Mechanism of Charge-Transfer Polymerization

I. Polymerizations of N-Vinylcarbazole with Some Quinones in a Non-Polar Solvent

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ABSTRACT: The polymerization of N-vinylcarbazole (VCZ) by *p*-chloranil (*p*-CA) and a few related quinoid compounds was studied in a non-polar solvent. The rapid charge-transfer polymerization of VCZ ostensibly initiated by *p*-CA turned out to be mainly a conventional cationic one initiated by a residual amount of 3,5,6-trichloro-2-hydroxy-*p*-benzoquinone which was retained in *p*-CA purified by recrystallizations or sublimations. Chromatography over calcium carbonate followed by recrystallizations and fractional sublimations was found to be an efficient purification method. The charge-transfer polymerization was accompanied by the formation of carbazole. The rate of polymerization followed the order: VCZ-*p*-BA > VCZ-*p*-CA > VCZ-2,6-dichloroquinone. 2,5-Dichloroquinone did not initiate the polymerization of VCZ under the same conditions. Some cationic species have been proposed in the initiation process of the polymerizations in view of the cationic propagation.

KEY WORDS Charge-Transfer Polymerization / N-Vinylcarbazole /
p-Chloranil / Quinoid / 3,5,6-Trichloro-2-Hydroxy-*p*-Benzoquinone /
Carbazole Formation /

In recent years rather extensive studies have been made on the charge-transfer polymerizations of N-vinylcarbazole (VCZ) with organic as well as inorganic electron acceptors.¹ However the polymerization mechanism has been controversial and definite mechanistic conclusions have not yet been drawn.

While a mesomeric polarization mechanism through partial electron transfer has been proposed by Ellinger² for polymerization in non-polar solvents or with weak organic electron acceptors especially such as acrylonitrile (AN) or methyl methacrylate (MMA), charge-transfer polymerizations of VCZ have been described as cationic in many systems. A Wurster radical-cation resulting from the complete electron transfer from VCZ to the acceptor has been postulated as the active species in the initiation process first by Scott *et al.*³ and by other researchers, but the interpretation has been different on the behavior or the fate of the Wurster radical-cation. Scott *et al.*³ suggested the same species as the propagating species, although they did not formulate in

detail. Tsuji *et al.*⁴ suggested that the radical in the Wurster radical-cation becomes delocalized over the carbazole ring during cationic polymerization, based on the observation of an ESR signal in the systems VCZ-halogens or VCZ-maleic anhydride (MAN). Pàc and Plesch⁵, in their detailed kinetic studies of the system VCZ-tetranitromethane(TNM)-nitrobenzene(NB), considered that the charge-transfer complex dissociates slowly to radical-ions and that the radical function becomes inactivated by the acceptor. Tazuke *et al.*⁶ insisted on the simultaneous occurrence of cationic and radical propagations from the radical-cation in the system of VCZ-AN.

It should be noted here that the Wurster radical-cation being the initiating species has not been confirmed in whole polymerization systems, especially in systems where non-polar solvents are employed. On the other hand, Szwarc *et al.*⁷ very recently demonstrated the formation of the carbonium ion $(C_6H_5)_2\dot{C}-CH_2NO_2$ from the charge-transfer complex between 1,1-diphenylethylene and TNM in NB. The result may imply

the possibility that this kind of σ -complex formed by the chemical reaction between the donor monomer and acceptor can be an initiator for cationic polymerization.

Thus, it is reasonable to think that the polymerization mechanism may vary in each system of the monomer-acceptor-solvent combination. Therefore full investigation of each system may be required.

A number of organic electron acceptors ranging widely in electron affinities have been described as effective initiators by Scott *et al.*³ and Ellinger², but surprisingly little quantitative data are available. In fact, the natures of initiating and propagating species or the fate of acceptors still appear to remain unsolved in many systems. Only a few systems have been studied in detail, *e.g.*, VCZ-AN,^{2,6} VCZ-TNM⁵, and VCZ-MAN^{4b}. The system VCZ-*p*-chloranil^{2,5,8} (*p*-CA) is also one of the typical charge-transfer polymerizations most studied to date, and yet it remains quite complicated.

We aimed at studying systematically the polymerization of VCZ with a series of quinones, one representative class of typical π -electron acceptors, including the reinvestigation of the system VCZ-*p*-CA. It may provide helpful suggestions for understanding the mechanism of the present systems to make comparison of the polymerization features and to examine the correlation between the magnitude of electron affinities of acceptors and their effectiveness as initiators among a variety of structurally analogous quinones. The effects of solvent polarity and light illumination on the polymerization are also the subjects of our investigation. This paper is concerned with the polymerizations of VCZ with *p*-CA and a few related quinoid compounds in benzene.*

EXPERIMENTAL

Materials

N-Vinylcarbazole (K & K Lab., Inc., U.S.A.) was recrystallized twice from purified *n*-hexane to give an overall yield of 50%, dried *in vacuo* for two or three days at room temperature, mp 65°C.

Purifications of *p*-CA, *p*-bromanil (*p*-BA),

* A part of this work has been published in previous communications.⁹

2,6-dichloroquinone (DQ) and 2,5-DQ (Wako Pure Chemical, Inc., Ltd., Japan) were made as follows. Commercially available materials of pure grade were first recrystallized from benzene, then passed through a column of freshly baked CaCO₃, using benzene as an eluent in order to remove acidic impurities, and recrystallized from it again. Finally, they were fractionally sublimed under reduced pressure. Alternatively commercial *p*-CA was purified by two recrystallizations from purified benzene followed by two fractional vacuum sublimations, where the intermediate fraction was collected in about 50–60% yield, the initial pale greenish-yellow fraction and final one being discarded.

Isobutyl vinyl ether (IBVE) was washed with aqueous potassium hydroxide, then with water and distilled under nitrogen over sodium wire.

Benzene was purified conventionally, refluxed over sodium wire for at least one week and redistilled from it immediately before use. Methanol was only distilled.

Spectroscopic Measurements and Polymerizations

Optical measurements were carried out soon after solutions were made up on a EPS-3 Hitachi recording spectrometer and a EPU-2A Hitachi spectrometer. The infrared spectra were taken with a EP1-G2 type Hitachi infrared spectrometer, where a cell of 0.5 mm thickness was used for the solution. The copolymer composition was determined using the ultraviolet absorption in benzene solution at 344 m μ . The molar extinction coefficient of polyvinylcarbazole at this wavelength was 3326.

Polymerizations were carried out in a glass tube or in a dilatometer. The polymerization tube was sealed in the presence or absence of N₂ after repeated of freezing and thawing at 10⁻¹ mm Hg. Some were carried out in air and under a high vacuum system (10⁻⁶ mm Hg) for comparison. The reaction mixture was poured into excess cold methanol after an appropriate time of polymerization and the polymer precipitated was filtered, washed with hot methanol, dried *in vacuo* and weighed. When *p*-BA was used as an acceptor, carbazole precipitated from the polymerization system in a few hours. In this case each reaction mixture was cooled in an ice bath for about ten minutes and carbazole was

filtered, the filtrate being poured into excess methanol to give a polymer. The polymer was a colloidal suspension and therefore coagulated by addition of one or two drops of concentrated hydrochloric acid solution.

RESULTS AND DISCUSSION

Spectroscopic Studies of VCZ-Quinones Systems

Intense coloration from red to mauve occurred on mixing VCZ with a set of quinones, which was ascribed to the formation of charge-transfer complexes. With all the quinones studied, two new bands appeared in the visible region, the band at a longer wavelength appearing as a broad shoulder. The position of the maxima of these charge-transfer bands shifted to longer wavelengths with increasing electron affinity of quinones, and a linear relationship was obtained between $h\nu_{CT}$ and the electron affinity (E_A) of acceptors. The results are given in Table I. Since all these charge-transfer complexes were found to be stable in benzene for a long time below room temperature, approximate values of association constants and molar extinction coefficients were calculated for a few polymerization systems from Benesi-Hildebrand plots, the complexation between benzene and quinones being neglected. (Table

II). Good straight lines in the Benesi-Hildebrand treatment indicated the 1:1 stoichiometry of these complexes.

Polymerizations

*VCZ-*p*-CA*

Although the polymerization of VCZ by *p*-CA has been investigated by Ellinger², Hatano *et al.*⁸ and Plesch *et al.*⁵, the results appear to be inconclusive and a mechanistic conclusion has not been reached. The polymerization in a non-polar solvent was studied by Ellinger, who reported that *p*-CA (e.g., 3-% concentration on monomer) effected rapid polymerization of VCZ in toluene at 80°C and that the polymerization rate increased with increasing monomer and acceptor concentrations, following second order both in the monomer and in the acceptor.¹

In sharp contrast to Ellinger's results we have now confirmed that the polymerization of VCZ by *p*-CA is extremely slow even at 80°C in a non-polar solvent as shown in Figure 1 (curve 2) and that almost no polymerization occurs below room temperature in the dark. The acceptor employed in this experiment was purified by two recrystallizations from benzene followed by two fractional sublimations as described above. In addition, we carried out the polymerization using *p*-CA purified by only one recrystallization and three

Table I. Charge-transfer bands between VCZ and a few quinones

Acceptor	E_A : Briegleb ¹⁰	Lyons ¹¹	$\lambda_{CT\max}$ in CCl ₄ (m μ) ^a	$h\nu_{CT\max}$ (eV)
<i>p</i> -BA	1.40	2.62	509 (595)	2.44
<i>p</i> -CA	1.37	2.59	506 (590)	2.45
2,6-DQ	1.15	2.34	462 (545)	2.68
2,5-DQ	1.10	2.54(2.30) ^b	452 (535)	2.74

^a The values in parenthesis describe approximate central positions in the broad shoulder-bands at longer wavelengths.

^b Calculated value from the present charge-transfer bands according to the equation, $h\nu_{CT1} - h\nu_{CT2} = E_{A2} - E_{A1}$, by use of *p*-CA as a standard.

Table II. Approximate association constants (*K*) and molar extinction coefficients for a few polymerization systems in benzene at 23°C

System	<i>K</i>	ϵ	λ (m μ)	Concentration range employed
VCZ- <i>p</i> -BA	0.39	1667	(506)	[D] = 4.85×10^{-2} – 17.73×10^{-2} mol/l [A] = 8.3925×10^{-3} mol/l
VCZ- <i>p</i> -CA	0.31	2500	(506)	[D] = 6.27×10^{-2} – 14.02×10^{-2} mol/l [A] = 8.79×10^{-3} mol/l
VCZ-2,5-DQ	0.27	1667	(452)	[D] = 5.94×10^{-2} – 13.54×10^{-2} mol/l [A] = 1.1511×10^{-2} mol/l

Figure 1. Polymerization of VCZ by *p*-CA in non-polar solvents.

1: Ellinger's result; [VCZ], 0.5 mol/l; [*p*-CA], 1.23×10^{-2} mol/l; Solvent, Toluene; Temp., 80°C.
2,3,4: [VCZ], 0.5 mol/l; [*p*-CA], 2.0×10^{-2} mol/l; Solvent, Benzene; Temp., 80°C.

2(●): *p*-Chloranil was recrystallized twice from benzene followed by two fractional sublimations *in vacuo*.

2(△): *p*-Chloranil was recrystallized from benzene and passed through a column of calcium carbonate, followed by two recrystallizations from benzene and one sublimation *in vacuo*.

3: *p*-Chloranil was recrystallized only once from benzene.

4: *p*-Chloranil was recrystallized three times from benzene.

recrystallizations from benzene and obtained the conversion curves 3 and 4 respectively shown in Figure 1, the former being quite similar to Ellinger's results.

These results suggested that some trace impurities, probably acidic impurities, which can be strong initiators for the polymerization of VCZ, are tenaciously retained in *p*-CA and that only one or two recrystallizations or simple sublimations are insufficient to remove them completely. The isolation and identification of a main component of acidic impurities have been achieved by the following procedures.

Commercial pure grade *p*-CA was dissolved in benzene and passed through a column of

freshly baked calcium carbonate. The column was washed well with benzene to elute *p*-CA and then a pink-violet zone was eluted with water to give a violet-colored aqueous solution. The solution was evaporated and the residue was extracted with benzene. From the benzene solution was isolated a yellow-orange compound which was purified by vacuum sublimation, mp 199°C (dec.). It was identified as 3,5,6-trichloro-2-hydroxy-1,4-benzoquinone (X) by comparison of the IR, UV and mass spectra with those of an authentic sample¹² and by the mixed melting point. Alternatively, direct water extraction of acidic impurities from a benzene solution of *p*-CA was followed in the belief that any of the acidic impurities (*e.g.*, chloranilic acid) absorbed in calcium carbonate might not be eluted with water. The water extract turned to purple and impurities were successfully extracted, among which X was found to be the main component. No coloration of the aqueous layer occurred from a benzene solution of *p*-CA shaken beforehand two or three times with water or chromatographed over calcium carbonate. *p*-Chloranil itself is neither affected by chromatographing over calcium carbonate nor undergoes any change in contact with cold water so long as it is for a short period of time. Trichlorohydroxyquinone (X) was likewise detected in *p*-CA purified simply by recrystallizations or sublimations. The commercial guaranteed grade *p*-CA contained spectroscopically *ca.* 0.25% of X.

Electronic spectrum (in H₂O):
 $\lambda_{\max}(\text{m}\mu)$; 222 (log ϵ 4.22),
297 (log ϵ 4.08),
536 (log ϵ 3.22).

Trichlorohydroxyquinone (X) proved to be a powerful initiator of the cationic polymerization of VCZ as shown in Figure II. It is therefore evident that the hitherto reported rapid charge-transfer polymerization of VCZ ostensibly initiated by *p*-CA in a non-polar solvent is mainly a conventional cationic one initiated by a trace amount of the impurity retained in *p*-CA.

Chromatography over calcium carbonate combined with two or three recrystallizations and a fractional sublimation *in vacuo* appears to be a

Figure 2. Polymerization of VCZ by 3,5,6-trichloro-2-hydroxy-*p*-benzoquinone (X) in benzene at 80°C.
1: [VCZ], 0.5 mol/l; [X], 5×10^{-5} mol/l.
2: [VCZ], 0.5 mol/l; [X], 4×10^{-6} mol/l.

generally efficient purification method of *p*-CA and other halogen substituted *p*-quinones. Employment of *p*-CA purified in this way resulted in almost the same conversion curve as that given in Figure 1 (curve 2), and this slow polymerization is assumed to be the charge-transfer initiated one.

Related to our finding is the recent observation by Plesch *et al.*¹³ that the polymerization rate of VCZ by mercuric chloride depends on the presence of the co-catalytic impurities contained in the monomer.

The following characteristic features have been observed with regard to the system VCZ-*p*-CA in benzene at 80°C. The polymerization was very slow and did not go to completion at all. Marked changes in color of the polymerization system were observed. The polymer yield increased linearly with the polymerization time for about 22 hrs and during that time the intense mauve color characteristic of the charge-transfer complex remained constant. But, when about 22 hrs elapsed after the polymerization had set in, the polymerization system gradually turned through brown to reddish brown and at the same time saturation of polymer yields occurred. After 30 to 35 hrs the initial color completely faded away and the polymerization system turned dark red. The polymers isolated within 20 hrs of polymerization time were very pale mauve

but the polymers after 25 hr of polymerization time were colored in brown or reddish brown even after repeated reprecipitations, the depth of the coloration increasing with the polymerization time. A dark red color developed when the colored polymer was dissolved in benzene. Elementary analyses of the polymer revealed that 1.5 to 4% of chlorine is contained in all the polymers, the amount of the content increasing in proportion to the intensity of the coloration of the polymer. The results are listed in Table IV. Particularly noteworthy is that the polymerization is accompanied by the formation of carbazole. When the polymerization was over 18 hr, a band at 3400 cm^{-1} ascribable to secondary NH stretching vibration began to appear in the infrared spectrum of the polymerization system and increased

Figure 3. Effect of temperature on polymerization of VCZ by *p*-CA in benzene.
[VCZ], 0.5 mol/l; [*p*-CA], 2.0×10^{-2} mol/l.
1: 80°C, 2: 60°C, 3: 30°C.

Figure 4. Effect of *p*-CA concentration on polymerization of VCZ in benzene at 80°C.
[VCZ], 0.5 mol/l.
1: [*p*-CA], 2.0×10^{-2} mol/l.
2: [*p*-CA], 1.0×10^{-2} mol/l.
3: [*p*-CA], 0.25×10^{-2} mol/l.

Table III. The effects of additives on the polymerization of VCZ by *p*-CA^a

Atmosphere	Additive	Polymerization time (hr)	Conversion (%)
1. N ₂	—	6 (12)	3.0 (6.5)
2. Vacuum (10 ⁻⁶ mmHg)	—	12	6.1
3. Air	(O ₂)	6 (12)	2.9 (5.9)
4. N ₂	DPPH (1 × 10 ⁻² mol/l)	6	3.3
5. N ₂	N (CH ₃) ₃ 30% aq. (1 × 10 ⁻² mol/l)	6 (12)	0 (0)

^a [VCZ], 0.5 mol/l, [*p*-CA], 2 × 10⁻² mol/l, Polymerization temp. 80°C.

its intensity with the polymerization time to a certain degree. When the system was allowed to polymerize for more than 50 hrs carbazole precipitated from the polymerization system, the polymer being dissolved in benzene. The yield of carbazole precipitated after 65 hrs amounted to approximately 25%, the polymer yield being 12–13%. Confirmation of carbazole was made by comparison of the infrared spectra with that of the authentic sample and the melting point of the mixture.

The apparent activation energy was calculated to be approximately 16.3 kcal/mol (Figure 3). The effect of acceptor concentration on the rate of polymerization has been studied (Figure 4). The polymerization appeared to follow first order in acceptor concentration. Copolymerization of VCZ and isobutyl vinyl ether (IBVE) initiated by *p*-CA gave a copolymer. [VCZ], 0.8 mol/l; [IBVE], 0.2 mol/l; polymerization time, 17 hr; polymerization temp., 80°C; yield, 3.7%; VCZ content in copolymer, 95.0%. Vinylcarbazole was copolymerized with IBVE when initiated by cationic catalysts, but radical copolymerization did not occur between them. Isobutyl vinyl ether alone did not undergo polymerization by *p*-CA in the dark. The results of the effect of additives on the polymerization are given in Table III. The polymerization was almost insensitive to oxygen or DPPH but inhibited by aqueous trimethylamine. Although the latter information on additive effects has a limited value in that organic bases interact strongly with *p*-CA, the above results indicate that the propagation is not radical, but cationic.

VCZ-*p*-BA and VCZ-2,6 and 2,5-DQ

No quantitative data concerning these systems have been recorded in the literature. The

conversion curves of the system VCZ-*p*-BA at 80°C are given in Figure 5. The effects of the monomer and acceptor concentration and variation of temperature on the rate of polymerization were determined by dilatometry. These results are shown in Figures 6, 7 and 8. The polymerization was inhibited by aqueous trimethylamine. The apparent activation energy calculated from the initial rate of polymerization was about 14.8 kcal/mol. As compared with the system VCZ-*p*-CA, the polymerization rate was much faster and such characteristic features as the saturation of polymer yields, the coloration of polymers or the formation of carbazole were more striking under the same conditions at 80°C, occurring only in a few hours. In addition, an acceleration period appeared to exist in this case, which was not observed with *p*-CA. Polymers contained bromine and showed a similar tendency as observed with *p*-CA (Table IV). The saturation of polymer yields is explained in terms of

Figure 5. Polymerization of VCZ by *p*-BA in benzene at 80°C.[VCZ], 0.5 mol/l; [*p*-BA], 2.0 × 10⁻² mol/l.

●: Dilatometry, △: Precipitation method.

Figure 6. Effect of monomer concentration on polymerization by *p*-BA in benzene at 80°C.

[*p*-BA], 2.0×10^{-2} mol/l.

1: [VCZ], 1.0 mol/l.

2: [VCZ], 0.5 mol/l.

3: [VCZ], 0.25 mol/l.

Figure 7. Effect of *p*-BA concentration on polymerization of VCZ in benzene at 80°C.

[VCZ], 0.5 mol/l.

1: [*p*-BA], 2.0×10^{-2} mol/l.

2: [*p*-BA], 1.0×10^{-2} mol/l.

3: [*p*-BA], 0.5×10^{-2} mol/l.

both monomer and acceptor consumptions. Consumption of the monomer is obvious in the light of the formation of carbazole. Analysis by means of infrared spectroscopy of the polymerization system (80°C) showed that the band at 3400 cm^{-1} (NH) began to appear in about 2 hr and that the bands at 1640 cm^{-1} (C = C), and 1685 cm^{-1} (C = O) and 1060 cm^{-1} (C-Br)¹⁴ characteristic of the monomer and acceptor respectively decreased their intensity in 1.5 to 2 hr and disappeared in 3 to 4 hr. The yields of carbazole precipitated from the polymerization

Figure 8. Effect of temperature on polymerization of VCZ by *p*-BA in benzene.

1: 80°C.

2: 60°C.

3: 45°C.

Table IV. Halogen contents in polymers^a

Acceptor	Polymerization time (hr)	Chlorine or bromine content (%)
<i>p</i> -CA	6	1.48
<i>p</i> -CA	28	2.60
<i>p</i> -CA	45	3.97
<i>p</i> -BA	1	1.27
<i>p</i> -BA	3	2.64
<i>p</i> -BA	5	4.80

^a Polymers were reprecipitated three times from benzene by addition of methanol.

Table V. Yields of carbazole precipitated from the polymerization system VCZ-*p*-BA

Reaction time (hr)	Yields (%)
3	10-17
4	32-36
5	35-41

system are listed in Table V.

Polymerization of VCZ by 2,6-DQ resulted in 2.3-%, 3.9-% and 4.8-% conversions after 8, 16, and 20 hrs respectively under the same conditions as employed in the case of *p*-CA or *p*-BA (VCZ, 0.5 mol/l, acceptor, 2×10^{-2} mol/l, 80°C) and the polymers obtained were almost white. 2,5-Dichloroquinone with concentrations of 2×10^{-2} and 5×10^{-2} mol/l did not initiate the polymerization of VCZ (VCZ, 0.5 mol/l) even after 22 hrs at 80°C. Neither the color change nor carbazole formation was observed with both 2,6- and 2,5-DQ.

Discussion on the Initiation Mechanism

In the present study polymerizations of VCZ with a set of structurally analogous quinones have been studied. The electron acceptors include *p*-BA, *p*-CA, 2,6-DQ and 2,5-DQ. Of these the polymerization initiated by the first two acceptors has turned out to be a complex one accompanied by the serious side reaction of carbazole formation. The transformation of VCZ into carbazole has been reported in the presence of a protonic acid^{2,15}, but the formation of carbazole from the polymerization system in which a catalytic amount of π acid is present but with no protonic acid initially present appears to be a new observation. The formation mechanism is not clear at present.

With regard to the polymerization mechanism, Ellinger² suggested that the polymerization of VCZ with organic electron acceptors in a non-ionizing solvent proceeds by partial electron transfer both in the initiation and propagation steps, although he did not formulate in detail concerning the system VCZ-*p*-CA. Hatano *et al.* regarded the charge-transfer complex as the initiator in the above system,⁸ but later showed that the polymerization is cationic from the result of copolymerization with 3,6-dibromovinyl-carbazole, suggesting the Wurster radical-cation as the initiator¹⁶.

It should be noticed, however, that their discussions have been based on the results obtained by the use of seemingly impure *p*-CA contaminated with acidic impurities. In fact, their results have been proved to be mainly conventional cationic polymerizations by X in the present study. The problem to be solved is the mechanism of the "slow" polymerization initiated by pure *p*-CA and related quinoid compounds free from acidic impurities in which the charge-transfer complexation appears to be associated with the polymerization.

Our present study using pure acceptors free from acidic impurities has now demonstrated

that the polymerizations are cationic in nature. It seems, therefore, to be reasonable to assume some cationic species as the active species for initiation in the present systems. Examination of polymerization features and their comparison among systems studied in connection with the values K and E_A allow us to propose two possibilities.

As shown in the following equilibria, the dissociation of the charge-transfer complex to radical ions may occur even in a non-polar solvent

where M and A denote the monomer (VCZ) and acceptor respectively. The equilibrium constants K_{II} and K_{III} are, of course, considered to be extremely small in a non-polar solvent. The ion-paired radical-cation, produced by the slow thermal electron transfer, the concentration of which is too small to be detected spectroscopically, may be assumed as the initiating species. This mechanism may account for the slow polymerization and also for the result that the rate of polymerization decreased in the order of decreasing values of K_I and E_A . In this case the absence of radical activity is ascribed to the reaction of the radical site with the acceptor, as Plesch *et al.* pointed out⁵, since quinones are inhibitors of radical reactions. This explains the fact that halogen is contained in the polymer. But the question arises as to whether the differences in the polymerization features observed between VCZ-*p*-CA and VCZ-*p*-BA systems are attributable solely to the slight differences in the magnitude of K_I or E_A .

As an alternative mechanism it may be possible to assume the cationic σ complex formed by the chemical reaction of VCZ with the acceptor as the initiator.

The following examples of nucleophilic displacement reactions on *p*-CA are also in support of this speculation. The reaction of *m*-phenylenediamine and *p*-CA has been demonstrated to proceed through the outer complex (π complex) and inner complex (σ complex) from spectrophotometric studies.¹⁷ Interaction of triethylamine with *p*-CA gives 2-diethylaminovinyl-3,5,6-trichloro-*p*-benzoquinone.^{18*} N-Vinylcarbazole monomer is reported to be strongly basic¹⁹ and the vinyl group is expected to be highly reactive towards electrophilic compounds as suggested from its π -electron density calculated by means of the LCAO method.²⁰ If this mechanism holds, the reactivity of the quinones as well as the degree of charge transfer will affect the polymerization. *p*-Bromanil may be assumed to be more reactive to form the σ complex than *p*-CA. It may be possible to interpret the difference in the polymerization rate between VCZ-*p*-CA and VCZ-*p*-BA as resulting from the difference in chemical reactivity between *p*-CA and *p*-BA. The incorporation of halogen in the polymer is also understandable from this mechanism.

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