transport mechanism in photoconductive polymers: dimer cations, which are one of hole traps, are dynamically formed by conformational changes in photoconductive polymer solids even below the glass transition temperature, and the dynamical formation is sensitive to sub-transitions such as β-relaxation in polymer solids.

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References and Notes

(1) Pearson, J. M.; Stolka, M. In *Poly(N-vinylcarbazole)*; Gordon and Breach, Science Publishers: New York, 1981; Chapter 4.
(2) Miyasaka, H.; Moriyama, T.; Ide, T.; Itaya, A. *Chem. Phys. Lett.* **1998**, *92*, 339−344.
(3) Miyasaka, H.; Khan, S. R.; Itaya, A. *J. Phys. Chem. A* **2002**, *106*, 2192−2199.
(4) Ito, S.; Yamashita, K.; Yamamoto, M.; Nishijima, Y. *Chem. Phys. Lett.* **1985**, *117*, 171−175.
(5) Ohmori, S.; Ito, S.; Yamamoto, M. *Ber. Bunsen-Ges. Phys. Chem.* **1989**, *93*, 815−824.
(6) Tsujii, Y.; Tsuchida, A.; Onogi, Y.; Yamamoto, M. *Macromolecules* **1990**, *23*, 4019−4023.
(7) Tsuchida, A.; Nagata, A.; Yamamoto, M.; Fukui, H.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1285−1289.
(8) Ohkita, H.; Nomura, Y.; Tsuchida, A.; Yamamoto, M. *Chem. Phys. Lett.* **1996**, *263*, 602−606.
(9) Yokoyama, M.; Akiyama, K.; Yamamori, N.; Mikawa, H.; Kusabayashi, S. *Polym. J.* **1985**, *17*, 545−548.
(10) Badger, B.; Brocklehurst, B. *Nature (London)* **1968**, *219*, 263.
(11) Tsujii, Y.; Takami, K.; Tsuchida, A.; Ito, S.; Onogi, Y.; Yamamoto, M. *Polym. J.* **1990**, *22*, 319−325.
(12) Yamamoto, M.; Tsujii, Y.; Tsuchida, A. *Chem. Phys. Lett.* **1989**, *154*, 559−562.
(13) Tsujii, Y.; Tsuchida, A.; Yamamoto, M.; Momose, T.; Shida, T. *J. Phys. Chem.* **1991**, *95*, 8635−8640.
(14) De Schryver, F. C.; Vandendriessche, J.; Toppet, S.; Demeyer, K.; Boens, N. *Macromolecules* **1982**, *15*, 406−408.
(15) Masuhara, H.; Tamai, N.; Mataga, N.; De Schryver, F. C.; Vandendriessche, J. *J. Am. Chem. Soc.* **1983**, *105*, 7256−7262.
(16) Tani, K.; Tohda, Y.; Takemura, H.; Ohkita, H.; Ito, S.; Yamamoto, M. *Chem. Commun.* **2001**, 1914−1915.
(17) Ohkita, H.; Ito, S.; Yamamoto, M.; Tohda, Y.; Tani, K. *J. Phys. Chem. A* **2002**, *106*, 2140−2145.
(18) Tsujii, Y.; Tsuchida, A.; Yamamoto, M.; Nishijima, Y. *Macromolecules* **1988**, *21*, 665−670.
(19) Yamamoto, M.; Ohkita, H.; Sakai, W.; Tsuchida, A. *Synth. Met.* **1996**, *81*, 301−304.
(20) Ohkita, H.; Sakai, W.; Tsuchida, A.; Yamamoto, M. *Macromolecules* **1997**, *30*, 5376−5383.
(21) Ohkita, H.; Ishii, H.; Ito, S.; Yamamoto, M. *Chem. Lett.* **2000**, 1092−1093.
(22) Ohkita, H.; Ishii, H.; Ogi, T.; Ito, S.; Yamamoto, M. *Radiat. Phys. Chem.* **2001**, *60*, 427−432.
(23) The transient absorption spectrum of *r*-DCzPe in DMF solutions containing *p*-dicyanobenzene (*p*-DCNB) had no absorption peak or shoulder at 785 nm.[12,13] This result indicates that in DMF solutions all Cz cations of *r*-DCzPe are dimer cations. Furthermore, it is assumed that all cations of *m*-DCzPe in DMF solutions are dimer cations because fully overlapped dimer cation is more stable than partially overlapped dimer cation.[12,13,18] Therefore, the amount of fully or

partially overlapped dimer cation in DMF solutions is the same as that of *p*-DCNB radical anion. The absorption of *p*-DCNB radical anion appears at 430 nm with 6500 mol^{-1} L cm^{-1} of molar absorption coefficient.[24] Thus, the molar absorption coefficients of LE and CR bands were calculated from the comparison of the absorbance of LE and CR bands with that of *p*-DCNB radical anion, on the assumption that the absorption coefficients of the Cz dimer cations at 430 nm are the same as that of radical cation of EtCz in PMMA solids (1900 mol^{-1} L cm^{-1}).

(24) Tsuchida, A.; Yamamoto, M.; Nishijima, Y. *J. Phys. Chem.* **1984**, *88*, 5062−5064.

(25) In the calculation, the absorbance at 785 nm was assumed to be ascribed to the isolated Cz cation only.

(26) Schmidt-Rohr, K.; Kulik, A. S.; Backham, H. W.; Ohlemacher, A.; Pawelzik, U.; Boeffel, C.; Spiess, H. W. *Macromolecules* **1994**, *27*, 4733−4745.

(27) Li, H. L.; Ujihara, S.; Tanaka, S.; Yamashita, T.; Horie, K. *J. Radioanal. Nucl. Chem.* **1996**, *210*, 543−553.

(28) Abe, A.; Kobayashi, H.; Kawamura, T.; Date, M.; Uryu, T.; Matsuzaki, K. *Macromolecules* **1988**, *21*, 3414−3419.

(29) Royal, J. S.; Victor, J. G.; Torkelson, J. M. *Macromolecules* **1992**, *25*, 729−734.

(30) Naito, T.; Horie, K.; Mita, I. *Macromolecules* **1991**, *24*, 2907−2911.

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