Charge-transfer Complexes of Vinyl Polymers with Large Pendant π-electron Systems. I. Poly(*N*-vinylcarbazole) and Related Compounds

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The absorption spectra and the thermodynamic constants (K_{CT}, ΔH, and ΔS of formation) of the charge-transfer (CT) complexes of poly-*N*-vinylcarbazole (PVCz), the oligomers of *N*-vinylcarbazole (VCzOlig I and II, $\overline{DP}=5$ and 10 respectively), poly-*N*-carbazolylethylvinylether (PCzEVE), and the monomeric model compounds were examined in solution in order to clarify the characteristics of the complexes of polymeric donors with large pendant π-electron systems. The apparent spectra were resolved into two CT bands. The complexes of PVCz and VCzOlig II showed a lower frequency shift in the absorption maximum of the first CT band and an increase in the intensity ratio of the first to the second CT bands as compared with those of the monomeric complexes. This behavior, regarded as a kind of so-called polymer effect, seems to arise from some electronic interaction between neighboring carbazolyl groups in one polymer chain; it can be explained by variation both in the electron-donating character and in the distribution of the orientational isomers between the PVCz complexes and the others. A comparison of the observed values of K_{CT}, ΔH, and ΔS among the donors suggested that a dominant factor in determining these values is the steric hindrance rather than the small difference in the electron-donating character in the case of the structurally related polymeric complexes. The steric hindrance is important in the complexes of PCzEVE and VCzOlig I, where the electronic interaction is hardly present.

There have been many spectrophotometric investigations concerning a charge-transfer (CT) complex in which the donor consists of a polymeric species. The characteristics of CT complexes of polymeric donors can be clarified by a detailed comparison of both the absorption spectra and the thermodynamic constants (equilibrium constant (K_{CT}), and enthalpy (ΔH), and entropy (ΔS) of formation) of polymeric CT complexes with those of the corresponding monomeric ones. However, such a comparison has been made for only a few polymers.[1–6] Iwatsuki and Arai have studied the CT complexes formed between either poly-*N*-dimethylaminostyrene, copolymers of *N*,*N*-dimethylaminostyrene with styrene, or *N*,*N*-dimethyltoluidine and maleic anhydride; they have found a bathochromic shift in the CT absorption maximum and increases both in K_{CT} and in ΔH with an increase in the mean sequence length of the *N*,*N*-dimethylaminostyrene units. They have concluded that the electron-donating character of the dimethylaniline group increases with an increase in the number of groups attached to one polymer chain. This may be regarded as a kind of "polymer effect."

On the other hand, of the vinylpolymers with large pendant π-electron systems, poly-*N*-vinylcarbazole (PVCz) has been studied by two groups of investigators. Rembaum and his co-workers[4] have reported that K_{CT} values determined by the Benesi-Hildebrand method[7] were higher for the monomeric model, *N*-ethylcarbazole (ECz), than for the polymer, while Boudevska[5] have reported the opposite result for K_{CT} values determined by a modification of the successive dilution. Furthermore, the CT absorption maxima, ΔH, and ΔS have never been compared in detail between PVCz and ECz. Thus, no information about the "polymer effect" has been obtained in the case of CT complexes of the vinylpolymers with large pendant π-electron systems.

Recently, the present authors[8] have found, from the absorption spectra of the vinylpolymers, that there is some electronic interaction between pendant π-electron systems in one polymer chain in solution only for the vinylpolymers with large pendant π-electron systems connected directly to the skeletal chain. It seemed that it would be very interesting to see how the interaction affects the properties of the polymeric CT complexes. In the present series of papers, the authors have examined systematically the CT complexes of the vinylpolymers with large pendant π-electron systems and their monomeric compounds. This paper will deal with the CT complexes of PVCz and related compounds.

Experimental

Materials. The donor compounds studied were the following seven compounds containing carbazolyl (Cz) groups.

The ECz, 1,4-bis(*N*-carbazolyl)butane (DCzB), and 1,3-bis(*N*-carbazolyl)propane (DCzP) were used as monomeric model compounds of PVCz. They were prepared from purified carbazole[9] according to the literature.[10]

The oligomers of *N*-vinylcarbazole (VCz) were prepared by the HCl-initiated polymerization of VCz in acetonitrile. A 10-ml portion of acetonitrile containing 5×10^{-5} mol of dry HCl was stirred into 150 ml of acetonitrile containing 5 g of purified VCz and 2 ml of methanol at 10 °C in the dark. After half an hour, the solution was poured into 500 ml of a methanol–water (1:1) mixture. The oligomer was then filtered off, reprecipitated twice from the acetone solution with a methanol–water (7:3) mixture, and dried in a vacuum. The oligomer thus prepared (VCzOlig I) melts at 119—123 °C and has a degree of polymerization ($\overline{DP}$) of about 5. When no methanol was present in the polymerization solution, the oligomer (VCzOlig II) with a $\overline{DP}$ of about 10 and a mp of 175—185 °C was obtained.

The PVCz was prepared by the polymerization of a 0.5 M benzene solution of VCz in the presence of 1 mol % azobisisobutyronitrile in an evacuated sealed tube at 60 °C for 5 hr and was reprecipitated three times from the benzene solution with methanol. The polymer has $\overline{\mathrm{DP}}$ of about 600.

The poly-*N*-carbazolylethylvinylether (PCzEVE) was used as a high molecular compound related to PVCz, in which the Cz groups are connected to the skeletal chain at a distance of about 4 Å by $-O-CH_2-CH_2-$ bonds. The polymer was prepared by the polymerization of a 0.2 M toluene solution of *N*-carbazolylethylvinylether in the presence of 3 mol % $BF_3O(C_2H_5)_2$ under a nitrogen atmosphere at −25 °C for 9 hr[11] and was reprecipitated three times from the benzene solution with methanol. The polymer has a $\overline{\mathrm{DP}}$ of 33 and melts at 137—148 °C.

Tetracyanoethylene (TCNE), tetracyanoquinodimethane (TCNQ), *p*-chloranil (CA), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), and 2,3,7-trinitrofluorenone (TNF) were used as acceptor compounds. The TCNE was recrystallized twice from monochlorobenzene and was subsequently sublimed *in vacuo*. The TCNQ, CA, and DDQ were recrystallized twice from acetonitrile, benzene, and methylene chloride respectively. The TNF was prepared from fluorenone according to the literature.[12]

The ethylene chloride used as a solvent was purified by the ordinary method.

Method. The absorption spectra and optical density were measured by means of two Shimadzu spectrophotometers, UV-200 and MPS-50 L, using 1-cm quartz cells and a temperature-regulated cell holder.

The K_{CT} was determined by the use of the Benesi-Hildebrand equation (1):[7]

$$[A]_0(l/A_\lambda) = (1/\varepsilon K_{CT}[D]_0) + (1/\varepsilon) \qquad (1)$$

where $[A]_0$ and $[D]_0$ are the initial concentrations of the acceptor and the donor respectively; l is the path length; A_λ is the absorbance at λ due only to the complex, and ε is the molar extinction coefficient of the complex at λ. This equation is valid for a 1:1 complex when $[D]_0 \gg [A]_0$.

The K_{CT} was determined at six different temperatures from 2 °C to 30 °C. The ΔH and ΔS of formation of a CT complex were calculated by using Eq. (2),

$$\ln K_{CT}\varepsilon = (-\Delta H/RT) + (\Delta S/R) + \ln \varepsilon \qquad (2)$$

Results and Discussion

The complexes with DDQ were unstable, and the CT spectra changed slowly with the time. Especially, the complexes with PCzEVE and VCzOlig I were more unstable and changes of the spectra began in a few minutes after the mixing. The other complexes were stable, and no change in absorbance with time was observed even after 12 hr. The 1: 1 stoichiometry of all the complexes studied was confirmed by the continuous-variation method.

CT Absorption Spectra. The absorption spectra of the complexes with TCNE, TCNQ, CA, and DDQ are shown in Figs. 1—3. The apparent CT absorption maxima (ν_{max}) and the shifts in ν_{max} ($\Delta\nu_{max}$) as compared with that of the ECz complex are listed in Table 1.

The apparent ν_{max} appears at lower frequencies for the polymeric donors than for the monomeric ones. This is especially clear in the case of the complexes with CA or DDQ. It is well-known that there is a linear relationship between the energy of the CT transition ($h\nu_{CT}$) and the ionization potential of the donor (I_p) for a series of complexes consisting of like donors and

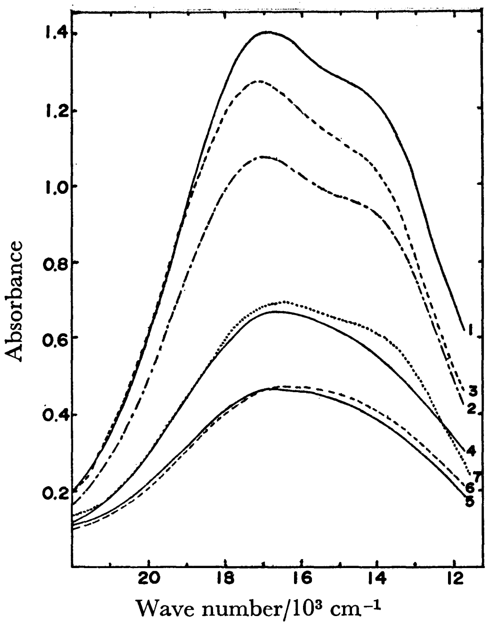


Fig. 1. CT spectra of TCNE complexes in ethylene chloride at 10 °C.

Donor	$[D]_0$	$[A]_0$
(1) ECz	0.0135 M	0.019 M
(2) DCzB	0.0135	0.019
(3) DCzP	0.016	0.023
(4) VCzOlig I	0.0185	0.023
(5) VCzOlig II	0.015	0.023
(6) PVCz	0.015	0.023
(7) PCzEVE	0.0134	0.007

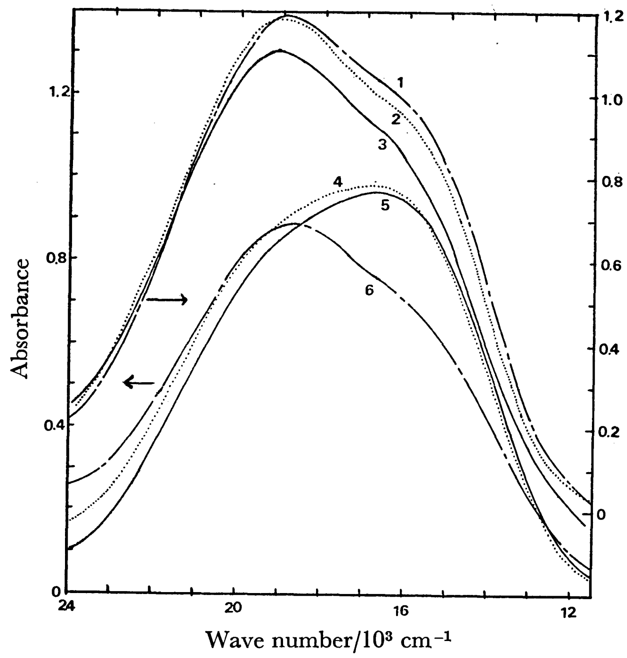
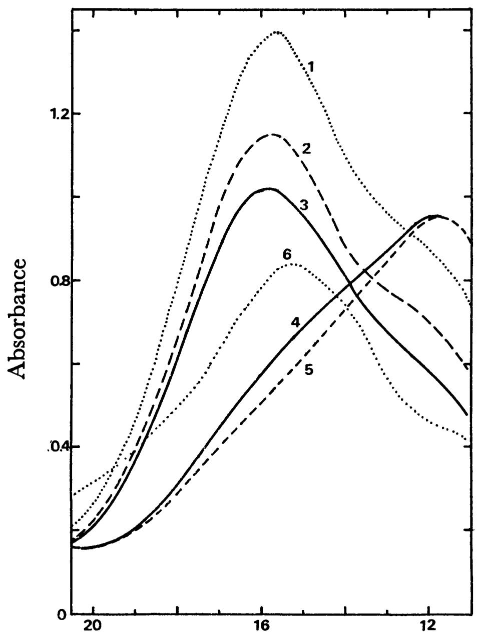


Fig. 2. CT spectra of CA complexes in ethylene chloride at 10 °C.

Donor	$[D]_0$	$[A]_0$
(1) ECz	0.050 M	0.011 M
(2) DCzB	0.050	0.011
(3) DCzP	0.050	0.011
(4) VCzOlig II	0.054	0.011
(5) PVCz	0.056	0.011
(6) PCzEVE	0.043	0.011



Wave number/10^3 cm^{-1}

Fig. 3. CT spectra of DDQ complexes in ethylene chloride at 10 °C.

Donor	$[D]_0$	$[A]_0$
(1) ECz	0.015 M	0.006 M
(2) DCzB	0.015	0.006
(3) DCzP	0.015	0.006
(4) VCzOlig II	0.030	0.006
(5) PVCz	0.030	0.006
(6) PCzEVE	0.008	0.003

Table 1. Apparent CT absorption maxima (ν_{max}) and the shifts in ν_{max} ($\Delta\nu_{max}$) as compared with that of the ECz complex[a)]

Donor	Acceptor	ν_{max}/cm^{-1}	$\Delta\nu_{max}$/cm^{-1}
ECz	TCNE	16810	—
DCzB		16950	140
DCzP		17090	280
VCzOlig I		16530	−280
VCzOlig II		16530	−280
PVCz		16260	−550
PCzEVE		16530	−280
ECz	TCNQ	17120	—
DCzB		17120	0
DCzP		17330	210
VCzOlig II		17010	−110
PVCz		16860	−260
PCzEVE		16640	−480
ECz	CA	18830	—
DCzB		18980	150
DCzP		19120	290
VCzOlig I		17550	−1280
VCzOlig II		17040	−1790
PVCz		16840	−1990
PCzEVE		18690	−140
ECz	DDQ	15720	—
DCzB		15800	80
DCzP		15820	100
VCzOlig II		11790	−3930
PVCz		11770	−3950
PCzEVE		(15270)	(−550)

a) at 10 °C in ethylene chloride; errors in ν_{max} and $\Delta\nu_{max}$ are ±20 cm^{-1}.

a common acceptor. However, in the present case, the lower frequency shift in the apparent ν_{max} should be considered not to correspond directly to a decrease in the I_p of the polymeric donors. This is because it is considered, for the following reasons that the spectra of all the complexes studied are composed of multiple overlapping bands: 1) in the spectra of the monomeric complexes, the absorption shoulders are apparently observed at frequencies lower than the apparent ν_{max}, and Klopffer has satisfactorily resolved the spectra of the complexes between *N*-isopropylcarbazole, one of the monomeric donors, and either TCNE or CA into two CT bands[13)]: 2) in the case of the polymeric donors, although the shoulders are hardly observed at all, the spectra have asymmetric bands with exceptionally large half bandwidths: 3) in the cases of CA and DDQ, although considerably shifted, the apparent absorption peaks for PVCz and VCzOlig II appear near the absortion shoulder for the monomeric donors.

Therefore, the spectra were resolved into two CT

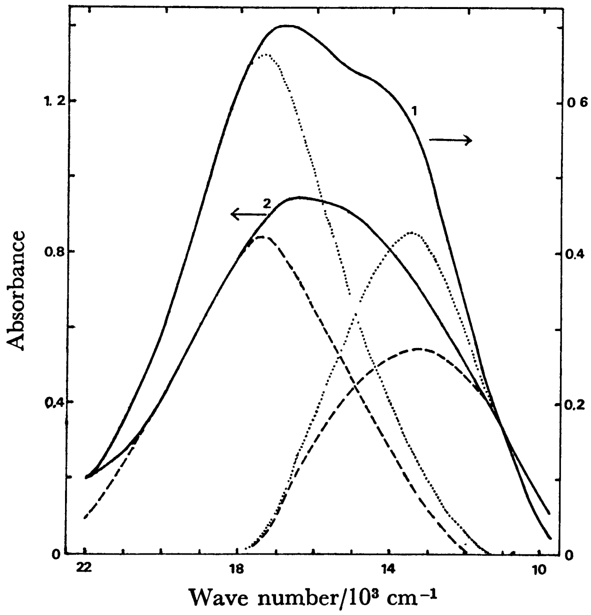


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Fig. 4. Resolution spectra of TCNE complexes of ECz (1) and PVCz (2).

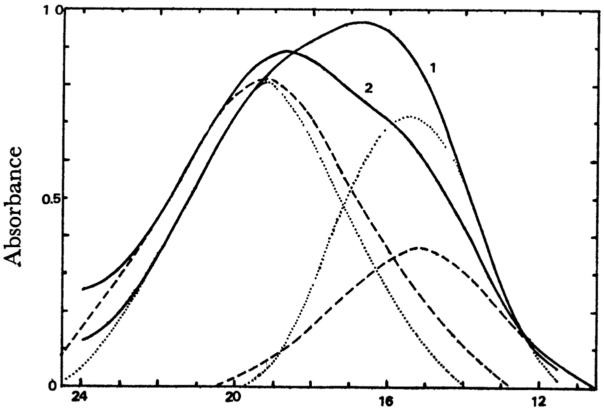

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Fig. 5. Resolution spectra of CA complexes of PVCz (1) and PCzEVE (2).

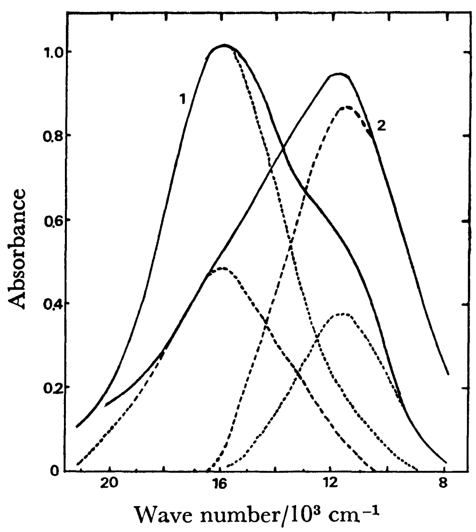

Fig. 6. Resolution spectra of DDQ complexes of DCzP (1) and PVCz (2).

Table 2. First and second CT band maxima (ν_1 and ν_2), the differences $\Delta\nu_{12}$ ($=\nu_2-\nu_1$) and $\Delta\nu_1$ ($\nu_1-\nu_{1\ \mathrm{ECz}}$), and intensity ratios of the first to the second CT bands (f_1/f_2)$^{a)}$

Donor	Acceptor	ν_1 cm^{-1}	ν_2 cm^{-1}	$\Delta\nu_{12}$ cm^{-1}	$\Delta\nu_1$ cm^{-1}	f_1/f_2
ECz	TCNE	13580	17400	3820	—	0.52
DCzB		13550	17400	3850	30	0.48
DCzP		13650	17400	3750	−70	0.40
VCzOlig I		13650	17400	3750	−70	0.45
VCzOlig II		13500	17400	3900	80	0.58
PVCz		13350	17400	4050	230	0.64
PCzEVE		13650	17400	3750	−70	0.54
ECz	TCNQ	12800	17100	4300	—	0.20
DCzB		12800	17100	4300	0	0.17
DCzP		12900	17300	4350	−100	0.17
VCzOlig II		12750	17100	4350	50	0.25
PVCz		12750	17100	4350	50	0.29
PCzEVE		12700	17200	4500	100	0.11
ECz	CA	15350	19250	3900	—	0.34
DCzB		15350	19250	3900	0	0.20
DCzP		15450	19250	3800	−100	0.25
VCzOlig I		15500	19250	3750	−150	0.42
VCzOlig II		15400	19250	3850	−50	0.63
PVCz		15500	19250	3750	−150	0.76
PCzEVE		15350	19250	3900	0	0.34
ECz	DDQ	11700	15900	4200	—	0.32
DCzB		11700	15900	4200	0	0.30
DCzP		11650	15900	4250	50	0.27
VCzOlig II		11500	15900	4400	200	1.4
PVCz		11400	15900	4500	300	1.7
PCzEVE		(11000)	(15300)	(4300)	(700)	(0.27)
ECz	TNF	18750	22900	4150		0.43
DCzP		(18750)	(23000)	(4250)		(0.41)
PVCz		(18750)	(23000)	(4250)		(0.49)

a) Errors in ν_1, ν_2, $\Delta\nu_{12}$ and $\Delta\nu_1$ are ± 100 cm^{-1} for the CA complexes of VCzOlig I, II and PVCz and ± 50 cm^{-1} for the other complexes. Errors in f_1/f_2 are $\pm 15\%$ for the former complexes and $\pm 10\%$ for the latter ones. The parenthesized numerical values are less reliable because of either decomposition of the complex or overlapping of absorption of TNF with that of the complexes.

bands by the use of a curve-analyzer, based on the assumptions that the individual resolved CT bands were symmetrical and that the location of the second CT band was almost the same for the complexes between a series of donors and a common acceptor. These assumptions seem reasonable judging from the spectra of the complexes with poly-1-vinylpyrene and related compounds.[14] The results were satisfactory, as is shown by the examples in Figs. 4—6. The absorption maxima of the first and the second CT bands (ν_1 and ν_2), the differences ($\Delta\nu_{12}$ and $\Delta\nu_1$ ($\Delta\nu_{12}=\nu_2-\nu_1$, and $\Delta\nu_1=\nu_1-\nu_{1\cdot\mathrm{ECz}}$)), and the intensity ratios (f_1/f_2) of the first to the second CT bands are listed in Table 2.

As the $\Delta\nu_{12}$ values are regarded to be constant at 4100 ± 400 cm^{-1} for all the complexes studied, irrespective of the acceptors, the first and the second CT bands are considered to be due to the CT from the highest occupied and the second highest occupied levels of the donor, respectively, to the lowest vacant level of the acceptor.

There is no appreciable difference in either ν_1 or f_1/f_2 among the monomeric donors, with the exception of ν_1 for DCzP. DCzP shows a little higher frequency shift in ν_1 as compared with the ν_1 values for the other monomeric donors. This is mainly due to the weakness of the electron-donating character of the substituent group per Cz ring as compared with that of an ethyl group, and not to some interactions between the two Cz rings connected at 1,3-positions, as was found in the study concerning the UV spectra.[8] PVCz and VCzOlig II show a lower frequency shift in ν_1 (50—300 cm^{-1}), with the exception of the ν_1 values for the CA complexes, and a considerable increase in f_1/f_2, especially in the cases of CA and DDQ, as compared with those for the monomeric donors. The changes are larger for PVCz than for VCzOlig II. VCzOlig I shows no clear shift in ν_1, but a small increase in f_1/f_2 only in the case of CA. On the other hand, PCzEVE shows no appreciable change in either ν_1 or f_1/f_2 as compared with those for the monomeric donors, in spite of the high value of $\overline{\mathrm{DP}}$.

It was thus clarified that the apparent complicated variation in the shape of the CT spectra between the monomeric and the polymeric donors results from the phenomena regarded as a kind of so-called polymer effect—namely, a lower frequency shift in ν_1 and a considerable increase in f_1/f_2 of the polymeric CT complexes as compared with those of the monomeric ones. It should be noted that the phenomena become clear with an increase in the $\overline{\mathrm{DP}}$, although they are unobservable for the pentamer, in a series of the polymers of VCz, and that they are not observed for PCzEVE, which has Cz groups apart from the skeletal chain in spite of the high value of $\overline{\mathrm{DP}}$ ($\overline{\mathrm{DP}}=33$). It is interesting that the $\overline{\mathrm{DP}}$ dependency of the shift in ν_1 mentioned above is quite different from that of the maleic anhydride complexes of poly-*N*,*N*-dimethylaminostyrene and related copolymers,[3] where the bathochromic shift results from the aminostyrene unit with a $\overline{\mathrm{DP}}$ value of only two.

The results mentioned above are closely related to the results obtained from the UV absorption spectra concerning the electronic interaction between pendant

π-electron systems in one polymer chain.[8] The phenomena mentioned above, therefore, seem to arise from some electronic interaction between neighboring Cz groups in one polymer chain.

The increase in f_1/f_2 upon a replacement of the monomeric donors by the polymeric ones is an interesting phenomenon which has hitherto never been reported, to the knowledge of the authors. It has been suggested that the complexes between either naphthalene or substituted benzenes and TCNE in solution have isomers differing in the mutual orientations of the symmetry axes of the donor and acceptor.[15] Kuroda and his co-workers[16] have made a theoretical treatment of the CT interaction in the TCNE complexes of naphthalene and pyrene, considering the effect of the interaction of higher CT states, and have concluded that the binding energy varies little with the angle between the symmetry axes of the donor and acceptor and that the energy barrier hindering the rotation of one molecule relative to its partner is less than 1 kcal/mol. Therefore, in some complexes, the orientational isomers are considered to coexist in solution with an almost equal probability because of the ease of the rotational interconversion among them. They have also suggested that f_1/f_2 is a parameter which offers information on the orientation of the donor molecule to the acceptor one.[16] The variation in f_1/f_2 in the present case may be a result of the orientational isomers, the distribution of which is affected by a perturbation effect of neighboring Cz groups to the complex. No detailed explanation can be offered at present.

TABLE 3. TEMPERATURE DEPENDENCE OF APPARENT CT ABSORPTION MAXIMA OF THE CA COMPLEXES OF PVCz AND VCzOlig II

	$\lambda_{\max}$ [nm][a)					
	2 °C	5 °C	10 °C	20 °C	35 °C	60 °C
VCzOlig II	590	586	585	573	556	—
PVCz	597	595	593	588	585	567

a) $[D]_0=0.156$ M (VCz unit), $[A]_0=0.007$ M in ethylene chloride.

In the complexes between either PVCz or VCzOlig II and CA, the apparent absorption maxima shifted reversibly to higher frequencies with an increase in the temperature, as is shown in Table 3. The shift was apparently due to a decrease in f_1/f_2 with an increase in the temperature and was larger for VCzOlig II than for PVCz. This suggests that the perturbation effect of neighboring Cz groups on the complex weakens according to the gradual disappearance of the local helical structure and/or the gradual ease of the internal rotation of a polymer chain with an increase in the temperature. The NMR measurements[17] have suggested that the internal rotation of the polymer chain, being restricted by neighboring bulky Cz groups, is sensitive to the temperature. In the PVCz (or VCzOlig II) complexes of TCNE and TCNQ, such a shift could not be observed, probably because of the small variation in f_1/f_2 between the PVCz and the ECz complexes.

The $h\nu_{\mathrm{CT}}$ for a series of complexes with a common acceptor can be described by the following expressions:

$$h\nu_{\mathrm{CT}} = (I_p - C_1) + C_2/(I_p - C_1) \quad (3)$$

$$h\nu_{\mathrm{CT}} = aI_p + b \quad (4)$$

where C_1, C_2, a, and b are constants for a given acceptor. The first and the second ionization potentials of ECz are determined to be 7.43 ± 0.03 eV and 8.02 ± 0.04 eV respectively by the use of sets of the constants for TCNE, TCNQ, CA, and TNF.[18] These values are in agreement with those reported by Klopffer,[13] and the first ionization potential (I_{p1}) is much smaller than the previously reported values, determined from the apparent absorption maxima.[4,19,20]

The lower frequency shift in ν_1 of the PVCz complexes as compared with the ν_1 of the monomeric complexes cannot be explained by supposing an effect of insufficient solvation due to both the polymer backbone and adjacent Cz groups, because such an effect would tend to cause a higher frequency shift, if it is present at all. The lower frequency shift in ν_1 may, therefore, be attributed to a decrease in the I_{p1} value of PVCz as compared with those of ECz due to some electronic interaction between neighboring Cz groups, assuming that the ν_1 varies little with a variation in the distribution of the orientational isomers. A decrease in the I_{p1} value of PVCz is evaluated to be about 0.03 eV from the variation in the ν_1 of the TCNE complexes, which is most reliable. This value seems reasonable, because it is comparable to the value of 0.04 eV for poly-1-vinylpyrene, the CT complexes of which show no variation in f_1/f_2 as compared with that of the monomeric CT complex.[14]

Thermodynamic Constants of the Formation of CT Complexes. For all the complexes studied, fairly good straight lines of Benesi-Hildebrand plots were obtained. The thermodynamic constants are listed in Table 4. Although Livina and his co-workers[20] have reported that the values of ε in the PVCz complexes have decreased with an increase in the temperature, ε was independent of the temperature in the region from 2 °C to 30 °C with the exception of the values of the complexes between either PVCz or VCzOlig II and CA. The data for the CA complexes are less reliable because of a little variation in the spectra with the temperature.

In a series of complexes with a common acceptor, the $\varepsilon_{\max}$ values are almost constant, contrary to the results reported by Boudevska.[5] The values of K_{CT}, $-\Delta H$, and $-\Delta S$ are in the following orders: ECz$>$DCzP$\sim$PCzEVE$>$VCzOlig$\sim$PVCz for K_{CT}; ECz$\sim$PCzEVE$>$PVCz$\gtrsim$VCzOlig$\gtrsim$DCzP for $-\Delta H$, and PVCz$>$VCzOlig$\sim$PCzEVE$>$ECz$>$DCzP for $-\Delta S$.

In general, there is a near-linear correlation between K_{CT} and $-\Delta H$ as well as between $-\Delta H$ and $-\Delta S$ for a set of complexes of a common acceptor with a series of structurally related donors.[21] In the present case, this correlation holds roughly only for the complexes with ECz and DCzP, where a dominant factor in determining K_{CT}, ΔH, and ΔS is the electron-donating character rather than the steric hindrance. The steric hindrance in a series of donors is considered to be in the order of: PVCz$>$VCzOlig$>$PCzEVE$>$DCzP$>$ECz. The values of K_{CT} and $-\Delta H$ of the complexes with PVCz and VCzOlig I and II are smaller than

TABLE 4. THERMODYNAMIC CONSTANTS OF FORMATION OF CT COMPLEXES[a)]

Donor	$[D]_0$ M	Acceptor	$[A]_0$ 10^3 M	ε_{max}[b)] (cm/M)	K_{CT} (M^{-1}) at 15 °C	$-\Delta H$ kcal/mol	$-\Delta S$ e.u.
ECz	0.02—0.2	TCNE	1.5	2500±150	2.8±0.2	3.2±0.2	8.9±0.5
DCzP	0.04—0.18		1.5	2500±150	1.9±0.2	2.5±0.2	7.0±1.0
VCzOlig I	0.08—0.3		3.0	2600±200	0.7±0.1	2.5±0.2	9.4±0.8
PVCz	0.06—0.3		3.0	2400±250	0.6±0.1	2.8±0.2	10.8±1.0
PCzEVE	0.04—0.2		3.0	2400±200	1.9±0.2	3.1±0.2	9.6±0.8
ECz	0.04—0.13	TCNQ	1.0	2600±200	3.5±0.3	3.8±0.2	10.8±0.7
DCzP	0.04—0.16		1.0	2600±200	2.0±0.2	3.1±0.2	10.2±1.0
PVCz	0.08—0.30		3.0	2300±300	0.9±0.2	3.2±0.2	11.4±1.0
ECz	0.06—0.2	CA	3.0	1720±150	1.3±0.2	3.0±0.2	9.4±0.6
DCzP	0.06—0.2		5.0	1800±200	1.0±0.2	2.7±0.2	10.2±0.8
VCzOlig II	0.06—0.2		6.0	1430±300[c)]	0.6±0.2	2.9±0.5	10.7±1.7
PVCz	0.05—0.2		6.0	830±120[c)]	1.0±0.2	3.4±0.4	12.0±1.5
ECz	0.02—0.1	TNF	2.0	2000±100	4.3±0.2	2.6±0.1	6.2±0.3
DCzP	0.03—0.18		2.0	2080±100	3.7±0.2	1.8±0.1	3.7±0.3
PVCz	0.05—0.2		3.0	1200±150	2.1±0.2	2.3±0.2	6.8±0.4

a) Solvent: methylene chloride for TNF and ethylene chloride for the other acceptors. b) at an apparent absorption maximum. c) at 15 °C.

those of ECz, in spite of a small enhancement in the electron-donating character of PVCz as compared with that of ECz. Futhermore, the value of K_{CT} of the PCzEVE complex is smaller than that of the ECz complex, in spite of no difference in the spectral properties (ν_1, ν_2, and f_1/f_2) between the former and the latter complexes. Therefore, it is clear that a dominant factor in determining K_{CT}, ΔH, and ΔS is the steric hindrance rather than a small difference in the electron-donating character in the case of the structurally related polymeric complexes. It should be noted that the situation is the same even in the case of VCzOlig I ($\overline{DP}=5$), as in the case of PVCz. This is quite different from the situation of the variation in both ν_1 and f_1/f_2 resulting from some electronic interaction between neighboring Cz groups.

The results presented above are in contrast to the results for the maleic anhydride complexes of poly-*N*,*N*-dimethylaminostyrene and related copolymers, where both K_{CT} and $-\Delta H$ increase with an increase in the $\overline{DP}$. This may be explained as follows. Poly-*N*,*N*-dimethylaminostyrene is one of the vinylpolymers with small pendant π-electron systems, although it is a fairly strong electron donor, and its electron-donating charater is to a considerable extent localized on the dimethylamino group. Therefore, the steric hindrance in forming a CT complex may not be serious in this polymer.

It is important to examine whether the interesting results for the PVCz complexes can be applied generally to the complexes of the other vinylpolymers with large pendant π-electron systems. A further study concerning the other polymeric complexes is now in progress.

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