Donor-Acceptor Interaction of Poly(N-methyl-3-vinylcarbazole)

Masaoki Furue, Kaoru Nakajima, Masao Saeki,
and Shun-ichi Nozakura

*Department of Polymer Science, Faculty of Science, Osaka
University, Toyonaka, Osaka 560, Japan.*

ABSTRACT: The formation of charge-transfer complexes of poly(N-methyl-3-vinyl-carbazole (P3VCA) with tetracyanoethylene (TCNE), 2,4,5,7-tetranitro-9-fluorenone (TeNF), chloranil (p-CA), and 1,3,5-trinitrobenzene (TNB) was investigated spectro-photometrically. The association constants (K) of P3VCA complexes were 2.5 to 7.1 times larger than those of the corresponding monomeric analog, N-methyl-3-ethyl-carbazole. To clarify the polymer effect, copolymers of N-methyl-3-vinylcarbazole with styrene and with the dimer model, 1,3-bis[3-(N-methylcarbazolyl)]propane, were studied to obtain the details of the complex formation. The complex of the dimer model was found to be less stable than those of the monomer analog and P3VCA. It is suggested that large stabilities in the polymer system do not simply result from the local concentration effect, but also from the favorable arrangements of the neighboring carbazole units.

KEY WORDS   Poly(N-methyl-3-vinylcarbazole) / N-Methyl-3-ethyl-carbazole / 1,3-Bis[3-(N-methylcarbazolyl)]propane / N-Methyl-3-vinylcarbazole—Styrene Copolymer / Charge-Transfer Complex / Donor—Acceptor Interaction / Polymer Effect /

Poly(N-vinylcarbazole) has been extensively studied in connection with the formation of charge-transfer complexes with various kinds of electron acceptors. Polymer complexes showed lower association constants than those of their monomeric and dimeric analogs.[1,2] The steric hindrance has been suggested as an important factor for the low stability of the polymer complex.

Poly(N-methyl-3-vinylcarbazole) (P3VCA) is a structurally related compound to PNVC, some NMR and emission studies have already been done.[3-5] In the present paper the charge-transfer complexes of P3VCA with tetracyanoethylene (TCNE), 2,4,5,7-tetranitro-9-fluorenone (TeNF), chloranil (p-CA), and 1,3,5-trinitrobenzene (TNB) were investigated spectrophotometrically. The association constants of P3VCA complexes, contrary to the case of PNVC, exhibited higher values than those of the corresponding monomeric analog, N-methyl-3-ethylcarbazole.

There are only a few examples in which positive polymer effects have been observed for vinyl polymers. Iwatsuki found in the system of p-dimethylaminostyrene polymers and acceptors a positive polymer effect with maleic anhydride and p-CA but a negative effect with trinitrotoluene.[6,7]

EXPERIMENTAL

Materials

N-Methyl-3-vinylcarbazole was prepared according to the method of Lopatinskii[8] and was recrystallized from ethyl alcohol before use; mp 70.5°C (lit.[8] mp 71°C).

N-Methyl-3-ethylcarbazole (3EtCA) was prepared according to the method of Buu-Hoi and Royer[9]; mp 28.5°C.

Anal. Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.17; H, 7.32; N, 6.58.

1,3-Bis[3-(N-methylcarbazolyl)]propane (1,3-BCAP) was newly synthesized by coupling the organic moiety of a lithium diarylcuprate with

that of an organic halide.[10] N-Methyl-3-carbazolyllithium was obtained as a white precipitate by the reaction of 20.8 g (0.08 mol) of N-methyl-3-bromo-carbazole in 60 ml of benzene and 17 ml of a hexane solution of n-butyllithium (5.0 M) for three hours at room temperature. After the reaction mixture was cooled to −78°C, the supernatant solution was removed by filtration; the solution was forced out through a glass-filter tube under nitrogen-gas pressure. The white precipitate was washed in portions with 400 ml of hexane, and dissolved in 250 ml of a dry mixture of ethyl ether and tetrahydrofuran (1 : 1 v/v) at −78°C. The yield of the lithium reagent was determined to be 80% by titration with a standard 0.1-N aq HCl solution. To the solution of the lithium reagent, copper(I) iodide (0.04 mol) was added in one portion under stirring and after five minutes 1,3-dibromo-propane (0.006 mol) was injected at −78°C. The resulting mixture, from which a yellow-green precipitate slowly separated, was stirred at −78°C for three hours, allowed to stand at room temperature for three days, and then poured onto 300 ml of a 10-% aq NH₄Cl solution. The organic layer was extracted with 300 ml of ethyl ether, washed with water, and dried over anhydrous magnesium sulfate. A green residual solid was obtained by evaporation of the solvents under reduced pressure and was subjected to chromatography on a 30 × 2.5 cm column of basic alumina. The first component eluted with hexane was N-methyl-carbazole. The second component eluted with hexane—benzene (1 : 1 v/v) was white crystals, which were recrystallized from benzene to yield 1,3-BCAP: yield 660 mg (27.4%); mp 162—164°C; m/e 402.

Anal. Calcd for $C_{29}H_{26}N_2$: C, 86.53; H, 6.51; N, 6.90. Found: C, 86.53; H, 6.45; N, 6.91.

TCNE was sublimed twice at atmospheric pressure. TeNF and TNB were recrystallized twice from glacial acetic acid. p-CA was recrystallized twice from acetone.

Dichloromethane for UV spectrophotometry was purified by the following procedure.[11] Commercial dichloromethane was washed with concentrated sulfuric acid, dilute sodium hydroxide, and distilled water. The washed material was left standing overnight over calcium

Table I. Copolymerization of N-methyl-3-vinylcarbazole (M_1) with styrene (M_2)

Expt no.	M_1 in feed, mol %	Polymerization time, hr	Conversion, %	M_1 unit in copolymer, mol %
1	12.6	3	7.6	16.4
2	23.5	3	7.5	29.1
3	35.6	3	6.6	42.6
4	40.6	4	8.1	46.7
5	47.1	3	6.9	55.4
6	58.4	3	8.1	65.8
7	70.1	3	7.4	76.6

chloride and fractionally distilled in a 50-cm Widmer column; bp 40—41°C.

Polymerization

Polymerization of N-methyl-3-vinylcarbazole. N-Methyl-3-vinylcarbazole (3 g) in 50 ml of toluene was placed in a 100-ml Schlenk tube under nitrogen. The solution was maintained at −78°C by a Dry Ice—acetone bath and then 2 ml of a hexane solution of boron trifluoride etherate (0.75 M) was added to the monomer solution. After two hours the reaction mixture was poured into 450 ml of methanol. The chloroform-soluble polymer was reprecipitated three times with methanol. Yield, 2.7 g. The molecular weight was found to be about 150,000 by a GPC measurement.

Copolymerization of N-methyl-3-vinylcarbazole with styrene. Free-radical copolymerization was carried out in benzene using AIBN at 60°C. Copolymers were isolated by precipitation with methyl alcohol and purified by at least two dissolution—precipitation steps, followed by drying under reduced pressure. Results of copolymerizations are shown in Table I. Monomer reactivity ratios of N-methyl-3-vinylcarbazole (M_1) and styrene (M_2) were $r_1 = 1.35 \pm 0.03$ and $r_2 = 0.741 \pm 0.007$. Q and e values of N-methyl-3-vinylcarbazole were calculated to be 1.35 and 0.8, respectively.

Method

Electronic absorption spectra were measured by a Hitachi Model 124 spectrophotometer with a thermostatically controlled cell compartment. Determination of the association constant of the charge-transfer complex was carried out by the Benesi—Hildebrand equation (I)

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$$[A_0] \cdot L/d = 1/K\varepsilon \cdot 1/[D_0] + 1/\varepsilon \qquad (1)$$

where $[A_0]$ and $[D_0]$ are the initial concentrations of the acceptor and the donor, respectively, d is the absorbance, L is the length of the optical cell, and K and ε are the association constant and molar extinction coefficient of the complex, respectively.

It was found that solutions of the complexes of P3VCA or 3EtCA with TeNF and p-CA were rather unstable at ambient temperature and turbidity slowly developed on standing. Therefore, absorptions were recorded immediately after the desired temperature was attained.

RESULTS

As an illustration the visible spectra of the complexes 3EtCA—TCNE and P3VCA—TCNE are shown in Figure 1. Spectral data for the complex formation of 3EtCA and P3VCA with various electron acceptors are presented in Table II. The Benesi–Hildebrand analysis gave good straight lines, suggesting 1 : 1 stoichiometry. To confirm this further, the continuous variation method was applied for 3EtCA—TCNE and P3VCA—TCNE complexes; the results showed maxima for both at 50 mol % of TCNE as can be seen is Figure 2.

As compared with the monomer complexes, the polymer complexes do not show any definite trend in the change of the absorption maxima
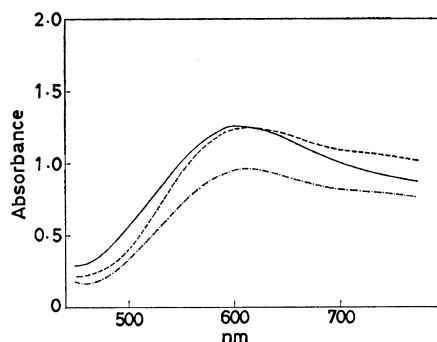

Figure 1. Spectra of charge-transfer complexes of P3VCA (——), 3EtCA (-----), and 1,3-BCAP (-·-·-) with TCNE: [P3VCA], $3.31 \times 10^{-2}\,M$; [TCNE], $1.26 \times 10^{-4}\,M$; [3-EtCA], 1.43×10^{-2}; [TCNE], $1.26 \times 10^{-3}\,M$; [1,3-BCAP], $2.99 \times 10^{-2}\,M$; [TCNE], $2.94 \times 10^{-3}\,M$; temp, 25°C; solvent, CH$_2$Cl$_2$.

and molar extinction coefficients of the charge-transfer band. However, the association constants of the polymer with TCNE, TNB, TeNF, and p-CA are 2.5, 5.8, 7.1, and 3.0 times larger than those of the monomeric analog, respectively.

The solutions of TCNE complexes in dichloromethane were stable, showing no drift of the absorptions after one day. In this regard the complexation with TCNE can be assumed to be suitable for further analysis of the polymer effect. Thermodynamic data were obtained in

Table II. Association constants (K) and molar[a] extinction coefficients (ε) of the P3VCA—, 3EtCA—, and 1,3-BCAP—acceptor system[b]

Acceptor	Temp, °C	K, ε, λ_{max}	P3VCA	3EtCA	1,3-BCAP
TCNE	25	K	18.5 ± 0.9	7.33 ± 0.85	3.88 ± 0.30
		ε	2700 ± 120	1500 ± 170	2400 ± 180
		λ_{max}, nm	605	608	608
TNB	30	K	16.6 ± 0.8	2.82 ± 0.11	1.96 ± 0.18
		ε	2270 ± 100	1710 ± 60	2120 ± 190
		λ_{max}, nm	405	405	405
TeNF	35	K	68.7 ± 1.9	9.60 ± 0.06	10.1 ± 0.48
		ε	1830 ± 30	1500 ± 10	1360 ± 60
		λ_{max}, nm	502	490	500
p-CA	27	K	5.46 ± 0.13	1.80 ± 0.52	
		ε	990 ± 20	1630 ± 470	
		λ_{max}, nm	548	540	

[a] Monomer unit concentration was applied.

[b] Solvent, dichloromethane.
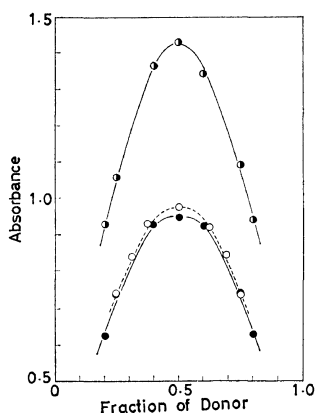
Figure 2. Continuous variation plots: a (◑), P3VCA—TCNE system, b (●), 3-EtCA—TCNE system; c (○), 1,3-BCAP—TCNE system: [P3VCA]+[TCNE], $1.1 \times 10^{-2} M$; [3-EtCA]+[TCNE], $1.1 \times 10^{-2} M$; [1,3-BCAP]+[TCNE], $4.0 \times 10^{-2} M$; temp, 25°C; solvent, CH_2Cl_2; absorbance, 610 nm.
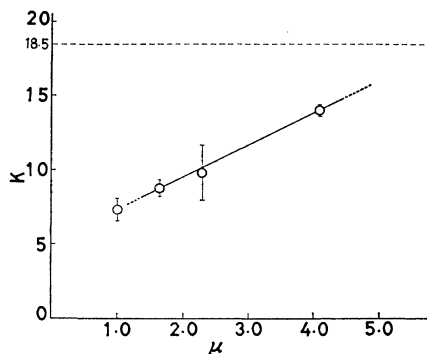
K were observed to be linearly dependent on the mean sequence length. The thermodynamic data of the copolymer—TCNE system is shown in Table III, indicating that there may be no substantial difference in the complex formation

Table III. Thermodynamic parameters in the formation of charge-transfer complexes with TCNE in CH_2Cl_2

Donor	$-\Delta H$, kcal/mol	$-\Delta S$, cal/mol·deg
P3VCA	6.17±0.69	15.6±2.6
3VCA—St copolymer (74/26)	6.75±0.27	17.3±1.1
3VCA—St copolymer (53/47)	5.77±0.79	14.7±3.0
3VCA—St copolymer (35/65)	6.45±0.27	17.4±1.0
3EtCA	2.83±0.27	5.43±1.00
1,3-BCAP	3.51±0.27	9.06±0.91

Table IV. K and ε of 3VCA-styrene copolymer—TCNE complexes at 25°C in CH_2Cl_2

Donor	K, l/mol	ε	λ_{max}, nm
P3VCA	18.5 ±0.9	2700±120	605
3VCA—St copolymer (74/26)	14.1 ±0.4	2310± 60	605
3VCA—St copolymer (53/47)	9.91±1.96	2310±450	605
3VCA—St copolymer (35/65)	8.78±0.66	1960±150	605
3EtCA	7.33±0.85	1500±170	608

regard to the complexation of P3VCA and 3EtCA with TCNE in methylene chloride; these are given in Table III. The changes of both enthalpy and entropy in the formation of the charge-transfer complex of P3VCA are larger than those of 3EtCA. The large increase of $-\Delta H$ is responsible for the increase in K of the polymer system. To clarify the favorable conditions under which P3VCA provides the complex formation, the systems of TCNE—copolymer with different sequence lengths of N-methyl-3-vinylcarbazole units were studied. Table IV shows λ_{max}, K, and ε of the chage-transfer complexes of these copolymers. With increasing N-methyl-3-vinylcarbazole content in the copolymers, the enhancement of K was observed, but λ_{max} remained unaltered at 605 nm.

The mean sequence lengths of N-methyl-3-vinylcarbazole units in these copolymers were calculated from eq 2 by assuming random distributions

$$\mu = r_2[M_2]/[M_1] + 1 \qquad (2)$$

where $[M_1]$ and $[M_2]$ are the molar concentrations of the monomers in the feed.[12] A relationship between K and the mean sequence lengths (μ) of N-methyl-3-vinylcarbazole units in the copolymer is shown in Figure 3. Values of

Figure 3. Relationship between K for the complex of copolymers with TCNE and the mean sequence length (μ) of N-methyl-3-vinylcarbazole unit. The dotted line denotes the value for P3VCA.

between the homopolymer and the copolymers and that there exist unambiguous differences between the polymeric systems and 3EtCA.

As seen in Figure 3, even short sequence lengths seem to provide a favorable condition for the charge-transfer interactions in these polymeric systems. Therefore, 1,3-BCAP, a dimeric analog, can be assumed to exhibit a favorable effect on the charge-transfer interaction. The stoichiometry of 1 : 1 with TCNE was ensured by the continuous variation method (Figure 2) and association constants with various acceptors were compared with the preceding results on the polymers and the monomer analog, as shown in Table II. Unexpectedly, the complexes of the dimer analog are found to be less stable than those of the monomer analog and the polymers. The thermodynamic data of the dimer complex showed intermediate values to those of the polymer and monomer complexes, as shown in Table IV.

DISCUSSION

Positive polymer effects were observed in P3VCA and *N*-methyl-3-vinylcarbazole—styrene copolymer systems, and the sequence length of the *N*-methyl-3-vinylcarbazole unit was found to play an important role in the complex formation. This fact suggests that a high local concentration of *N*-methyl-3-vinylcarbazole units of the polymer chain is fovorable for the complex formation. In the case of the dimer-complex (Table II), however, the enhancement of K was not observed and the K with TCNE was equal to almost one-half the value for the 3EtCA complex. It may be deduced that the formation of the charge-transfer complex with one carbazolyl group of the dimer sterically prevents the complex formation of the other carbazolyl group. Thus, the large stability which was found in the polymer system does not simply result from the local concentration effect.

Both $-\Delta H$ and $-\Delta S$ are larger for the polymer systems than for the monomeric system. The positive polymer effect came from the large value of $-\Delta H$, which overcame the disadvantage in the large value of $-\Delta S$. In the case of the dimer model the increase in $-\Delta H$ could not overcome the disadvantage in the increased value of $-\Delta S$. The large value of $-\Delta H$ in the polymer system may suggest the possibility of a difference of the charge-transfer complex itself, but no substantial changes of λ_{max} were observed for the complexes with TCNE, indicating that this may not be the case. The decrease of the ionization potential of the carbazole units in the polymer can also be ruled out. The large stability in the polymer system may be derived from the favorable arrangement of the neighboring carbazole units, which is in turn defined by the conformation of the polymer chain. The details of the suitable arrangement for the complex formation cannot yet be visualized. However, it may be speculated the dipole—dipole repulsion between carbazole groups in the polymer chain is one of the reasons for the large value of $-\Delta H$ and that this force is released on complexation. A molecule of TCNE may swing to and fro between two adjacent carbazole units. In the case of the dimer analog, two carbazolyl groups can be so remote as to minimize the repulsion, and hence $-\Delta H$ becomes smaller.

In the case of a structurally related compound, poly(*N*-vinylcarbazole) the formation of charge-transfer complexes is entropically less favorable and the value of $-\Delta H$ is almost the same as that for the monomeric and dimeric analogs; this results in a negative polymer effect.[1] On the other hand, P3VCA exhibited a positive polymer effect. It has been suggested on the the basis of NMR studies that, as compared with P3VCA, poly(*N*-vinylcarbazole) appears to represent the polymeric environment in which the carbazole groups are much more tightly packed.[3] The large difference in the complex formation between the two systems may be understood by this difference in the arrangement of the neighboring carbazole units.

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