Mechanism of Charge-Transfer Polymerization. IV. Multiplicity of the Reaction Course in the Photosensitized Reaction of *N*-Vinylcarbazole in the Presence of the Organic Electron Acceptor[1]

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ABSTRACT: Comprehensive studies have been made on the photosensitized reaction of *N*-vinylcarbazole (VCZ) in the presence of various organic electron acceptors for the purpose of elucidating the nature of the reaction. It was found that the reaction involves cationic polymerization, cyclodimerization, radical polymerization, and in certain cases radical copolymerization with an electron-accepting monomer and that the reaction course is strongly solvent dependent. Multiplicity of the reaction course is systematically explained in terms of the dual reactivity, cationic and radical, of the intermediate VCZ cation radical formed by the electron transfer from VCZ to the electron acceptor in the excited state. The factors which determine the reaction course are discussed.

Polymerization of electron-donating monomers by electron acceptors, the so-called charge-transfer polymerization, has currently been a topic of great interest and received much attention especially with regard to *N*-vinylcarbazole (VCZ). Although rather extensive studies have been made on the thermally induced charge-transfer polymerization of VCZ,[2] only a few independent systems have been reported to date on the photosensitized polymerization of VCZ in the presence of the electron acceptor and the nature of the reaction has not been fully clarified.

As typical examples, we have reported that cationic polymerization of VCZ took place in the systems VCZ–*p*-quinoid compounds in benzene.[3] Occurrence of cationic polymerization has also been reported in the system VCZ–2,4,7-trinitrofluorenone in nitrobenzene.[4] On the other hand, cyclodimerization of VCZ to yield *trans*-1,2-dicarbazylcyclobutane has been reported in the system VCZ–chloranil (CA) in methanol or in acetone.[5]

The charge-transfer complex which is stable in the ground state generally has a polar structure in the excited state.[6] Also the charge-transfer complex that is formed only in the excited state of either donor or acceptor molecule, the exciplex, has a polar structure.[7] Thus occurrence of the photochemical electron transfer has been shown in many donor–acceptor systems.[8] Likewise, it has been postulated that the photochemical electron transfer occurs from VCZ to the electron acceptor to give VCZ cation radical which initiates the polymerization of VCZ. In fact, we have recently demonstrated the photochemical formation of ion radical intermediates in the system VCZ–CA by means of flash spectroscopy.[9] If the reaction involves the intermediate VCZ cation radical, the dual reactivity, cationic and radical, should be expected, since VCZ monomer undergoes both cationic and radical reaction. However, no systematic study has been carried out on this point. Moreover, we have recently found that the reaction of VCZ in the presence of the electron acceptor is greatly influenced by trace impurities retained in the electron acceptor[10] or by the atmosphere[11]; thus some experimental errors are found in the literature. In the present study we endeavored to make comprehensive investigation on the photosensitized reaction of VCZ using various organic electron acceptors for the purpose of elucidating the nature of the reaction, attention being paid to the solvent effect on the reaction, in particular. Preliminary results have been reported in the previous communication.[12]

Experimental Section

Materials. *Monomers. N*-Vinylcarbazole (BASF Chemicals Ltd.) was recrystallized twice from purified methanol, then once from purified *n*-hexane to give an overall yield of 50%; it was dried *in vacuo* for 3 days at room temperature. Styrene was purified in the usual way, dried over calcium chloride, and distilled twice under reduced pressure immediately before use.

Electron Acceptors. All organic electron acceptors were obtained commercially as extra pure grade or guaranteed grade reagents from WAKO Pure Chemical Industries Ltd. or Nakarai Chemical Ltd. Purifications of bromanil (BA), chloranil (CA) and 2,5-dichloro-*p*-benzoquinone (2,5-DQ) were made as described in the previous paper.[13] Particular care was taken to remove acidic impurities tenaciously retained in them. *p*-Benzoquinone (*p*-BQ) was recrystallized twice from purified *n*-hexane and fractionally sublimed twice *in vacuo*. Pyromellitic dianhydride (PMDA) and tetrachlorophthalic anhydride (TCPA) were fractionally sublimed twice *in vacuo* immediately before use. Maleic anhydride (MA) and phthalic anhydride (PTA) were recrystallized twice from purified benzene and fractionally sublimed twice *in vacuo* immedi-

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(1) Part III of this series: Y. Shirota, K. Kawai, N. Yamamoto, K. Tada, T. Shida, H. Mikawa, and H. Tsubomura, *Bull. Chem. Soc. Jap.*, **45**, 2683 (1972).

(2) (a) J. Pác and P. H. Plesch, *Polymer*, **8**, 237, 252 (1967); (b) R. Gumbs, S. Penczek, J. Jagur-Grodzinski, and M. Szwarc, *Macromolecules*, **2**, 77 (1969); (c) T. Nakamura, M. Soma, T. Onishi, and K. Tamaru, *Makromol. Chem.*, **135**, 241 (1970); (d) C. E. H. Bawn, A. Ledwith, and M. Sambhi, *Polymer*, **12**, 209 (1971); (e) P. H. Bowyer, A. Ledwith, and D. C. Sherrington, *ibid.*, **12**, 509 (1971); and references cited therein.

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(6) For examples, see (a) R. Potashnik and M. Ottolenghi, *Chem. Phys. Lett.*, **6**, 525 (1970); (b) H. Masuhara and N. Mataga, *ibid.*, **6**, 608 (1970).

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(9) Y. Shirota, K. Kawai, N. Yamamoto, K. Tada, H. Mikawa, and H. Tsubomura, *Chem. Lett.*, 145 (1972).

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(11) Y. Shirota, K. Tada, M. Shimizu, S. Kusabayashi, and H. Mikawa, *Chem. Commun.*, 1110 (1970).

(12) K. Tada, Y. Shirota, S. Kusabayashi, and H. Mikawa, *Chem. Commun.*, 1169 (1971).

(13) T. Natsuume, M. Nishimura, M. Fujimatsu, M. Shimizu, Y. Shirota, H. Hirata, S. Kusabayashi, and H. Mikawa, *Polym. J.*, **1**, 181 (1970).

ately before use. 1,3,5-Trinitrobenzene (TNB) was recrystallized three times from purified methanol and dried *in vacuo* for 3 days at room temperature. Dimethyl terephthalate (DMTP) was recrystallized three times from absolute ethanol and fractionally sublimed twice *in vacuo* immediately before use. CCl_4 was washed with dilute aqueous sodium carbonate, then with water, dried over magnesium sulfate, and distilled twice over calcium hydride immediately before use. CBr_4 was recrystallized three times from absolute ethanol and sublimed twice *in vacuo* immediately before use. Fumaronitrile (FN) was recrystallized three times from purified benzene and fractionally sublimed twice *in vacuo* immediately before use. Diethyl fumarate (DEF) was first dried over calcium chloride and then fractionally distilled twice over calcium hydride under reduced pressure immediately before use.

Solvents. Benzene was purified and dried in the usual way, and fractionally distilled twice from sodium wire immediately before use. Dichloromethane was washed with concentrated sulfuric acid, then with dilute aqueous sodium hydroxide, and with water, dried over calcium chloride, and fractionally distilled twice from calcium hydride immediately before use. H_4furan was refluxed over potassium hydroxide for a long time, distilled from it, and refluxed over sodium wire for 3 days under dry nitrogen atmosphere and distilled from it immediately before use. Acetone was refluxed with potassium permanganate, distilled from it, dried over calcium sulphate, and fractionally distilled over Drierite under dry nitrogen atmosphere immediately before use. Acetonitrile was refluxed over phosphorus pentoxide overnight and distilled from it, this procedure being repeated twice or three times. Then it was refluxed over anhydrous potassium carbonate for a long time and fractionally distilled twice from it immediately before use. Methanol was refluxed with small amounts of sodium metal and fractionally distilled twice immediately before use. *N,N*-Dimethylformamide and Me_2SO were dried over molecular sieves (Type 4A) for 3 days and fractionally distilled over calcium hydride under reduced pressure immediately before use.

Reaction Procedure. All reactions were carried out in a glass tube, 1.5 cm in diameter, connected to a vacuum line. The electron acceptor was dissolved in a solvent contained in the tube and VCZ monomer was introduced to the solution under dry nitrogen atmosphere, and the solvent was again introduced to the constant volume. All solutions freshly prepared in this way were evacuated at 10^{-6} mm of Hg by several freeze-pump-thaw cycles and then sealed. In acetonitrile or when relatively high concentration of the electron acceptor was used, the monomer solution and the acceptor solution were independently evacuated at 10^{-6} mm of Hg and they were mixed immediately before irradiation. The reaction system was irradiated at 10–20° for an appropriate time, mostly 5 hr, with light of wavelength longer than 310 nm at a distance of about 2 cm from a 500-W high-pressure mercury lamp (type PIH-500, Eikosha Co. Ltd.). Some systems were irradiated in the charge-transfer band using appropriate filter solutions. In the copolymerization experiment with styrene as a comonomer light of wavelength longer than 350 nm was irradiated using a filter solution of aqueous solution of $Cu(NO_3)_2 \cdot 3H_{20}$ (5 g/10 ml) so as to avoid the excitation of styrene. Under these conditions thermal reactions were negligible in all systems studied. The concentration of VCZ monomer was usually 0.5 *M* (in acetonitrile 0.25 *M*, in methanol 2.5×10^{-2} *M*) and that of the electron acceptor was usually 5.0×10^{-3} *M* (in acetonitrile 2.5×10^{-3} *M*, in methanol 1.0×10^{-3} *M*). The reaction mixtures were poured into excess cold methanol. The reaction products precipitated were filtered with a glass filter weighed beforehand, washed with methanol, dried *in vacuo* at room temperature for 2 days, and weighed. When the precipitates were mixtures of different products, they were separated by means of fractionation with appropriate solvents.

Analyses. Identification of the products was made on the basis of their melting point, solubility, and ir, uv, nmr spectra, and elementary analyses.

VCZ homopolymer was easily soluble in benzene, but difficultly soluble in CCl_4 or in acetone. The copolymer of VCZ with FN was entirely insoluble in benzene but soluble in H_4furan. The copolymer of VCZ with DEF was soluble in benzene and in CCl_4. VCZ homopolymer and the copolymers of VCZ with styrene and VCZ with DEF were reprecipitated from benzene–methanol. The copolymer of VCZ with FN was reprecipitated from H_4furan–methanol. The cyclodimer of VCZ, *trans*-1,2-dicarbazylcyclobutane, was difficultly soluble in cold methanol, but soluble in benzene or in acetone. It was recrystallized from acetone–methanol, mp 192.1–193.4° (lit.[14] mp 191.0–193.5°), and identified by comparison with the authentic sample.[14] The copolymers obtained between VCZ and FN, and between VCZ and DEF are white powders with molecular weights in the range 3000–7000 and 3000–10,000, respectively (Table VII). Although in some solvents the values of the molecular weight above 10,000 were obtained, it should be noted that these do not seem to be precise ones since these are beyond the capability of the Mechrolab VPO instrument. The VCZ–FN copolymer did not soften below 300°: the VCZ–DEF copolymer softened at 178–225°. The ir spectra of the VCZ–FN copolymer and the VCZ–DEF copolymer show a weak C≡N absorption at 2250 cm^{-1}, a strong C═O absorption at 1740 cm^{-1}, respectively. The facts that the characteristic peaks due to the vinyl group in VCZ and the *trans* out-of-plane ═C—H deformation vibration at 965 and 975 cm^{-1} observed in FN and DEF, respectively, disappeared in the copolymers indicated that the copolymerization proceeded at the olefinic double bonds of both monomers. Noticeably, these copolymers were characteristic in their electronic absorption spectra. The absorption maxima due to the carbazyl moiety observed at 344 and 330 nm in VCZ homopolymer shifted toward the violet region by about 10 and 5 nm in the VCZ–FN copolymer (λ_{max} 333, 320 nm) and the VCZ–DEF copolymer (λ_{max} 338, 325 nm), respectively. By contrast, VCZ–styrene copolymers showed no such violet shift. The copolymer compositions were determined from the absorption band due to the carbazyl group together with the nitrogen analyses, these being in good agreement. The compositions of the VCZ–styrene copolymers were determined at λ_{max} 344 nm in H_4furan. The compositions of VCZ–FN and VCZ–DEF copolymers were determined in H_4furan at λ_{max} 333 and 338 nm, respectively. In calculation of the copolymer compositions it was assumed that the molar extinction coefficient value of the carbazyl group does not change between VCZ homopolymer and the copolymer at their absorption maxima. The copolymers of VCZ with FN and VCZ with DEF were found to be 1:1 in their compositions irrespective of two or three different monomer feed ratios (Table VII) and were assigned to be the alternating copolymers since FN and DEF did not polymerize alone under the present condition.

In preliminary examinations, it was found that in most systems the reaction product is regulated by the solvent and consists of a single product, *e.g.*, VCZ homopolymer, or copolymer, or VCZ cyclodimer. However, when the electron acceptor acts as a monomer at the same time, the reaction products were frequently mixtures of VCZ homopolymer, VCZ cyclodimer, and the copolymer. They were successfully separated by fractionation with solvents. Typical examples are shown in Chart I.

Apparatus. Ir spectra were taken with a Hitachi EPI-G2 ir spectrometer. Uv spectra were taken with a Hitachi 124 spectrophotometer. Nmr spectra were obtained with a Japan Optics Laboratory JNM 3H-60 spectrometer. Emission spectra were obtained with a Hitachi MPF Model 3 spectrophotofluorometer. Molecular weights were determined with a Mechrolab VPO Model 302 in pyridine at 65°.

Results and Discussion

Charge-Transfer Interaction between VCZ and Various Organic Electron Acceptors. The organic electron acceptors used in the present study are as follows: *p*-quinoid compounds: BA, CA, 2,5-DQ, *p*-BQ; acid anhydrides: PMDA, MA, PTA, TCPA; nitro compound: TNB; electron-accepting monomers: FN, DEF; others: CBr_4, CCl_4, DMTP. The solutions of VCZ and each of these electron acceptors are colored except CBr_4, CCl_4, and DMTP, indicating the existence of the charge-transfer interaction in the ground state. The systems VCZ–BA, VCZ–CA, and VCZ–2,5-DQ showed two charge-transfer absorption bands with λ_{max} (in CCl_4) at 595 and 509, 590 and 506, 535 and 452 nm, respectively, the first band appearing as a shoulder. The charge-transfer band of the system VCZ–*p*-BQ was overlapped with the absorption of *p*-BQ. In the systems VCZ–PMDA and VCZ–TNB new broad shoulder

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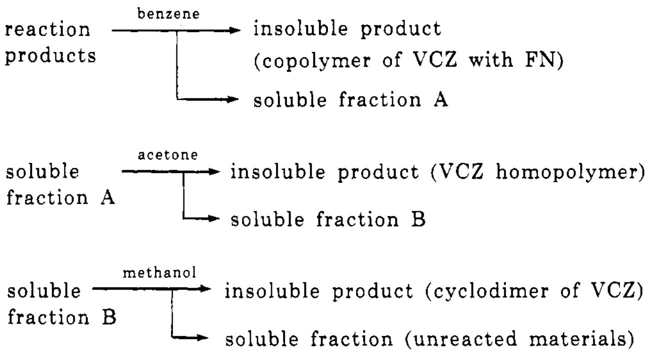
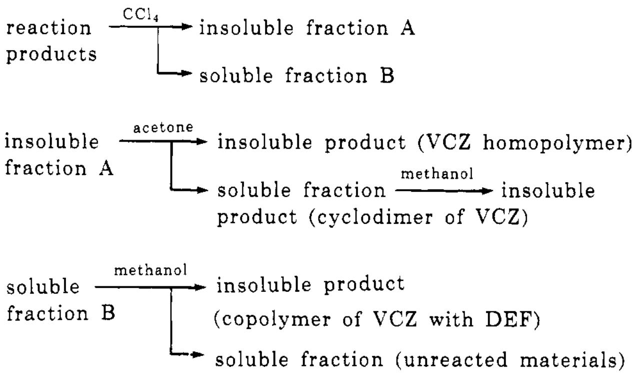
[14] (a) L. P. Ellinger, J. Feeney, and A. Ledwith, *Monatsch. Chem.*, **96**, 131 (1965); (b) S. McKinley, J. W. Crawford, and C. H. Wang, *J. Org. Chem.*, **31**, 1963 (1966).

Chart I
VCZ-FN System



VCZ-DEF System



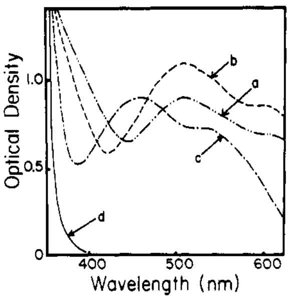


Figure 1. The absorption spectra of the systems VCZ-electron acceptors in carbon tetrachloride. (a) VCZ-BA system (– – – – – –), (b) VCZ-CA system (— — — —), (c) VCZ-2,5-DQ system (— — — —), and (d) VCZ (————). [VCZ] = 0.2 *M*, [acceptor] = 1.0×10^{-2} *M*.

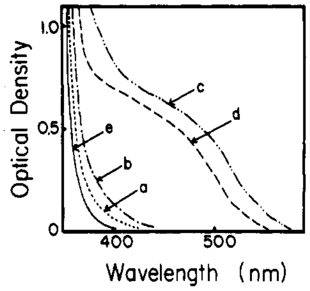


Figure 2. The absorption spectra of the systems VCZ-electron acceptors in chloroform. (a) VCZ-PTA system (- - - - - - -), (b) VCZ-MA system (— — — —), (c) VCZ-PMDA system (— – — – —), (d) VCZ-TNB system (———), (e) VCZ (————). [VCZ] = 0.2 *M*, [acceptor] = 1.0×10^{-2} *M* ([TNB] = 1.0×10^{-3} *M*.)

bands due to the charge-transfer complexes appeared at wavelengths longer than 390 nm. In the systems VCZ-MA, VCZ-PTA, and VCZ-FN, no distinct charge-transfer bands appeared, but the absorption spectra of these systems shifted to the red region as compared with the sum of the absorptions of VCZ and the electron acceptor of the same concentration, the intensity of the absorptions being increased with increasing concentration of the electron acceptor. The absorption spectrum of the system VCZ-DEF showed only slightly red shift and the color of the solution was only slightly pale yellow, its color deepening when cooled. Formation of the 1:1 charge-transfer complex was confirmed in the systems, *e.g.*, VCZ-FN and VCZ-DEF by means of a continuous variation method in the absorption band due to the charge-transfer complex.[15] The absorption spectra are shown in Figures 1 and 2. In the systems VCZ-CCl_4 and VCZ-DMTP, the charge-transfer interaction in the ground state appears to be negligible since these solutions are colorless and the absorption spectra of these systems were almost the same with the absorption of VCZ of the same concentration. However, formation of the exciplex has been demonstrated spectroscopically in the system VCZ-DMTP in benzene[16] and it has also been reported that dynamic quenching of the fluorescence of VCZ occurs by CCl_4 or CBr_4,[17] indicating the charge-transfer interaction in the excited state of VCZ. In the systems VCZ-FN and VCZ-DEF, weak charge-transfer interaction was observed in the ground state, but also formation of the exciplex was demonstrated. When FN or DEF was added to a benzene solution of VCZ, the fluorescence of VCZ was quenched and a new emission band due to the exciplex was observed with λ_{max} 550 and 540 nm, respectively, as shown in Figures 3 and 4. In more polar solvents, *e.g.*, dichloromethane or acetonitrile, no new emission band was observed and only stronger quenching of the VCZ fluorescence occurred probably due to the predominance of the electron-transfer process. The Stern-Volmer plots for the quenching of the VCZ fluorescence by FN or DEF in benzene and in acetonitrile are depicted in Figures 5 and 6; the upward deviation of the plots observed especially in the case of FN in the ranges of rather high concentrations of the quencher appears to be as due to the participation of the static quenching, that is, the charge-transfer interaction in the ground state.

Reactions. In the present study all reactions were carried out in high vacuum systems and under conditions in which thermal reactions were negligible; the reaction systems were in most cases irradiated with light of wavelength longer than 310 nm. Thus, the primary process of the reaction involves the excitation of both VCZ monomer and the charge-transfer complex formed in the ground state; in some systems the electron acceptor (*e.g.*, *p*-quinoid compounds) is also excited.

As a result of the investigation on the solvent effect on the photosensitized reaction of VCZ in the presence of various organic electron acceptors, we have found that the reaction courses are regulated principally by the solvent used. In less basic solvents such as benzene, dichloromethane, or nitrobenzene a general reaction course is cationic homopolymerization of VCZ, although a very weak electron acceptor such as DMTP is used, almost no polymerization occurs in nonpolar benzene. We have already clarified that cationic homopolymerization of VCZ proceeds in benzene in the systems VCZ-BA, VCZ-CA,

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(16) M. Yamamoto, T. Ohmichi, M. Ohoka, K. Tanaka, and Y. Nishijima, *Rept. Progr. Polym. Phys. Jap.*, **12**, 457 (1969).
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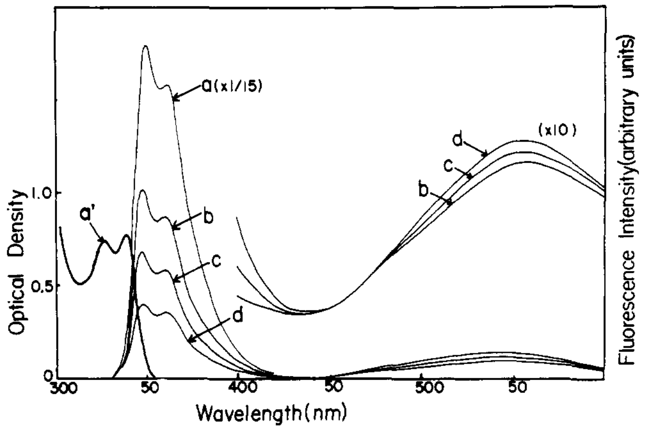

Figure 3. Absorption and fluorescence spectra of VCZ and the system VCZ-FN in benzene at room temperature. a′: Absorption spectrum of VCZ. [VCZ] = 1.79×10^{-4} *M*. a: Fluorescence spectrum of VCZ (corrected). [VCZ] = 1.79×10^{-4} *M*. b, c, d: Fluorescence spectra of the system VCZ-FN (cor). Excitation wavelength: 340 nm. b: [VCZ] = 1.79×10^{-4} *M* and [FN] = 5.17×10^{-2} *M*. c: [VCZ] = 1.79×10^{-4} *M* and [FN] = 7.70×10^{-2} *M*. d: [VCZ] = 1.79×10^{-4} *M* and [FN] = 0.105 *M*.

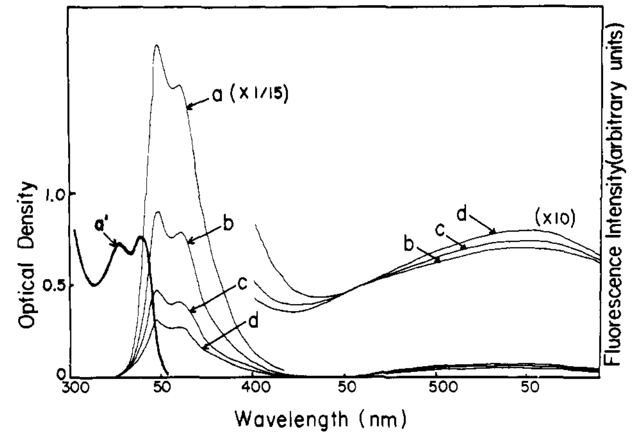

Figure 4. Absorption and fluorescence spectra of VCZ and the system VCZ-DEF in benzene at room temperature. a′: Absorption spectrum of VCZ. [VCZ] = 1.79×10^{-4} *M*. a: Fluorescence spectrum of VCZ (cor). [VCZ] = 1.79×10^{-4} *M*. b, c, d: Fluorescence spectra of the system VCZ-DEF (cor). Excitation wavelength: 340 nm. b: [VCZ] = 1.79×10^{-4} *M* and [DEF] = 0.200 *M*. c: [VCZ] = 1.79×10^{-4} *M* and [DEF] = 0.305 *M*. d: [VCZ] = 1.79×10^{-4} *M* and [DEF] = 0.412 *M*.

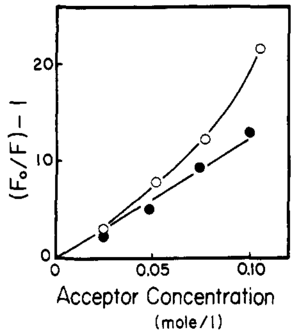

Figure 5. Stern–Volmer plots for the quenching of the VCZ fluorescence by FN or DEF in benzene. F_0 and *F* represent the VCZ fluorescence intensities in the absence and in the presence of an acceptor, respectively. (○) VCZ-FN system. [VCZ] = 1.79×10^{-4} *M*. (●) VCZ-DEF system. [VCZ] = 2.36×10^{-4} *M*.

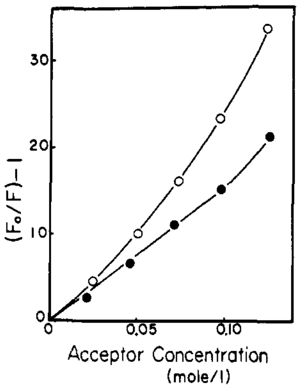

Figure 6. Stern–Volmer plots for the quenching of the VCZ fluorescence by FN or DEF in acetonitrile. F_0 and *F* represent the VCZ fluorescence intensities in the absence and in the presence of an acceptor, respectively. (○) VCZ-FN system. [VCZ] = 1.86×10^{-4} *M*. (●) VCZ-DEF system. [VCZ] = 1.86×10^{-4} *M*.

VCZ-2,5-DQ, and VCZ-*p*-BQ and that not only the excitation of VCZ monomer but also the selective excitation of the charge-transfer complex initiates the cationic homopolymerization of VCZ.[3] In the literature it has been reported that the photosensitized cationic homopolymerization of VCZ proceeds in the systems VCZ-CBr_4 in benzene[18] and VCZ-2,4,7-trinitrofluorenone in nitrobenzene.[4] Cationic homopolymerization of VCZ was found to occur also in the system VCZ-MA in benzene, the polymer yields being dependent upon the irradiation time and the wavelength of the incident light (Figure 7). The polymerization was not greatly affected by the addition of 1,1-diphenyl-2-picrylhydrazyl (DPPH) but inhibited by the addition of small amounts of triethylamine. Cationic homopolymerization of VCZ was also found to occur in dichloromethane with various organic electron acceptors; the results are listed in Table I. The characteristic colors due to the charge-transfer complexes faded after irradiation for 5 hr and the homopolymers of VCZ which were light brown were obtained as single products. That the homopolymerization was not radical but cationic in nature was confirmed from the effect of additives and the copolymerization with styrene. The homopolymerization was not retarded by the addition of DPPH, but inhibited by the addition of small amounts of dimethylformamide. The compositions of the copolymers between VCZ and styrene examined in the systems, *e.g.*, VCZ-CA and VCZ-PTA, were quite different from those reported in the radical copolymerization with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator.[19] The results are shown in Table II and Figure 8.

By contrast, it was found that in such polar, basic solvents as acetone, acetonitrile or methanol, cyclodimerization of VCZ to give *trans*-1,2-dicarbazylcyclobutane generally takes place exclusively with a variety of organic electron acceptors except CBr_4 and CCl_4. Cyclodimerization of VCZ took place only in the presence of catalytic amounts of the organic electron acceptor under deaerated condition, although no cyclodimerization of VCZ occurs in the absence of the electron acceptor. The cyclodimerization was also initiated by the selective excitation of the charge-transfer band as was found in the systems VCZ-BA and VCZ-CA where the charge-transfer bands are well separated from the component absorption bands. Cyclodimerization of VCZ also took place even in the relatively less

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(19) R. Hart, *Makromol. Chem.*, 47, 143 (1961).

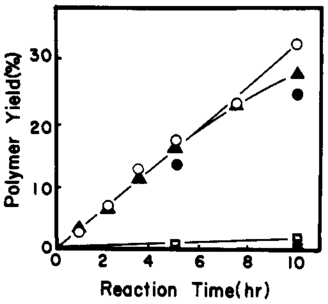


Figure 7. Photopolymerization of VCZ with MA in benzene at 10–20°. [VCZ] = 0.5 M. [MA] = 3.0×10^{-2} M. (○) Irradiated with light of wavelength longer than 310 nm. (▲) Irradiated with light of wavelength longer than 350 nm. (□) Irradiated with light of wavelength longer than 390 nm. (●) DPPH was added. [DPPH] = 1.0×10^{-4} M. Irradiated with light of wavelength longer than 310 nm. (■) Triethylamine was added. [Triethylamine] = 1.0×10^{-2} M. Irradiated with light of wavelength longer than 310 nm.

Table I
Photosensitized Polymerization of VCZ in the Presence of Various Organic Electron Acceptors in Dichloromethane[a]

Acceptor	Additives[b]	Yield of Polymer (%)
BA	None	73.1
CA	None	58.0
CA	DPPH	52.3
CA	DMF[c]	0
2,5-DQ	None	71.2
p-BQ	None	70.0
PDA	None	73.1
MA	None	96.2
PTA	None	80.0
PTA	DMF	0
DMTP	None	79.9
TNB	None	80.0
FN	None	97.8
FN	DMF	0
DEF	None	88.0
DEF	DMF	0

[a] Irradiated with light of wavelength longer than 310 nm for 5 hr at 10–20°. [VCZ] = 0.5 M, [acceptor] = 5.0×10^{-3} M. [b] [DPPH] = 1.0×10^{-4} M; [DMF] = 2.0×10^{-2} M. [c] DMF = dimethylformamide.

Table II
Compositions of Copolymers Obtained under Irradiation in the Systems VCZ(M_1)-Styrene-CA and VCZ(M_1)-Styrene-PTA in Dichloromethane[a]

M_1 (Molar Ratio)	Conversion (%)	Concn (mg/50 ml of H_4furan)	A (at 344 nm)	m_1 (Molar Ratio)
I. VCZ(M_1)-Styrene-CA System				
0.25	9.5	2.6	0.709	0.776
0.50	6.0	3.0	0.872	0.865
0.75	7.4	2.6	0.805	0.969
II. VCZ(M_1)-Styrene-PTA System				
0.25	8.5	2.8	0.758	0.767
0.50	5.9	2.7	0.775	0.847
0.75	6.1	2.7	0.838	0.973

[a] Irradiated with light of wavelength longer than 350 nm at 10–20°. The copolymer compositions were calculated based on the extinction coefficient value of the VCZ homopolymer prepared with AIBN catalyst in benzene; the absorbance of the VCZ homopolymer (2.93 mg/50 ml of H_4furan at 344 nm was 0.923. [VCZ] + [styrene] = 1.0 M, [acceptor] = 5.0×10^{-3} M.

Table III
Photosensitized Cyclodimerization of VCZ to Give *trans*-1,2-Dicarbazylcyclobutane in Polar, Basic Solvents[a]

	Yield of Cyclodimer (%) in		
Acceptor	Acetone	Acetonitrile	Methanol[b]
BA	44.5[c]	33.1[i]	28.2
CA	45.5[d]	25.0[i]	23.8
2,5-DQ	57.4[e]	37.8[i]	31.4
p-BQ	55.2[f]	45.1[i]	18.5
PDA[g]	43.0	56.3	
MA[h]	77.8	75.1	
TCPA	40.8	37.5[i]	
PTA	72.3	74.8	
DMTP	63.0	75.2	
TNB	44.0	70.8[i]	
CCl_4	0[j]	0[k]	
CBr_4		0[l]	
FN	69.5	24.9[i]	
DEF	46.7	35.8[i]	

[a] Irradiated with light of wavelength longer than 310 nm for 5 hr at 10–20°. [VCZ] = 0.5 M, [acceptor] = 5.0×10^{-3} M. [b] [VCZ] = 2.5×10^{-2} M, [acceptor] = 1.0×10^{-3} M. [c] 18.0% cyclodimer when irradiated in the charge-transfer band, $h\nu > 430$ nm. [d] 34.0% cyclodimer when irradiated in the charge-transfer band, $h\nu > 430$ nm. [e] [2,5-DQ] = 0.25 M, 57.6% homopolymer of VCZ. [f] [*p*-BQ] = 0.5 M, 69.9% homopolymer of VCZ. [g] In H_4furan, 32.4% cyclodimer of VCZ. [h] In H_4furan, 44.0% cyclodimer of VCZ. [i] [VCZ] = 0.25 M, [acceptor] = 2.5×10^{-3} M. [j] 54.1% homopolymer of VCZ; chlorine contents, 0.81%. [k] 76.7% homopolymer of VCZ; chlorine contents, 0.68%. [l] 71.9% homopolymer of VCZ; bromine contents, 1.48%.

polar solvent H_4furan in the systems, *e.g.*, VCZ–PMDA and VCZ–MA, while with a very weak electron acceptor, *e.g.*, DMTP, the cyclodimerization did not proceed in H_4furan, occurring only in polar, basic solvents. The results are summarized in Table III.

On the other hand, in strongly basic solvents such as dimethylformamide or Me_2SO, the general reaction course was found to be radical homopolymerization of VCZ instead of the cyclodimerization reaction. The homopolymerization of VCZ proceeded with, *e.g.*, acid anhydrides, DMTP, FN, DEF, *p*-benzoquinone, and its derivatives as shown in Table IV. The polymer yield was relatively low with such electron acceptors as BA or CA which act as radical traps, and almost no polymerization occurred with TNB as an electron acceptor. This was also the case with 2,5-DQ when it was present in rather high concentration. The polymer yield was in general higher in Me_2SO than in dimethylformamide. Radical nature of the polymerization in dimethylformamide or in Me_2SO was indicated from the effect of additives and the copolymerization with styrene. The results of copolymer compositions are shown in Table V and Figure 8, which are in good agreement with the reported values in the radical copolymerization.[19]

The above generalized reactions, *i.e.*, cationic homopolymerization of VCZ in less basic solvents, cyclodimerization of VCZ in basic solvents, and radical homopolymerization of VCZ in strongly basic solvents dimethylformamide and Me_2SO, are all rationalized as initiated by VCZ cation radical, ion-paired cation radical in nonpolar solvents or dissociated cation radical in polar solvents, formed by the photochemical electron transfer from VCZ to the electron acceptor. Indeed, we have obtained direct evidence for the formation of VCZ cation–radical and the anion radical of the electron acceptor in some systems

Table IV
Photosensitized Polymerization of VCZ in the Presence of Various Organic Electron Acceptors in Dimethylformamide and in Me_2SO[a]

Acceptor	Additives[b]	Yield of Polymer (%) in DMF	Yield of Polymer (%) in Me_2SO
BA	None	1.7	19.3
CA	None	13.7	17.1
CA	DPPH	0	0
2,5-DQ	None	27.6	32.0
2,5-DQ[c]	None	0.7	
p-BQ	None	15.3	39.0
PDA	None	17.3	53.2
MAn	None	10.1	45.1
PTA	None	10.5	68.1
PTA	DPPH	0	0
DMTP	None	30.1	71.1
TNB	None	1.5	0.8
FN	None	26.0	58.8
FN	DPPH	0	0
DEF	None	11.5	81.8

[a] Irradiated with light of wavelength longer than 310 nm for 5 hr at 10–20°; [VCZ] = 0.5 *M*, [acceptor] = 5.0×10^{-3} *M*. [b] [DPPH] = 1.0×10^{-4} *M*. [c] [2,5-DQ] = 0.25 *M*.

Table V
Compositions of Copolymers Obtained under Irradiation in the Systems VCZ(M_1)-Styrene-CA and VCZ(M_1)-Styrene-PTA in Dimethylformamide[a]

M_1 (Molar Ratio)	Conversion (%)	Concn (mg/50 ml of H_4furan	*A* (at 344 nm)	m_1 (Molar Ratio)
	I. VCZ(M_1)-Styrene-CA System			
0.25	8.6	14.1	0.335	0.042
0.50	4.1	4.1	0.229	0.105
0.75	2.3	4.2	0.572	0.289
	II. VCZ(M_1)-Styrene-PTA System			
0.25	7.4	5.7	0.188	0.043
0.50	3.3	5.3	0.295	0.104
0.75	0.6	2.0	0.210	0.294

[a] Irradiated with light of wavelength longer than 350 nm at 10–20°. The copolymer compositions were calculated based on the extinction coefficient value of the VCZ homopolymer prepared with AIBN catalyst in benzene; the absorbance of the VCZ homopolymer (2.93 mg/50 ml of H_4furan at 344 nm was 0.923. [VCZ] + [styrene] = 1.0 *M*, [acceptor] = 5.0×10^{-3} *M*.

such as VCZ-CA[1,9] or VCZ-PMDA[20] by means of flash spectroscopy. The electron transfer occurs by the selective excitation of the charge-transfer complex or *via* the interaction of the excited VCZ with the electron acceptor in the ground state or *vice versa*. It should be noted that the electron-transfer process depends upon the polarity of solvent; thus when a very weak electron acceptor is used, the electron transfer to give ion-radical species may not occur in nonpolar solvents as revealed in the system, *e.g.*, VCZ-DMTP in benzene, where no appreciable reaction occurs.

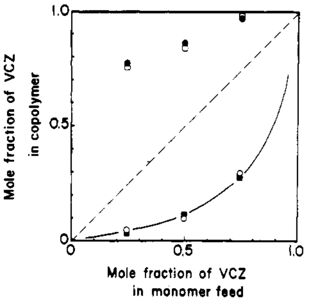
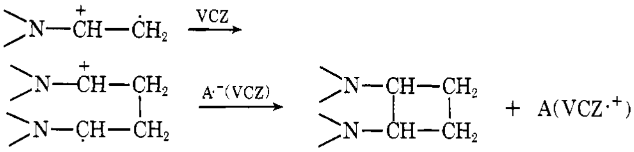


Figure 8. Compositions of VCZ-styrene copolymers obtained in the systems VCZ-styrene-CA and VCZ-styrene-PTA in dichloromethane and in dimethylformamide under irradiation with light of wavelength longer than 350 nm. [VCZ] + [styrene] = 1.0 *M*, [acceptor] = 5.0×10^{-3} *M*. (●) VCZ-CA system in dichloromethane. (□) VCZ-PTA system in dichloromethane. (○) VCZ-CA system in dimethylformamide. (■) VCZ-PTA system in dimethylformamide. (—) Composition curve obtained in the radical copolymerization with AIBN catalyst.[19]

In contrast to the cationic homopolymerization of VCZ, the cyclodimer of VCZ is most reasonably understood as formed by a radical reaction of VCZ cation radical with the VCZ monomer to give VCZ dimer cation radical, followed by the electron back-transfer to it and cyclization.[5,12,21] That the reaction is radical in nature was confirmed by the fact that addition of small amounts of DPPH inhibited the formation of the cyclodimer.



>N–, carbazyl group
A, electron acceptor

Cation solvation by the basic solvent is considered to be responsible for the cyclodimerization reaction. VCZ monomer is well known to be strongly basic, and easily undergoes cationic polymerization.[22] Thus, in less basic solvents such as benzene, dichloromethane, or nitrobenzene, cationic reactivity in VCZ cation radical predominates over radical reactivity, leading to cationic homopolymerization of VCZ. By contrast, in basic solvents, such as acetone, acetonitrile, or methanol, cationic reactivity in VCZ cation radical may be suppressed due to cation solvation; hence radical reactivity in VCZ cation radical becomes preferential, leading to the cyclodimerization reaction. The relative magnitude of basicity, that is, cation-solvating ability, of a solvent has been determined from the position of the absorption band of the deuterated hydroxy group (O—D) in the ir spectrum in each solvent containing a small quantity of methanol-*d*. With benzene as a standard, the relative magnitudes of basicity of the solvents have been shown to increase in the order[23]: dichloromethane (−12) < benzene (0) < nitrobenzene (21) < acetonitrile (49) < acetone (64) < dimethylformamide (107) < Me_2SO (141); the values in the parentheses repre-

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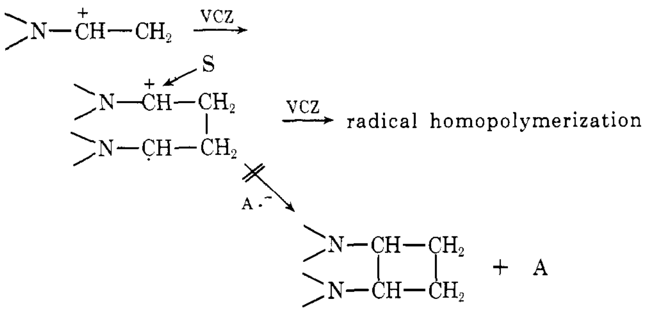
(20) T. Tomikawa, K. Tada, Y. Shirota, T. Nogami, N. Yamamoto, H. Tsubomura and H. Mikawa, unpublished results, presented at the 4th Symposium on the Charge-Transfer Complex, Nagoya, Japan, Oct. 1972, Reprint p 67.

(21) It was pointed out by a referee that a mechanism involving a monomer triplet state might be possible for the cyclodimerization reaction. However, the mechanism of the radical reaction of VCZ cation radical with the VCZ monomer seems to be most reasonable based on the following reasons. (a) Formation of VCZ cation radical and the anion radical of the electron acceptor has been demonstrated directly. (b) The cyclodimerization reaction takes place only in basic solvents. (c) In the absence of the electron acceptor, no cyclodimerization reaction occurs.

(22) H. Scott, T. P. Konen, and M. M. Labes, *J. Polym. Sci., Part B*, 1, 413 (1963).

(23) H. Kagiya, Y. Sumida, and T. Inoue, *Bull. Chem. Soc. Jap.*, 41, 767 (1968).

sent $\Delta\nu_D$(cm^{-1}), where $\Delta\nu_D$(cm^{-1}) = ν_D(benzene) − ν_D(other solvents). The value of methanol is unknown but it is generally understood to have a rather strong cation-solvating ability. The occurrence of radical homopolymerization of VCZ in dimethylformamide or in Me_2SO is also attributed as due to the cation solvation by these strongly basic solvents. Although it is not very clear at present why radical homopolymerization predominates over the cyclodimerization in dimethylformamide or in Me_2SO, it may be rationalized on the basis of the very powerful cation solvation by these solvents. That is, the very powerful cation solvation by these solvents impedes back electron transfer to the VCZ dimer cation radical formed from the radical reaction of VCZ cation radical with the VCZ monomer. Hence subsequent radical addition of VCZ monomer occurs leading to homopolymerization of VCZ.



>N−, carbazyl group
A, electron acceptor
S, solvent (dimethylformamide or Me_2SO)

A notable exception to the above generalization is the system using σ acceptors such as CCl_4 or CBr_4; that is the cyclodimerization reaction did not take place in polar, basic solvents such as acetone or acetonitrile, VCZ homopolymer being produced (Table III). Although further studies are necessary for the clarification of the detailed mechanism of the polymerization, it is suggested from the effects of additives that the homopolymerization of VCZ with CBr_4 or CCl_4 as an electron acceptor in acetone or in acetonitrile proceeded mainly cationically; the polymerization was greatly retarded by the addition of small amounts of dimethylformamide and also the polymerization occurred only very slightly in the formamide solvent, while the polymerization was not greatly affected by the addition of DPPH or hydroquinone. It is suggested that the electron-transfer process in these systems is accompanied by the cleavage of the electron-acceptor molecules as in the following.[18] Radical species ($\cdot CX_3$) thus formed may add to the radical site of VCZ cation radical, the resulting species probably initiating the cationic polymerization of VCZ even in basic solvents. In fact, the incorporation of halogen atoms into the polymer was confirmed by the elementary analyses of the resulting polymers.

$$VCZ + CX_4 \xrightarrow{h\nu} VCZ^{\cdot+} + X^{\cdot-} + \cdot CX_3$$
$$X = Br, Cl$$

An important factor also to be noted as influencing the reaction course is the radical-trapping ability of the electron acceptor or of the solvent. The solvent nitrobenzene in which cationic homopolymerization of VCZ takes place is relatively weak in its cation-solvating ability, and at the same time acts as an efficient radical trap. Also, it was anticipated, in view of radical nature of the cyclodimerization reaction, that when the electron acceptor which acts as a strong radical scavenger is present in a rather high concentration instead of in catalytic amounts, the cyclodimerization would not take place. This was indeed found to be the case with *p*-quinoid compounds as shown in Table III.

Table VI
Photosensitized Copolymerization of VCZ with the Electron-Accepting Monomers, FN and DEF, in Various Solvents[a]

Solvent	Reaction Product (%) Electron-Accepting Monomers: Fumaronitrile (FN)	Reaction Product (%) Electron-Accepting Monomers: Diethyl Fumarate (DEF)
Benzene	34.1 (HP) and 35.7 (CP)	0.6 (HP) and 1.8 (CP)
Dichloromethane	95.2 (HP) and 2.6 (CP)	88.1 (HP) and 2.9 (CP)
Acetone	61.7 (CP)	17.5 (CP) and 11.9 (CD)
Acetone[b]	23.5 (CP) and 41.8 (CD)	
Acetone[c]	9.6 (CP) and 43.9 (CD)	
Acetonitrile[d]	39.8 (CP)	19.4 (CP) and 1.8 (CD)
DMF	84.4 (CP)	10.4 (CP)
Me_2SO	97.4 (CP)	42.1 (CP)

[a] The symbols CP, HP, and CD represent the alternating copolymer of VCZ with the electron-accepting monomer, VCZ homopolymer, and the cyclodimer of VCZ, respectively. Irradiated with light of wavelength longer than 310 nm for 5 hr at 10–20°; [VCZ] = 0.5 *M*, [electron-accepting monomer] = 0.5 *M*. [b] [VCZ] = 0.5 *M*, [FN] = 0.25 *M*. [c] [VCZ] = 0.5 *M*, [FN] = 0.05 *M*. In the cases of *b* and *c*, the copolymer yields were calculated based on the FN concentration. [d] [VCZ] = 0.25 *M*, [electron-accepting monomer] = 0.25 *M*.

As stated above, the reaction course, especially dual cationic and free-radical nature of the reaction, was found to be clearly regulated mainly by the solvent. Furthermore, it was expected that when the electron acceptor is at the same time a monomer capable of undergoing radical polymerization or copolymerization, more information would be obtained with respect to the nature of the reaction. From this viewpoint we have studied the polymerization of the systems VCZ-FN and VCZ-DEF in the presence of high concentrations of FN or DEF, directing our attention to the solvent effect. The monomers FN and DEF, in general, have been known to show very little tendency to polymerize alone but known to copolymerize with other vinyl monomers such as styrene in a radical mechanism.[24,25] The results obtained lent further support to the solvent regulation of the reaction as described above. It is also of interest to note that first examples of alternating copolymerization were observed with respect to the VCZ monomer. When the system containing equimolar amounts of VCZ and the electron-accepting monomer, FN or DEF, was irradiated in benzene, simultaneous cationic homopolymerization of VCZ and alternating radical copolymerization between VCZ and FN or DEF took place. In dichloromethane also, cationic homopolymerization of VCZ and alternating radical copolymerization occurred simultaneously, although the former predominated much over the latter in this solvent. However, in such basic solvents as acetone or acetonitrile, no cationic homopolymerization of VCZ occurred but alternating radical copolymerization proceeded accompanied by the cyclodimerization of VCZ. As the concentration of the electron-accepting monomer decreased, the proportion of the cyclodimerization to the alternating copolymerization increased. In dimethylformamide or Me_2O only alternating radical copolymerization took place. The results are summarized in Table VI. The analyses of the copoly-

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(24) G. E. Ham, *J. Polym. Sci., Part A*, **45**, 169 (1960).

(25) C. Walling and E. A. McElhill, *J. Amer. Chem. Soc.*, **73**, 2819 (1951).

Table VII
Compositions of the Copolymers, VCZ–FN and VCZ–DEF, Obtained in Various Solvents[a]

Solvent	Mol Fraction of VCZ in Monomer Feed	Concn (mg/50 ml of H_4furan)	*A* (at 333 nm for a; at 338 nm for b)	Anal. N(%)	Mol Fraction of VCZ in Copolymer[b]	Mol Wt
			a. VCZ–FN Copolymer			
Benzene	0.25	4.0	0.908	14.48	0.510 (0.545)	7,600
Benzene	0.40	4.1	0.937	14.37	0.516 (0.550)	3,700
Benzene	0.50	3.5	0.780	14.90	0.494 (0.526)	3,300
Benzene	0.60	3.0	0.684	14.45	0.514 (0.546)	3,900
Benzene	0.75	3.5	0.791	14.60	0.506 (0.540)	4,100
Dichloromethane	0.50	3.1	0.690	15.07	0.493 (0.519)	
Acetone	0.50	2.8	0.650	14.91	0.531 (0.526)	
Acetonitrile[c]	0.50	2.9	0.645	15.00	0.493 (0.522)	
DMF	0.25	4.6	1.040	15.44	0.507 (0.502)	7,700
DMF	0.40	4.2	0.982	15.37	0.538 (0.505)	3,700
DMF	0.50	2.8	0.630	15.22	0.503 (0.512)	3,600
DMF	0.60	3.0	0.680	15.14	0.509 (0.516)	5,700
DMF	0.75	3.9	0.861	14.62	0.486 (0.539)	3,400
Me_2SO	0.50	4.0	0.905	16.47	0.496 (0.460)	6,700
			b. VCZ–DEF Copolymer			
Benzene	0.25	3.6	0.618	4.29	0.516 (0.563)	8,200
Benzene	0.40	4.1	0.670		0.499	4,200
Benzene	0.50	6.6	1.120	3.75	0.510 (0.488)	5,000
Benzene	0.60	4.1	0.685	3.37	0.502 (0.436)	7,700
Benzene	0.75	2.3	0.398	3.44	0.516 (0.446)	
Dichloromethane	0.50	5.6	0.965	3.74	0.518 (0.487)	
Acetone	0.50	4.0	0.650		0.487	
Acetonitrile[c]	0.50	5.6	0.960	4.29	0.513 (0.563)	2,800
DMF	0.40	2.6	0.430		0.495	
DMF	0.50	3.5	0.600	3.95	0.515 (0.516)	8,100
DMF	0.60	5.4	0.903	3.41	0.502 (0.442)	10,400
DMF	0.75	4.4	0.732	3.79	0.499 (0.494)	9,500
Me_2SO	0.50	7.4	1.260	3.49	0.512 (0.452)	18,200

[a] Concentrations, [VCZ] + [electron-accepting monomer] = 1.0 *M*. [b] The copolymer compositions were calculated from the extinction coefficient value of the VCZ homopolymer prepared with AIBN catalyst in benzene and from the nitrogen analysis (in parentheses). The absorbance of VCZ homopolymer (2.93 mg/50 ml of H_4furan) at 344 nm is 0.923. Calculated values of nitrogen analyses for 1:1 VCZ–FN and 1:1 VCZ–DEF copolymers are 15.49 and 3.83%, respectively. [c] Concentrations, [VCZ] + [electron-accepting monomer] = 0.5 *M*.

Table VIII
Generalized Reaction Courses in the Photosensitized Reaction of *N*-Vinylcarbazole in the Presence of the Organic Electron Acceptor

	Various Organic Electron Acceptors (Catalytic Amounts)	Electron-Accepting Monomers Capable of Undergoing Radical Copolymerization (FN, DEF) (Large Amounts)
Less basic solvents (*e.g.*, benzene, dichloromethane, nitrobenzene)	Cationic homopolymerization of VCZ	Cationic homopolymerization of VCZ. (In benzene, radical copolymerization takes place simultaneously.)
Basic solvents (*e.g.*, acetone, acetonitrile, methanol)	Cyclodimerization of VCZ (exception CBr_4, CCl_4)	Radical copolymerization of VCZ with the electron-accepting monomer plus cyclodimerization of VCZ
Strongly basic solvents (*e.g.*, DMF, Me_2SO)	Radical homopolymerization of VCZ	Radical copolymerization of VCZ with the electron-accepting monomer

mer compositions are described in Table VII. That the homopolymerization of VCZ is cationic and the copolymerization of VCZ with the electron-accepting monomer is radical in nature was indicated from the effect of additives.[26] Addition of small amounts of dimethylformamide or DPPH in the system greatly retarded or inhibited the homopolymerization of VCZ or the copolymerization between VCZ and the electron-accepting monomer, respectively. Also, occurrence of alternating copolymerization of VCZ with FN or with DEF irrespective of the widely varied monomer feed ratios was confirmed in thermal polymerizations with AIBN as an initiator.[15,28]

The polymerization features observed in the system VCZ–electron-accepting monomer are rationalized on the basis of dual cationic and free radical nature of the VCZ cation radical intermediate formed through the excited

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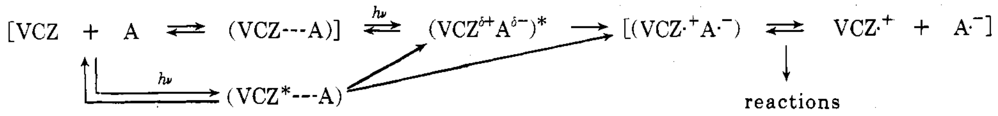
(26) In their extensive studies on the copolymerization of donor–acceptor complexes in the presence of metal halides or organometal halides, N. G. Gaylord and his coworkers proposed that alternating copolymers result from the homopolymerization of donor–acceptor complex.[27]

(27) For an example, see N. G. Gaylord, *J. Polym. Sci., Part C,* **31**, 247 (1970).

(28) M. Yoshimura, Y. Shirota, and H. Mikawa, Polymer Science, Reprint Vol. 2, 1972, p 481.

Scheme I
Primary Process in the Photosensitized Reaction of *N*-Vinylcarbazole in the Presence of the Organic Electron Acceptor (A)



charge-transfer complex and mainly through the charge-transfer interaction in the excited state of VCZ. Solvent effects on the dual nature of VCZ cation radical observed in the systems using rather high concentrations of the electron-accepting monomer are in good agreement with those observed in the systems with catalytic amounts of various organic electron acceptors as shown in Scheme I and Table VIII where the generalized reaction courses are summarized.

Summary

The photosensitized reaction of VCZ in the presence of the organic electron acceptor has been found to take entirely different reaction courses depending upon the reaction conditions. They are classified into four major groups: (1) cationic homopolymerization of VCZ, (2) cyclodimerization of VCZ, (3) radical homopolymerization of VCZ, and (4) radical copolymerization between VCZ and an electron-accepting monomer. Cationic homopolymerization of VCZ occurred in less basic solvents such as benzene, dichloromethane or nitrobenzene, while cyclodimerization of VCZ generally took place exclusively in such polar, basic solvents as acetone, acetonitrile or methanol. On the other hand, radical homopolymerization of VCZ proceeded in dimethylformamide or in Me$_2$SO. When the electron acceptor is a monomer capable of undergoing radical polymerization or copolymerization and is present in relatively large amounts instead of in catalytic amounts, radical copolymerization between VCZ and the electron-accepting monomer took place in addition to cationic homopolymerization and cyclodimerization of VCZ, the reaction course also being dependent upon the solvent and the concentration of the electron-accepting monomer.

The multireaction courses are systematically explained in terms of the intermediacy of VCZ cation radical formed by the photochemical electron transfer from VCZ to the electron acceptor. The VCZ cation radical exhibits the dual cationic and free radical activity. The cationic reactivity of VCZ cation radical is shown as cationic homopolymerization of VCZ, while its radical reactivity leads to either cyclodimerization of VCZ or radical homopolymerization of VCZ. Radical homopolymerization of VCZ is naturally replaced by radical copolymerization when the electron acceptor is a monomer which can copolymerize with VCZ. The choice of the multireaction courses may be determined by the following factors: (a) polarity of solvent, (b) basicity, that is, cation-solvating ability of solvent, (c) stability of the anion radical of the electron acceptor formed as a counterpart for VCZ cation radical, (d) radical trapping ability of the electron acceptor or of the solvent, and (e) polymerizability of the electron acceptor. It must be stressed that among these factors, basicity, that is, cation-solvating ability, of the solvent is almost decisively important in determining the reaction course in the photosensitized reaction of VCZ in the presence of the organic electron acceptor.

Stereospecific Polymerization of Aliphatic Monoaldehydes

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ABSTRACT: Stereospecific polymerization of acetaldehyde to give the isotactic polymer was investigated by using a series of effective catalysts: R$_2$AlOCR′NPh and its acetaldehyde complexes R$_2$AlOCR′NPh·MeCHO. The most characteristic feature of this type of catalyst is the formation of the monomer-catalyst complex in a quantitative yield by the reaction with acetaldehyde above the ceiling temperature (−40°) of the polymerization and that of the isotactic polyacetaldehyde below that temperature in a high yield. The catalyst behavior of this type of catalyst and its derivatives under various conditions are discussed in relation to their structures. Water and peracetic acid proved to be indispensable cocatalysts. A novel molecular mechanism of the stereospecific polymerization of acetaldehyde is proposed based on these experimental results.

Rather extensive work has been reported on the stereospecific polymerization of acetaldehyde by several research groups.$^{1-5}$ The importance of the coordination of the monomer to the catalyst in the initiation step of the polymerization was shown using organoaluminum catalysts and a coordinate anionic mechanism was proposed for in-

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(1) J. Furukawa, T. Saegusa, and H. Fujii, *Makromol. Chem.*, **37**, 149 (1960).

(2) G. Natta, G. Mazzanti, P. Corradini, and I. W. Bassi, *Makromol. Chem.*, **37**, 156 (1960).

(3) O. Vogl, *J. Polym. Sci., Part A*, **46**, 261 (1960).

(4) S. Ishida, *Kobunshi Kagaku*, **18**, 187 (1961); *J. Polym. Sci., Part A*, **62**, 1 (1962).

(5) H. Takida and K. Noro, *Kobunshi Kagaku*, **21**, 23 (1964); **21**, 109 (1964).