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Mechanism of Initiation of Alkyl Vinyl Ether Polymerization by Electron Acceptors

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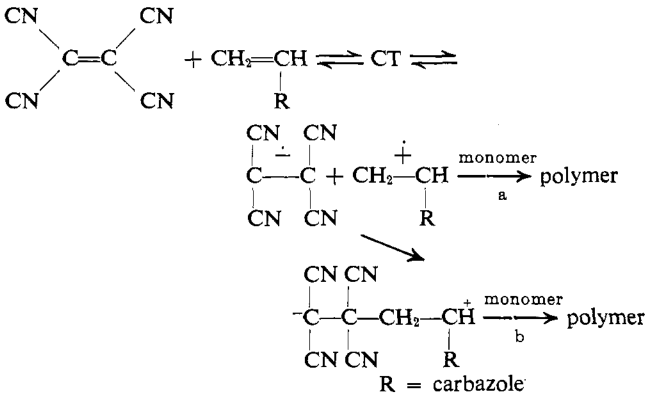
ABSTRACT: Alkyl vinyl ethers were polymerized in the presence of tetracyanoquinodimethane and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in polar solvents. Tetracyanoethylene, which contained the acidic impurity tricyanoethenol, also initiated polymerization of alkyl vinyl ethers. Pure tetracyanoethylene did not initiate polymerization, but reacted with the alkyl vinyl ethers to give 1-alkoxy-2,2,3,3-tetracyanocyclobutane. Kinetic studies showed that the alkyl vinyl ether and acceptors reacted in a second-order manner, first order each in monomer and initiator. The reactivity of the various alkyl vinyl ethers in the formation of the cyclobutane adduct and in polymerization decreased in the order: *tert*-butyl > isopropyl > ethyl ≃ *n*-butyl ≃ isobutyl, corresponding to the order of inductive effects of the alkyl group. The highest polymerization yields and highest molecular weights (40,000–80,000) of the resulting polymers were obtained with isopropyl vinyl ether. The esr of the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone radical anion was observed in the reaction of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and ethyl vinyl ether. A 1:1 molar reaction of alkyl vinyl ether with tetracyanoquinodimethane and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone produced oligomer and a 1:1 reaction product, respectively. These oligomers contained both the vinyl ether and electron acceptor, supporting an initiation mechanism involving a coupling reaction of the donor monomer and acceptor initiator.

The importance of charge-transfer complexes in the initiation of cationic polymerization has been recognized only recently.[1] Although the polymerization of vinyl monomers containing electron-donating substituents by organic acceptors have been reported,[2] the initiation reaction is still not completely understood and the exact mechanistic steps have not been determined. The proposed mechanism of initiation involves a charge-transfer complex, followed by a "T-class" (thermal) electron-transfer reaction to give a radical cation and a radical anion.

$$D + A \rightleftharpoons [D \longrightarrow A] \rightleftharpoons D\cdot^{+},A\cdot^{-} \rightleftharpoons D\cdot^{+}(\text{solv}) + A\cdot^{-}(\text{solv})$$

Since solvation of the charged species will accelerate the electron transfer, ionization becomes more facile in polar solvents.[3]

In studies[4] of the tetracyanoethylene initiation of the polymerization of *N*-vinylcarbazole in methylene chloride, the radical-anion concentration was proportional to the polymerization rate, and a polymerization resulting from the radical cation of *N*-vinylcarbazole was proposed (path a). However, from similar studies in benzene, it was concluded[5] that the intermediate radical anion and radical cation coupled to form the zwitterion **1**, and polymer was found as a result of path b. The polymerization of *N*-vinylcarbazole initiated by chloranil has also been proposed[6] to proceed by a mechanism similar to that shown in path b.



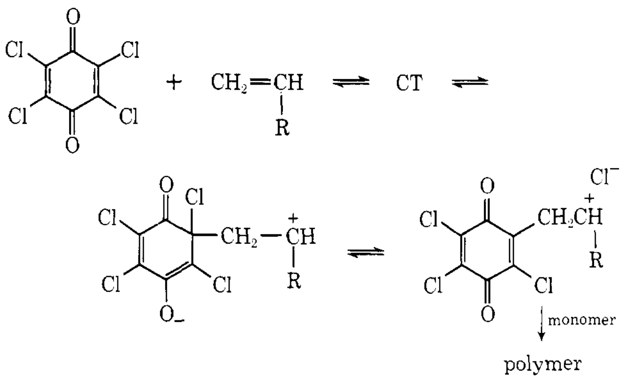


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Table I
Polymerization of Alkyl Vinyl Ethers
Initiated by Tetracyanoquinodimethane[a]

Monomer	Solvent	Yield, %	η_{sp}/C
Isopropyl vinyl ether	CH_3CN	43	0.72[c]
b	CH_3CN	67	0.23
	CH_3NO_2	90.0	0.07
	$(CH_2)_2Cl_2$	Trace	
	Toluene	Trace	
Ethyl vinyl ether	CH_3CN	22	0.19
	CH_3NO_2	36	0.24
n-Butyl vinyl ether	CH_3CN	23	0.13
	CH_3NO_2	20	0.13
Isobutyl vinyl ether	CH_3CN	32	0.28
	CH_3NO_2	24	0.19
tert-Butyl vinyl ether	CH_3CN	3	0.19
	CH_3NO_2	12	0.08

[a] Conditions: [monomer] = 2 *M*, [tetracyanoquinodimethane] = 5×10^{-3} *M*, 20 hr at 25°. [b] Also contained 1.1×10^{-4} mol of hydroquinone. [c] The intrinsic viscosity for this polymer (0.66) corresponds to a molecular weight of 70,000–80,000 as determined by the Mark–Houwink equation [J. A. Manson and G. J. Arquette, *Makromol. Chem.*, **12**, 37, 187 (1960)].

Table II
Polymerization of Alkyl Vinyl Ethers Initiated by
2,3-Dichloro-5,6-dicyano-*p*-benzoquinone[a]

Monomer	Solvent	Yield, %	η_{sp}/C
Isopropyl vinyl ether	CH_3CN	100	0.53[b]
	CH_2Cl_2	0	
Ethyl vinyl ether	CH_3CN	62	0.05
	Neat	0	
Isobutyl vinyl ether	CH_3CN	70	0.06
tert-Butyl vinyl ether	CH_3CN	23	0.08

[a] Conditions: [alkyl vinyl ether] = 2.0 *M*, [2,3-dichloro-5,6-dicyano-*p*-benzoquinone] = 5×10^{-3} *M*, 20 hr at 25°. [b] The intrinsic viscosity of this polymer (0.48) corresponds to a molecular weight of 40,000–50,000 as determined by the Mark–Houwink equation (see the reference of footnote *c*, Table I).

Tetracyanoethylene also affords cyclobutane derivatives in reactions with *N*-vinylcarbazole,[4,5,7] alkyl vinyl ether,[7-9] and various para-substituted styrenes.[10] Both the initiation of *N*-vinylcarbazole polymerization and the formation of the cyclobutane derivatives with tetracyanoethylene have been postulated to take place through a charge-transfer complex of the donor and acceptor.[4,5] The reaction path (to cyclobutane or polymer) and the ease with which it takes place depend on such factors as the molar ratio of donor to acceptor, the polarity of the solvent, and the structure of the acceptor.

This work reports the mechanism of the initiation of the polymerization of alkyl vinyl ethers in the presence of the strong electron acceptors, tetracyanoquinodimethane, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, and tetracyanoethylene.[11]

Results and Discussion

Polymerization. Alkyl vinyl ethers were polymerized in the presence of tetracyanoquinodimethane and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in polar solvents (Tables I and II). Relatively high molecular weight poly(isopropyl vinyl ether) could be obtained in good yield under anhydrous and high-purity conditions employing tetracyanoquinodimethane as the initiator. With tetracyanoquinodimethane as the initiator, the relative rates of initiation of the various alkyl vinyl ethers as observed by the first appearance of precipitation in the polymerization solvent followed the order *tert*-C_4H_9 (1 min) >$(CH_3)_2CH$ (10 min) >C_2H_5 (30 min). (Since the rate of polymer propagation in comparison to the rate of initiation in the polar solvent acetonitrile would be large for all of the alkyl vinyl ethers investigated, the rate of propagation could not affect the time for polymer precipitation. Therefore, it was assumed that the time for polymer precipitation was proportional to the rate of initiation.) The initial yellow color of the charge-transfer complex obtained on mixing the vinyl ether and the acceptor slowly faded to water white over the polymerization period, except in the case of *tert*-butyl vinyl ether, where a fast reaction occurred and the yellow color of the polymerization system changed to green almost immediately. The *tert*-butyl vinyl ether polymerization mixture contained the radical anion of tetracyanoquinodimethane, as evidenced by electronic absorption at 740 and 840 nm, which are the same as the maxima for tetracyanoquinodimethane radial-anion lithium salt (Figure 1). The spectra for the authentic radical anion and that produced by the reaction mixture was identical. A single adsorption was also observed by esr, but the hyperfine splitting could not be resolved, probably because of radical exchange in the polymerization mixture.

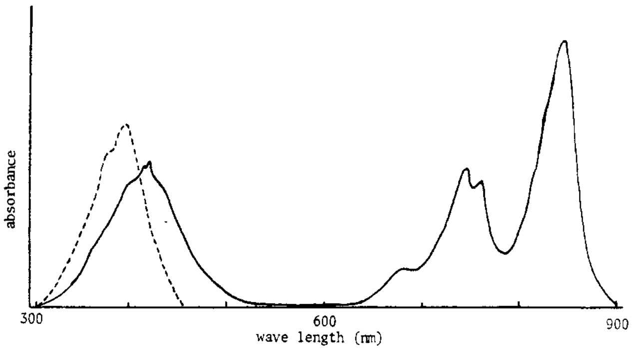

Figure 1. Visible and near-ir spectra of tetracyanoquinodimethane (– – –) and tetracyanoquinodimethane radical-anion lithium salt in acetonitrile (——).

A dark red color appeared immediately upon mixing alkyl vinyl ether with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in acetonitrile and then disappeared. All of the poly(alkyl vinyl ethers) were observed to precipitate within a few seconds after mixing the monomer and initiator; high molecular weight poly(isopropyl vinyl ether) was isolated in a quantitative yield after the polymerization had proceeded for 20 hr.

Temperature and solvent polarity were found to influence these polymerization reactions. Polymerization initiated by tetracyanoquinodimethane and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone took place in the polar solvents acetonitrile and nitromethane, but did not take place in ethylene chloride or toluene (Tables I and II). Neither acetonitrile nor nitromethane alone was an initiator for the polymerization, although it has been shown[12] that nitromethane initiates the polymerization of *N*-vinylcarbazole at higher temperatures.

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Table III
Effect of Temperature on the Polymerization of Alkyl Vinyl Ethers

Alkyl vinyl ether	Initiator[a]	Temp, °C	First appearance of polymer precipitation, min	Polymerization time, hr	Yield, %
Isobutyl	TCNQ	75	5	2	21
	TCNQ	60	15	6	27
	TCNQ	40	30	8	26
	TCNQ	25	60–120	5	20
	DDQ	25	<1	20	70
	DDQ	0	≃660	20	<5
	DDQ	−40		20	0
Isopropyl	TCNQ	25	10	20	70
	TCNQ	10	150	20	80
	TCNQ	0		4	0
	TCNQ	−30		4	0

[a] TCNQ = tetracyanoquinodimethane and DDQ = 2,3-dichloro-5,6-dicyano-*p*-benzoquinone.

Table IV
Polymerization of Alkyl Vinyl Ethers by Tricyanoethenol in Tetracyanoethylene[a]

Alkyl vinyl ether	Tetracyanoethylene	Solvent	Polymer yield, %	η_{sp}/C
Isopropyl	*b*	CH_3CN	85.1	0.10
Isopropyl	*b*	CH_3NO_2	70.1	0.11
Isopropyl	*b*	$(CH_2Cl)_2$	63.4	0.31
tert-Butyl	*b*	CH_3CN	25.0	0.06
n-Butyl	*b*	CH_3CN	13.3	0.05
n-Butyl	*b*	CH_3NO_2	6.9	0.06
Isobutyl	*b*	GH_3CN	6.9	0.05
Isobutyl	*b*	CH_3NO_2	8.1	0.06
Ethyl	*b*	CH_3CN	Trace	
Ethyl	*b*	CH_3NO_2	Trace	
Isopropyl	*c*	CH_3CN	42.2	
Isopropyl	*c*	CH_3NO_2	39.7	
Isopropyl	*c*	$(CH_2Cl)_2$	88.3	0.16
Isopropyl	*d*	CH_3CN	10.8	
Isopropyl	*d*	CH_3NO_2	4.5	
Isopropyl	*d*	$(CH_2Cl)_2$	0	

[a] $[C_3H_7OC_2H_3] = 2.0\ M$, [tetracyanoethylene] = $5 \times 10^{-3}\ M$, 25°, 20 hr. Tetracyanoethylene purified by three recrystallizations from chlorobenzene followed by two sublimations at 1.0 mm did not initiate polymerization of the monomers. [b] Purified by one recrystallization from chlorobenzene followed by one vacuum sublimation. [c] After 3 months aging at 25° in the atmosphere. [d] Obtained from Aldrich Chemical Co., Inc., and used without further purification.

Table V
Effect of Water on the Polymerization of Isopropyl Vinyl Ether with Highly Purified Tetracyanoethylene in Acetonitrile

[Water]/[tetracyanoethylene]	Aging time, hr	First appearance of polymer precipitation, min	Yield, %	η_{sp}/C
1/1	0		0	
1/1	4.5		0	
1/1	24	60	27	0.06
1/1	48	10	70	0.08
1/2	24	30	31	0.13
2/1	24		0	

Ethyl vinyl ether did not polymerize in the presence of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone without solvent.

Higher polymerization temperatures had no affect on the overall yield, but the initiation rate increased with increasing temperature (Table III). By lowering the polymerization temperature, the initiation rate was greatly decreased and the polymerization stopped below 0° for both tetracyanoquinodimethane and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. At −30°, no polymer formation was observed within a 4-hr period with ultraviolet or visible light irradiation employing tetracyanoquinodimethane as the initiator. Precipitation of polymer did occur within 10 min after the reaction ampoules were warmed to room temperature at the end of the 4-hr observation period. Irradiation of the polymerization by ultraviolet light not only retards the polymerization but also lowers the molecular weight of the polymer.[13] These results are in agreement with the observations that a "T-class" reaction,[14] in which a complete one-electron transfer from donor to acceptor takes place thermally, is promoted by higher temperatures and polar solvents, and would not be enhanced by light.

Highly purified tetracyanoethylene would not initiate the polymerization of alkyl vinyl ethers, even in polar solvents such as acetonitrile and nitromethane. However, when a catalytic amount of tetracyanoethylene, which was incompletely purified (containing traces of tricyanoethenol, *vide infra*), was added ([tetracyanoethylene]:[alkyl vinyl ether] = 1:400) polymerization took place, depending on the solvent and purity of the tetracyanoethylene. The results of the polymerization of various alkyl vinyl ethers are given in Table IV.[15]

This effect of impurities on the polymerization is similar to that found for the polymerization of *N*-vinylcarbazole initiated by *p*-chloranil.[6] In this case, the initiator was found to be an acidic impurity in the chloranil, 3,5,6-trichloro-2-hydroxyl-*p*-benzoquinone.

In polymerizations initiated with impure tetracyanoethylene, the red-orange color of the charge-transfer complex appeared immediately on mixing the tetracyanoethylene and alkyl vinyl ether in acetonitrile, but disappeared within a few seconds. Precipitation of the polymer from the solvent, however, did not occur until 10–30 min after mixing, and polymerization continued in the colorless media. Thus it appeared that the charge-transfer complex was not responsible for polymerization, since the color of the complex was not present throughout the polymerization, and it is unlikely that any cationic species formed *via* the charge-transfer reaction would be long lived enough to continue the polymerization after 30 min. Highly purified tetracyanoethylene showed the transient color characteristics of the charge-transfer complex, but did not initiate the polymerization of alkyl vinyl ethers; instead the cyclobutane product of tetracyanoethylene and the vinyl ether was found (*e.g.*, 1-isopropoxy-2,2,3,3-tetracyanocyclobutane).

Highly purified tetracyanoethylene could be converted to an active catalyst by addition of water to its acetonitrile solution (Table V).[15] Equal molar or less than equal molar amounts of water and tetracyanoethylene produced an active polymerization catalyst. The reaction with water was slow; the optimum aging time in acetonitrile at room temperature was about 48 hr. Unreacted water inhibited polymerization

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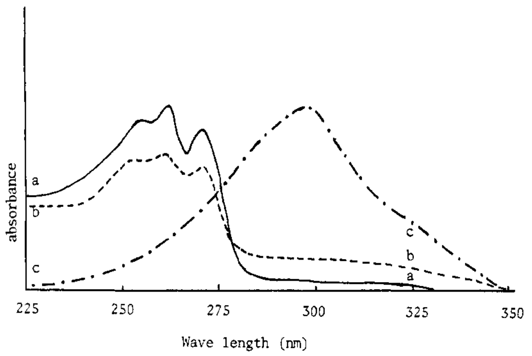

Figure 2. Uv spectra: (a) tetracyanoethylene in acetonitrile, ϵ_{262} 7300, (b) reaction mixture of tetracyanoethylene and water in acetonitrile without vinyl ether after 24 hr, (c) tricyanoethenol in water, ϵ_{295} 7250.

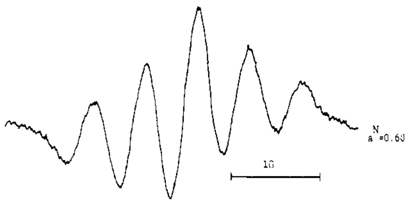

Figure 3. Electron spin resonance of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone radical-anion lithium salt.

at higher water concentrations. Tetracyanoethylene is known[16] to react with water to form tricyanoethenol (pK_a = 1.9) and this alcohol is resistant to further hydrolysis. Tricyanoethenol was isolated, in fact (as a tetramethylammonium salt), from the reaction of tetracyanoethylene and water in acetonitrile. The uv spectrum of the reaction of tetracyanoethylene and water in acetonitrile showed a decrease in the tetracyanoethylene absorptions and a concurrent increase at 298 nm, the maximum absorption of tricyanoethenol (Figure 2). A prepared sample of tricyanoethenol[17] initiated the polymerization of isobutyl vinyl ether. Therefore, it appears that the true catalyst in polymerizations involving incompletely purified tetracyanoethylene is tricyanoethenol.

Effect of Additives. Hydroquinone. Alkyl vinyl ethers are believed[18] to homopolymerize by a cationic mechanism only, but can copolymerize under free-radical conditions. In a polymerization system which contained hydroquinone in a slight molar excess of the tetracyanoquinodimethane, the polymerization proceeded normally, except the polymer solution was orange instead of the usual water white at the end of the 20-hr polymerization period (Table I). The initial color of the mixture was bright orange. Since hydroquinones are known[19] to inhibit free-radical polymerization, the propagation mechanism is probably cationic in this polymerization.[20]

Table VI

Effect of Water on the Polymerization of Isopropyl Vinyl Ether by Tetracyanoquinodimethane in Acetonitrile

[Water]/[tetracyanoquinodimethane]	Yield, %	η_{sp}/C
0[a]	75	0.46
0	36	0.48
1	28	0.44
2	37	0.51
5	28	Methanol soluble

[a] Tetracyanoquinodimethane was sublimed into a reaction ampoule which had been dried with a flame under high vacuum.

Water. Since water is a common impurity and could react in the presence of tetracyanoquinodimethane to provide a protonic initiator, a series of polymerizations containing various amounts of water were carried out to determine whether water participates in the initiation step. However, it can be seen from Table VI that water acts only as a chain-transfer agent at high concentrations, *e.g.*, at a water to tetracyanoquinodimethane molar ratio of 5:1. The highest yield of polymer was obtained when the polymerization system had been very carefully dried and the tetracyanoquinodimethane was sublimed into the polymerization ampoule. This procedure produced a higher yield of polymer, but had no affect on the molecular weight, indicating that the molecular weight is governed by a monomer-transfer reaction.[18] Water only becomes involved in the transfer step at higher concentrations.

Electron Spin Resonance. Tetracyanoquinodimethane. Both the presence[4] and the absence[5] of free radicals have been reported in the polymerization of *N*-vinylcarbazole by tetracyanoethylene. An attempt to observe a free-radical intermediate in the reaction of tetracyanoquinodimethane and isopropyl vinyl ether was carried out. No free radicals were observed by esr in this system either under reduced pressure or in an atmosphere of argon. During these experiments polymer formation was noted by the clouding of the esr solution; and in the case where the system was blanketed with argon, a 34% yield of polymer was obtained. A concurrent polymerization under the same conditions produced the normal yield of polymer. The tetracyanoquinodimethane radical anion can also be observed in the visible region of the spectrum at 740 and 840 nm (Figure 1). Under the polymerization conditions in which the reagents were highly purified and the system was very carefully dried, no absorptions were observed at these wavelengths, in agreement with the esr results. However, this does not eliminate the transient existence of the tetracyanoquinodimethane radical anion, for if the rate-controlling step involves an electron transfer, and the subsequent reactions are relatively fast and occur before the radical anion and radical cation are solvent separated, the tetracyanoquinodimethane radical anion would not be observed.

2,3-Dichloro-5,6-dicyano-*p*-benzoquinone. Since the reaction of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone with isobutyl vinyl ether is much faster than the analogous reaction with tetracyanoquinodimethane, its esr was studied by employing flow techniques. The 2,3-dichloro-5,6-dicyano-*p*-benzoquinone radical anion was observed for both a 1:1 and a 1:400 molar ratio of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and isobutyl vinyl ether. The lithium salt of the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone radical anion showed a five-line spectrum in acetonitrile (Figure 3). During the flow of the reaction mixture of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and isobutyl vinyl ether in acetonitrile, an unresolved spectrum

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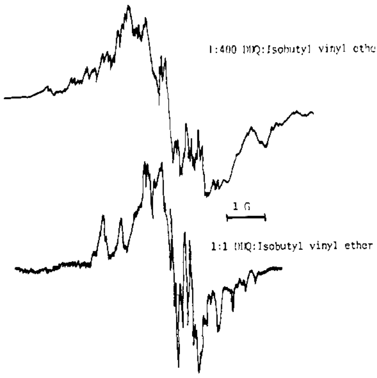

Figure 4. Electron spin resonance of the reaction mixture of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and isobutyl vinyl ether in acetonitrile.

(Figure 4) of the same width as the authentic lithium 2,3-dichloro-5,6-dicyano-*p*-benzoquinone radical-anion esr signal was observed. With a 1:1 molar ratio of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone to isobutyl vinyl ether, the signal disappeared within 30 sec after the flow was stopped, and a new signal of lower intensity was observed in approximately 15 min. This latter signal was stable for hours. A 1:400 molar ratio of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone to isobutyl vinyl ether reaction mixture displayed a similar signal (Figure 4) during flow, and although the intensity of this signal was greatly diminished after the flow was stopped, it never completely disappeared. Even at very high amplification, no overlapping alkyl radical absorptions were observed. Since alkyl radicals are most often observed only at low temperatures and show a broad absorption spectrum (25–50 G),[21] the esr signals observed for these flow experiments were assigned to the DDQ radical anion.

These results are similar to the flow esr results obtained for the reaction of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and *p*-phenylenediamine[22] in acetonitrile and the reaction of chloranil and tetramethyl-*p*-phenylenediamine in ethanol.[23] In these experiments the radical cation of the donor, which did not undergo subsequent reactions, was observed along with the radical anion of the acceptor. However, the flow esr experiments of chloranil and dimethylaniline showed only the chloranil radical anion absorption.[23]

The 2,3-dichloro-5,6-dicyano-*p*-benzoquinone radical anion was unstable in solution when it was electrolytically generated and showed a less-well-resolved spectrum than solutions in which the radical anion was produced by electron transfer from *p*-phenylenediamine.[22] The unresolvable spectra observed for our alkyl vinyl ether and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone system are consistent with exchange between radical anion and unreacted 2,3-dichloro-5,6-dicyano-*p*-benzoquinone or products.

Although the relative reactivities of the radical anions of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and tetracyanoquinodimethane cannot be predicted from this study, under the conditions they are probably of the same order. The buildup of the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone radical anion is due to its fast formation in the reaction of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and alkyl vinyl ethers and its relatively slow subsequent reaction and disappearance.

TABLE VII
KINETICS OF THE REACTION OF TETRACYANOQUINODIMETHANE AND ISOPROPYL VINYL ETHER[a]

[Isopropyl vinyl ether]/[tetracyanoquinodimethane][b]	Temp, °C	Second-order rate constant, l. mol^{-1} sec^{-1}
400	25.0	$1.67 \times 10^{-4} \pm 0.08 \times 10^{-4}$
400	30.0	$2.23 \times 10^{-4} \pm 0.56 \times 10^{-4}$
400	35.0	$3.85 \times 10^{-4} \pm 0.42 \times 10^{-4}$
800	30.0	$2.21 \times 10^{-4} \pm 0.56 \times 10^{-4}$
		$\Delta H^{\ddagger} = 14.6 \pm 2.5$ kcal/mol
		$\Delta S^{\ddagger} = -27 \pm 5$ eu

[a] The disappearance of tetracyanoquinodimethane was followed at 393.5 nm under pseudo-first-order conditions. All rates are from averages of two or more runs. [b] [Tetracyanoquinodimethane] = 2.5×10^{-4} *M*, [isopropyl vinyl ether] = 0.1 *M* or 0.2 *M*.

Since the tetracyanoquinodimethane radical-anion formation is slower, as shown by the slow disappearance of tetracyanoquinodimethane in the presence of isopropyl vinyl ether (Table VII) and the 10–30 min induction periods for the polymerization of alkyl vinyl ethers initiated by tetracyanoquinodimethane, this explains why the tetracyanoquinodimethane radical anion could not be observed. Its disappearance would be relatively fast compared to its formation and its concentration never builds up appreciably.

Tetracyanoethylene. Neither the tetracyanoethylene radical anion nor the alkyl vinyl ether radical cation was observed with flow esr experiments in methylene chloride or acetonitrile. This is reasonable for a reaction in which the intermediate radicals couple rapidly before they are solvent separated.

Kinetics. Tetracyanoquinodimethane. The charge-transfer complex of tetracyanoquinodimethane with alkyl vinyl ethers was not observed. Either the charge-transfer band is masked by the tetracyanoquinodimethane absorptions or its lifetime is short enough so that its concentration never builds up appreciably. Calculations[11] predict the charge-transfer band for tetracyanoquinodimethane and isopropyl vinyl ether to be observed at 423 nm. The following equilibria and derivation, which applies the steady-state assumption for the charge-transfer complex, show that tetracyanoquinodimethane and alkyl vinyl ether would react following second-order kinetics, first order in each reagent.

$$\mathrm{TCNQ} + \mathrm{iPVE} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{CT}$$

TCNQ = tetracyanoquinodimethane
iPVE = isopropyl vinyl ether

$$\mathrm{CT} \xrightarrow{k_3} \mathrm{A}$$

CT = charge-transfer complex

$$\mathrm{A} + \mathrm{iPVE} \longrightarrow \text{polymer}$$

A = some initiating species

Assume that the CT concentration is always very small and k_3 is rate controlling.

$$\frac{-\mathrm{d[TCNQ]}}{\mathrm{d}t} = k_1[\mathrm{TCNQ}][\mathrm{iPVE}] - k_2[\mathrm{CT}] \qquad (1)$$

Steady-state assumption

$$\frac{\mathrm{d[CT]}}{\mathrm{d}t} = k_1[\mathrm{TCNQ}][\mathrm{iPVE}] - k_2[\mathrm{CT}] - k_3[\mathrm{CT}] = 0$$

$$k_1[\mathrm{TCNQ}][\mathrm{iPVE}] = k_2[\mathrm{CT}] + k_3[\mathrm{CT}] = (k_2 + k_3)[\mathrm{CT}]$$

$$[\mathrm{CT}] = k_1/(k_2 + k_3)[\mathrm{TCNQ}][\mathrm{iPVE}]$$

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(22) N. H. Kolodny and K. W. Bowers, *J. Amer. Chem. Soc.*, **94**, 1113 (1972).

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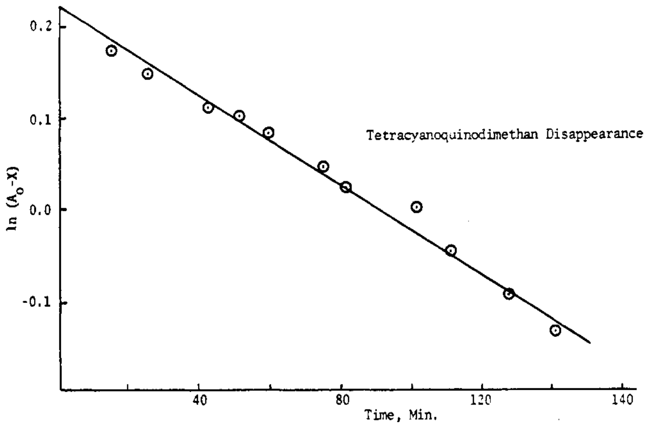


Figure 5. Kinetic data from visible spectra study of TCNQ + $(CH_3)_2CH—O—CH=CH_2 \rightarrow$ products.

Table VIII

Visible Spectra of 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone and Related Species[a]

	λ_{max}, nm
DDQ	272, 280, 374
$DDQ\cdot^-$	290, 353, 590
DDQ + iPVE	270, 340, 350 (590)[b]

[a] Solvent = acetonitrile, DDQ = 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, iPVE = isopropyl vinyl ether. [b] This absorption is only transient.

Substituting into eq 1 gives

$$\frac{-d[TCNQ]}{dt} = k_1[TCNQ][iPVE] - \frac{k_2k_1}{k_2 + k_3}[TCNQ][iPVE] = \left[k_1 - \frac{k_2k_1}{k_2 + k_3}\right][TCNQ][iPVE]$$

Under pseudo-first-order conditions tetracyanoquinodimethane was observed to disappear in a first-order manner (Figure 5 and Table VII) and by doubling the concentration of the isopropyl vinyl ether the rate doubled, indicating that the reaction is first order in each reagent. Since the kinetics were studied over a relatively narrow temperature range, only tentative conclusions can be made from the entropy and enthalpy of the overall reaction. The enthalpy and entropy are consistent with a very ordered transition state to give maximum overlap for the electron-transfer reaction. The enthalpy is approximately of the same magnitude as that of the reaction of tetracyanoethylene and *N*-vinylcarbazole.[13]

Table IX

Kinetics of the Reaction of 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone and Alkyl Vinyl Ethers[a]

Alkyl vinyl ether	Second-order rate constant, l. mol^{-1} sec^{-1}
Ethyl vinyl ether	0.417 ± 0.014
Isopropyl vinyl ether	0.323 ± 0.005
tert-Butyl vinyl ether	0.546 ± 0.035

[a] Conditions: [2,3-dichloro-5,6-dicyano-*p*-benzoquinone] = 0.05 *M*, [alkyl vinyl ether] = 0.5 *M*, temp = 25.0°, solvent = acetonitrile.

Table X

Kinetics of the Cycloaddition Reaction of Tetracyanoethylene and Alkyl Vinyl Ethers

Alkyl vinyl ether	[VE], *M*	[TCNE], *M*	Maximum abs of CT complex, nm	Solvent	First-order rate constant,[a] sec^{-1}
tert-Butyl	0.1	0.1	436	CH_3CN	0.180 ± 0.020
	0.5	0.01	436	CH_3CN	0.920 ± 0.100
Isopropyl	0.1	0.1	430	CH_3CN	0.085 ± 0.005
	0.5	0.1	430	CH_3CN	0.196 ± 0.033
	0.5	0.05	430	CH_3CN	0.197 ± 0.009
	0.1	0.01	430	CH_3CN	0.120 ± 0.008
	0.5	0.01	430	CH_3CN	0.133 ± 0.013
Ethyl	0.1	0.1	419	CH_3CN	0.017 ± 0.009
	0.5	0.01	419	CH_3CN	0.080 ± 0.003
tert-Butyl	0.5	0.02	436	CH_2Cl_2	0.987 ± 0.067
	0.4	0.02	436	CH_2Cl_2	0.759 ± 0.054
	0.3	0.02	436	CH_2Cl_2	0.915 ± 0.093
	0.2	0.02	436	CH_2Cl_2	0.617 ± 0.088
Isopropyl	0.5	0.05	430	CH_2Cl_2	0.1126 ± 0.0109
	0.45	0.05	430	CH_2Cl_2	0.1199 ± 0.0192
	0.3	0.05	430	CH_2Cl_2	0.0970 ± 0.0169
	0.1	0.05	430	CH_2Cl_2	0.0631 ± 0.0097
	0.5	0.02	430	CH_2Cl_2	0.0414 ± 0.0141
	0.4	0.02	430	CH_2Cl_2	0.0457 ± 0.0083
Isopropyl	0.3	0.02	430	CH_2Cl_2	0.0472 ± 0.0050
	0.2	0.02	430	CH_2Cl_2	0.0462 ± 0.0096
Ethyl	0.5	0.02	419	CH_2Cl_2	0.0100 ± 0.0005
	0.4	0.02	419	CH_2Cl_2	0.0137 ± 0.0021
	0.3	0.02	419	CH_2Cl_2	0.0073 ± 0.0004
	0.2	0.02	419	CH_2Cl_2	0.0034 ± 0.0005

[a] Determined by following the charge-transfer complex disappearance at 25 ± 0.2°.

2,3-Dichloro-5,6-dicyano-*p*-benzoquinone. Mixtures of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone with isopropyl, ethyl, or *tert*-butyl vinyl ether were all found to have a transient absorption at 590 nm. This apparently is not a charge-transfer absorption, since it is at the same wavelength for the different alkyl vinyl ethers. Calculations[11] show that this charge-transfer absorption would fall about 412 nm, but no absorptions were found which could be assigned to a charge-transfer complex between 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and alkyl vinyl ethers. Since 2,3-dichloro-5,6-dicyano-*p*-benzoquinone does not absorb at longer wavelengths than 374 nm and the radical anion of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone does absorb at 590 nm, this transient absorption can only be assigned to the production and disappearance of the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone radical anion (Table VIII). If a charge-transfer complex exists, it probably is present only in small concentrations, since the electron transfer to form the radical anion and radical cation is extremely fast as observed by visible spectroscopy and esr. Following the disappearance of the 590-nm absorption employing a stopped-flow instrument showed that the reaction was second order with similar rates for various alkyl vinyl ethers (Table IX). Since the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone radical anion and probably the alkyl vinyl ether radical cation were formed almost instantaneously, and the overall reaction rate as observed by the disappearance of the radical anion was second order, it was concluded the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone radical anion was coupling with the alkyl vinyl ether radical cation in the initiation of polymerization.

Cycloaddition Reaction of Tetracyanoethylene and Alkyl Vinyl Ethers. Since in the cycloaddition reaction of an alkyl vinyl ether with tetracyanoethylene to form 1-(alkoxy)-2,2,3,3-tetracyanocyclobutane, the appearance and disappearance of the red-orange color of the charge-transfer complex formed between this donor and acceptor could not be followed by conventional methods, the kinetics of this reaction were obtained by stopped-flow techniques (Table X). The wavelength of maximum absorbance in acetonitrile for the charge-transfer complex of tetracyanoethylene with isopropyl and *tert*-butyl vinyl ethers could not be determined exactly because of the fast disappearance of color. The charge-transfer complex of ethyl vinyl ether with tetracyanoethylene was found to absorb at 419 nm both in the polar solvent acetonitrile, as well as the slightly polar solvent methylene chloride. Therefore, it was assumed that the charge-transfer complexes of tetracyanoethylene with isopropyl and *tert*-butyl vinyl ethers in acetonitrile absorb at or near the λ_{max} found[8] in methylene chloride. Rates determined at 5 nm above and below the wavelengths given in Table X were within the experimental error and decreased with increasing wavelength.

For the derivation of the overall rate equation, the equilibrium between reactants and complex, k_1/k_2, was assumed to be rapid, and the rate-controlling step was assumed to be the disappearance of the charge-transfer complex.

Rate equation for the reaction of TCNE with iPVE

$$\text{TCNE} + \text{iPVE} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{CT} \xrightarrow{k_3} \text{products} \qquad (2)$$

$$\frac{-\mathrm{d}[\text{CT}]}{\mathrm{d}t} = k_3[\text{CT}] + k_2[\text{CT}] - k_1[\text{TCNE}][\text{iPVE}] \qquad (3)$$

$$\frac{k_1}{k_2} = \frac{[\text{CT}]}{[\text{TCNE}][\text{iPVE}]} \text{ or } [\text{CT}] = \frac{k_1}{k_2}[\text{TCNE}][\text{iPVE}] \qquad (4)$$

$$\frac{-\mathrm{d}[\text{CT}]}{\mathrm{d}t} = k_3\frac{k_1}{k_2}[\text{TCNE}][\text{iPVE}] + \frac{k_2k_1}{k_2}[\text{TCNE}][\text{iPVE}] - k_1[\text{TCNE}][\text{iPVE}] \qquad (5)$$

$$\frac{-\mathrm{d}[\text{CT}]}{\mathrm{d}t} = \frac{k_3k_1}{k_2} + k_1 - k_1[\text{TCNE}][\text{iPVE}] = \frac{k_3k_1}{k_2}[\text{TCNE}][\text{iPVE}] \qquad (6)$$

$$\text{rate of CT disappearance} = k_{obsd}[\text{TCNE}][\text{iPVE}] \qquad (7)$$

The formation of the charge-transfer complex (rate constant k_1) was faster than the upper limit of the stopped-flow apparatus, and only the disappearance of the charge-transfer complex could be followed by this technique. Therefore, k_1 and k_2 could not be determined. If k_1/k_2 is large and rapid, the following derivation from eq 3 is in agreement with the observed results. Assuming k_1/k_2 is large and rapid, eq 4 can be rewritten

$$[\text{TCNE}][\text{iPVE}] = \frac{k_2}{k_1}[\text{CT}] \qquad (8)$$

and substituted into eq 3 to give

$$\frac{-\mathrm{d}[\text{CT}]}{\mathrm{d}t} = k_3[\text{CT}] + k_2[\text{CT}] - k_1\frac{k_2}{k_1}[\text{CT}] \qquad (9)$$

$$\frac{-\mathrm{d}[\text{CT}]}{\mathrm{d}t} = k_3[\text{CT}] \qquad (10)$$

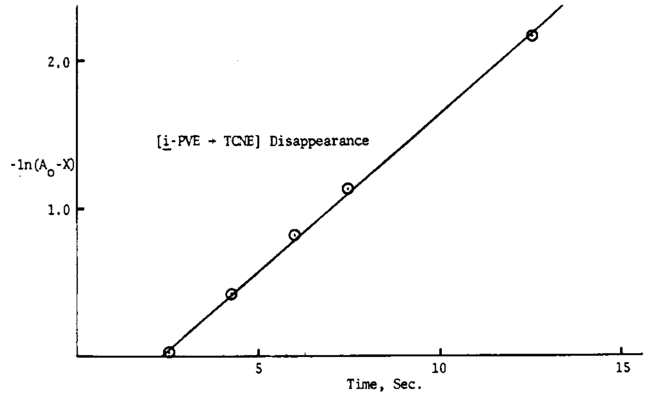
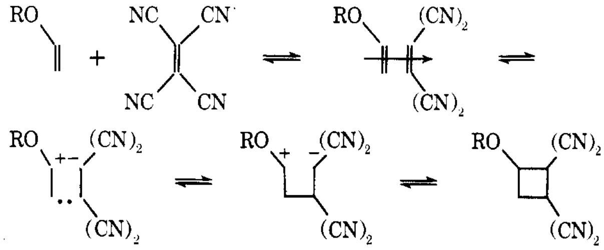


Figure 6. Kinetic data from stopped-flow visible spectral study of TCNE + *i*-PVE ⇌ [*i*-PVE → TCNE] → *i*-PVE·$^+$, TCNE·$^-$ ($k_{obsd}{}^d$) → → products (fast).

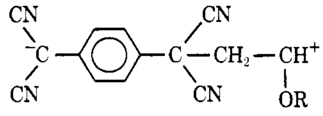
At high concentration ratios of vinyl ether to TCNE, the equilibrium (eq 2) is driven to the right and the rate expression (eq 10) holds. The disappearance of the charge-transfer complex is first order for *tert*-butyl, isopropyl, and ethyl vinyl ethers (Figure 6). If the ratio is small, the collapse of the charge-transfer complex to starting materials becomes important, and the kinetics became more complicated (*e.g.*, eq 3).

From the rate of disappearance of the charge-transfer absorption, the rate of cyclobutane formation followed the order ethyl < isopropyl < *tert*-butyl. The reaction was faster in the polar solvent acetonitrile than in the slightly polar solvent methylene chloride. The order of the increasing rate of cyclobutane formation is the same as the order of decreasing ionization potential and is consistent with a charge-transfer complex intermediate and electron-transfer step in the cycloaddition reaction (eq 11). The effect of the polarity of the solvent is also in agreement with this mechanism.



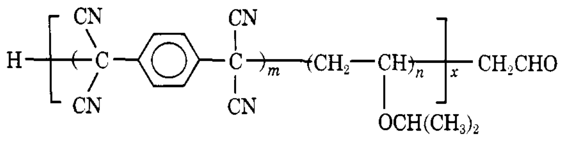
(11)

Preparation and Structure of Oligomers. Tetracyanoquinodimethane. If an electron transfer *via* a charge-transfer complex is the initiating step in the polymerization of alkyl vinyl ethers by tetracyanoquinodimethane, the radical anion and radical cation must react rapidly before they are solvent separated in order not to be observed by esr. An intermediate such as **2** would then be formed. The dropwise addition of a dilute acetonitrile solution of isopropyl vinyl ether to a large excess of tetracyanoquinodimethane in refluxing acetonitrile produced an oligomer which contained both the tetracyanoquinodimethane and isopropyl vinyl ether. From the molecular weight, integration of the aliphatic and aromatic regions of the nmr spectrum, and combustion analysis, it was determined that the reaction product had a structure which



2

approximates 3, the major portion being $m = 1$, $n = 2$, and $x = 2$ in combination with smaller amounts of $n = 1$ and $n = 3$. Carbonyl absorptions in the ir spectrum of 3 supported an aldehyde end group. By varying the reaction time or temperature the molecular weight could also be varied, but the ratio of tetracyanoquinodimethane and isopropyl vinyl ether contained in the oligomer remained fairly constant. This oligomer did not initiate the polymerization of isopropyl vinyl ether.



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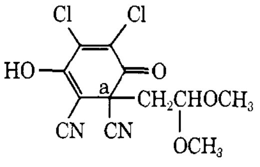
2,3-Dichloro-5,6-dicyano-*p*-benzoquinone. The initiation of alkyl vinyl ether polymerization is faster with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone compared to tetracyanoquinodimethane. Therefore, it would be expected that in a reaction with a 1:1 molar ratio of catalyst to monomer, the higher activity of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone could allow a 1:1 addition product to be obtained since at the same rate of propagation, the ratio of the rates of initiation to propagation would be greater.

Reactions carried out with a 1:1 molar ratio of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and alkyl vinyl ether in acetonitrile gave a large amount of poly(alkyl vinyl ether) and oligomers which contained both 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and vinyl ether as shown by ir analysis.

However, mixing acetonitrile solutions of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and methyl vinyl ether (1:1 molar ratio) for a few seconds and then quenching in methyl alcohol produced a 1:1 reaction product which has been assigned structure 4. The nmr spectrum of this product agrees with this assignment. The methoxy proton absorption appeared as two singlets with equivalent integration intensities which indicated that the methoxy groups were diastereomeric in relation to the asymmetric center, a, of structure 4. The methine proton appeared as two overlapping doublets at 4.47 ppm, in agreement with the acetal structure. The methylene protons absorb at 2.7; this is about 2 ppm upfield from the expected value for the vinyl ether being attached to the carbonyl oxygen. The cyano absorption in the ir appeared as a broad singlet, which was in agreement with attachment of the vinyl ether at a cyano-substituted ring carbon as shown in structure 4.



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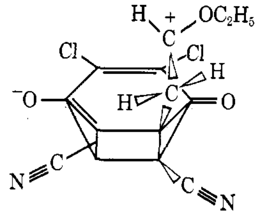
The mass spectral and combustion analyses were also in agreement with structure 4. An extremely weak parent peak at *m/e* 318 and fragmentation peaks corresponding to the acetal structure appeared in the mass spectrum.

The reaction of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and ethyl vinyl ether (1:1 molar ratio) in acetonitrile, which was quenched in methyl alcohol produced the methyl ethyl analog of 4. The alkoxy proton absorptions in the nmr spectrum were split into two overlapping absorptions in a 40:60 ratio, which indicated that the product was a mixture of two diastereomers. The two methoxy absorptions at 3.14 and 3.09 ppm appeared in a ratio of 40:60, respectively, and corresponded in size to the two ethoxy triplets centered at 0.96 and 1.00 ppm which absorbed in a ratio of 40:60, respectively. The formation of one diastereomer in excess results from a preferred conformation of the intermediate zwitterion 5. Since attack of methyl alcohol would occur almost exclusively from above the ring, one diastereomer would be formed preferentially. The reaction of methyl vinyl ether and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, which was quenched with ethyl alcohol, produced the same diastereomeric mixture, except the opposite diastereomer was produced in excess as shown by nmr analysis (*e.g.*, the two methoxy absorptions at 3.14 and 3.09 ppm appeared in a ratio of 60:40, respectively). The methylene and methine absorptions were similar to those of 4.



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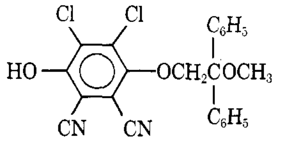
The structure of these compounds showed that both 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and alkyl vinyl ether are incorporated together in these reactions and probably follow the same reaction path to initiate the polymerization of alkyl vinyl ethers.

Since in these experiments isolation of an oligomer is hindered by the very rapid formation of polymer relative to the rate of initiation, the reaction of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone with 1,1-diphenylethylene was studied, since in this reaction only a dimer could form.[28] An addition product of 1,1-diphenylethylene and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, (6), was isolated from a 1:1 reaction mixture in acetonitrile after quenching with methanol. The methylene protons absorbed in the nmr spectrum at 5.0 ppm and no carbonyl absorptions were present in the ir spectrum, in agreement with the *p*-phenoxy structure 6. This structure is different than 4 which showed methylene absorptions at 2.8 ppm in the nmr and carbonyl absorptions in the ir. Possibly the steric hindrance of the phenyls prevented coupling to the ring carbons as was found for ethyl vinyl ether.



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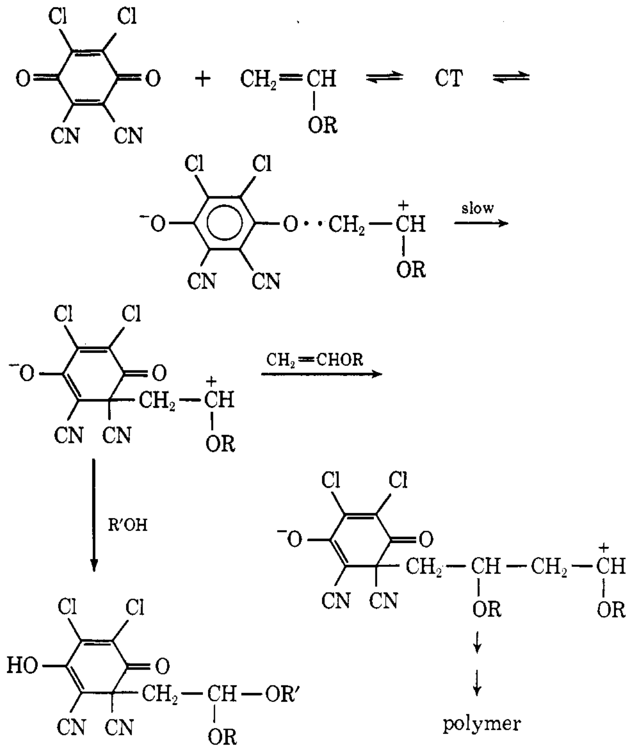
Mechanism. From these results the following initiation mechanism for the polymerization of vinyl ether can be written, as represented by the acceptor 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. In acetonitrile, this acceptor and alkyl vinyl ethers undergo a rapid one-electron transfer through a charge-transfer complex to yield a radical anion of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and a radical cation of the alkyl vinyl ether. These radicals mainly couple to give a dipolar intermediate that initiates the cationic polymerization of the alkyl vinyl ether in the presence of excess alkyl



vinyl ether.[24] Initiation with tetracyanoquinodimethane proceeds by an analogous mechanism in acetonitrile.

This mechanism agrees with the results for all three acceptors studied with alkyl vinyl ethers. The main difference in the results for the various acceptors is the relative rates of the mechanistic steps; this is due to the relative electron affinities and structure of the acceptors. The order of electron affinity,[10] 2,3-dichloro-5,6-dicyano-*p*-benzoquinone > tetracyanoethylene > tetracyanoquinodimethane, is the same order as the relative rates of reaction with alkyl vinyl ethers. Tetracyanoethylene readily forms a stable cyclic product with alkyl vinyl ethers, and no polymer formation can occur; therefore, the rate of cyclization is greater than the rate of polymer propagation. The acceptors, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and tetracyanoquinodimethane, do not form cyclic products with alkyl vinyl ethers and can only initiate polymerization.

Experimental Section

Materials. Tetracyanoethylene was recrystallized three times from a large excess of chlorobenzene and sublimed twice at 78° (1.0 mm), mp 200–202° in a sealed tube (lit.[25] mp 200–202°). Tetracyanoquinodimethane was recrystallized three times from ethyl acetate and sublimed twice with activated carbon at 170° (1 mm), mp 297–299° (lit.[26] mp 293.5–296°). 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone was recrystallized three times from benzene–chloroform (1:4) and sublimed twice at 180° (1 mm), mp 217–219° (lit.[27] 215–217°).

The alkyl vinyl ethers were washed with water, dried over potassium hydroxide, distilled over metallic sodium, and stored over a metallic sodium mirror after the removal of air by several freeze–thaw cycles under reduced pressure. Acetonitrile was distilled over phosphorus pentoxide and stored over phosphorus pentoxide after the removal of air by several freeze–thaw cycles under reduced pressure.

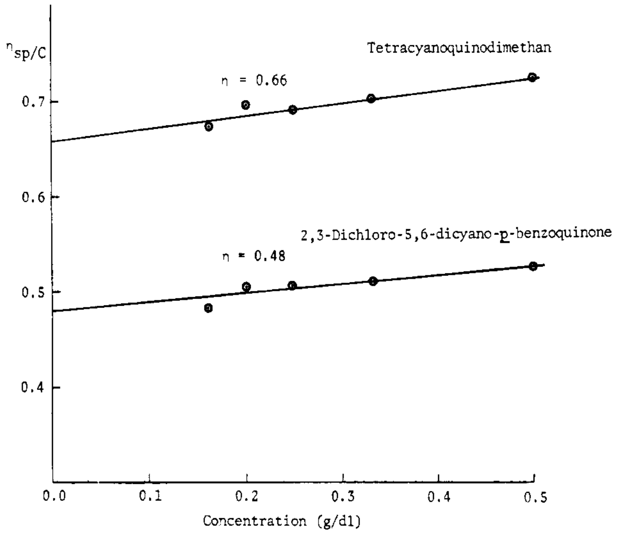


Figure 7. Intrinsic viscosity of poly(isopropyl vinyl ether).

General Polymerization Procedure. Polymerizations were carried out in Pyrex glass ampoules under reduced pressure (10^{-4}–10^{-5} mm). The dried monomer and solvent were transferred by trap-to-trap distillation into an ampoule into which a weighed amount of catalyst had been placed, and the ampoule was sealed. After a given period of time, the ampoule was opened and the polymer produced was isolated by evaporating the volatile substances. The polymeric product was washed three times by dissolving it in methylene chloride and pouring this solution into methanol.

The solution viscosities of the resulting polymers, η_{sp}/C, were determined in benzene (C = 0.5 g/dl) at 30°.

Reactions of Alkyl Vinyl Ethers with Tetracyanoquinodimethane. Polymerization of Alkyl Vinyl Ethers with Tetracyanoquinodimethane. Polymerization. The polymerizations were carried out as described in the general procedure employing 0.020 g (10^{-4} mol) of tetracyanoquinodimethane and 4.6 ml (3.4 g, 0.04 mol) of isopropyl vinyl ether, 3.8 ml (2.9 g, 0.04 mol) of ethyl vinyl ether, or 5.2 ml (4.0 g, 0.04 mol) of butyl vinyl ether. After the reaction ampoule was sealed and warmed to room temperature, it was shaken until the tetracyanoquinodimethane dissolved. The yields and specific viscosities of the resulting polymers are given in Table I. Figure 7 shows the determination of the intrinsic viscosity, η, of poly(isopropyl vinyl ether) initiated by tetracyanoquinodimethane.

The Effect of Additives. Hydroquinone. The regular polymerization procedure was followed with 12 mg (1.1×10^{-4} mol) of hydroquinone present in a slight molar excess of the catalyst to yield 2.281 g (67%) of polymer. The polymer solution at the end of the 20-hr polymerization period was orange instead of the usual water white.

Water. Polymerizations to determine the effect of water (Table VI) were carried out by the general method, except that distilled water was added to the catalyst cup along with the tetracyanoquinodimethane. Polymerization no. 1 was carried out in the same manner except that the catalyst cup was placed in a side arm which had been added to the reaction ampoule. The ampoule was flamed while under high-vacuum pumping. After cooling, the side arm was warmed, thereby subliming the tetracyanoquinodimethane evenly onto the ampoule walls. A slight coloring of green was noted in the normally yellow tetracyanoquinodimethane. The side arm was removed with a torch to remove any residue after sublimation.

Low-Temperature Studies. The general polymerization procedure was followed, except after sealing the polymerization ampoule it was placed in an alcohol–ice bath at −30° or a water–ice bath at 0°. Three polymerization trials were carried out at each temperature. Two of the ampoules were irradiated, one with a Universal 93 tungsten lamp and the other a high-pressure uv lamp, respec-

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(24) M. Szwarc, "Carbanions, Living Polymers, and Electron Transfer Processes," Interscience, New York, N. Y., 1968.

(25) R. A. Carboni, "Organic Syntheses," Collect. Vol. 4, Wiley, New York, N. Y., 1963, p 877.

(26) D. S. Acker and W. R. Hertler, *J. Amer. Chem. Soc.*, **84**, 3370 (1962).

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tively; the third ampoule was protected from light. No polymer precipitation occurred during a 4-hr period, but in all six cases precipitation of polymer occurred within 10 min after the reaction ampoules were warmed to room temperature at the end of the 4-hr observation period.

Reaction of Isopropyl Vinyl Ether and Tetracyanoquinodimethane in a 1:1 Molar Ratio. To a 500-ml round-bottom flask containing 5 g (0.025 mol) of tetracyanoquinodimethane dissolved in 300 ml of acetonitrile at 80° was added dropwise a solution of 3 ml (4 g, 0.046 mol) of isopropyl vinyl ether in 100 ml of acetonitrile. The addition took approximately 4 hr. The volatiles, which consisted only of acetonitrile as shown by glc, were then removed and the tarry residue was extracted with benzene. The insoluble portion of the residue was unreacted tetracyanoquinodimethane, 3.1 g. The addition of Skelly B to the benzene extraction solution caused the precipitation of a green sticky substance. After several washings with Skelly B to remove the poly(isopropyl vinyl ether), this sticky substance became a fine green powder, mp 115–119°. Decoloration with charcoal gave 0.9 g (18% yield) of tan solid, mp 117–120°. Integration of the nmr spectrum was in agreement with a 2:1 incorporation of isopropyl vinyl ether and tetracyanoquinodimethane, respectively; ir 3010 (aromatic C–H), 2936 (aliphatic C–H), 2245 (–CN), 1900 (para-substituted phenyl), 1715 (C=O), 1660, 1500, 1440, 1410, 1370, 1315, 1170, 1100 (alkyl ethers), 1040, 1015, 910, and 820 cm^{-1} (para-substituted phenyl). The structure is probably an oligomer made up of two molecules of tetracyanoquinodimethane and four molecules of isopropyl vinyl ether.

Anal. Calcd for $C_{44}H_{48}N_8O_4$: C, 70.19; H, 6.42; N, 14.88; mol wt, 753. Found: C, 70.29; H, 5.73; N, 16.10; mol wt, 723 (vapor pressure osmometer in acetone).

Reactions of Alkyl Vinyl Ethers with 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone. Polymerization of Alkyl Vinyl Ethers with 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone. The polymerizations were carried out as described in the general procedure employing 0.0227 g (10^{-4} mol) of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and 4.6 ml (3.4 g, 0.04 mol) of isopropyl vinyl ether, 3.8 ml (2.9 g, 0.04 mol) of ethyl vinyl ether, or 5.2 ml (4.0 g, 0.04 mol) of butyl vinyl ether. Upon warming the polymerization ampoule to room temperature, polymer precipitation occurred immediately with the evolution of heat. The yields and specific viscosities are given in Table II. Figure 7 shows the determination of the intrinsic viscosity, η, of poly(isopropyl vinyl ether) initiated by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone.

Reaction of Methyl Vinyl Ether and 2,3-Dichloro-5,6-*p*-benzoquinone in a 1:1 Molar Ratio. Two 20-ml acetonitrile solutions of 4.54 g (0.02 mol) of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and 1.50 ml (1.16 g, 0.02 mol) of methyl vinyl ether were simultaneously added into the top of a 10-cm vigreaux column which was fitted to a 50-ml round-bottom flask containing 25 ml of methanol and a magnetic stirring bar. After the addition, the volatiles were removed under reduced pressure and 4.7 g (82%) of light yellow solid, **4**, was recovered and recrystallized from small volumes of acetonitrile: mp 173–175.5° dec; nmr ($(CD_3)_2CO$) δ 4.48 (two doublets, 1 H, $-CH_2C\mathit{H}-$), 3.28 (variable, broad singlet, –OH), 3.28 and 3.23 (two singlets, 6 H, $-OCH_3$), and 2.68 (two overlapping doublets, 2 H, $-C\mathit{H}_2CH-$); ir (Nujol) 3300 (OH), 2240–2260 (CN), 1728 and 1700 (C=O, quinone), 1110 and 1130 (alkoxy); uv λ_{max} (CH_3CN) 231, 270, 280, and 357 nm (ϵ 10,444, 9525, 6034, and 1504); mass spectrum (20 eV) *m/e* 318, 289, 285, 267, 242, 228, 89, and 75. *Anal.* Calcd for $C_{12}H_{10}Cl_2N_2O_4$: C, 45.44; H, 3.18; N, 8.84. Found: C, 44.90; H, 2.43; N, 8.58.

Reaction of Ethyl Vinyl Ether and 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone in a 1:1 Molar Ratio. Two 20-ml acetonitrile solutions of 4.54 g (0.02 mol) of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and 1.94 ml (1.44 g, 0.02 mol) of ethyl vinyl ether were simultaneously added into the top of a 10-cm vigreaux column which was fitted to a 50-ml round-bottom flask containing 25 ml of methanol and a magnetic stirring bar. After the addition, the volatiles were removed under reduced pressure and the non-volatiles were triturated several times with Skelly B, which gave 4.2 g (70%) of yellow-colored solid. This product was recrystallized from small volumes of acetonitrile: mp 140–142° dec; nmr (CD_3CN) δ 4.48 (broad triplet, 1 H, $-CH_2C\mathit{H}-$), 3.47 (two overlapping quartets, 2 H, $-OC\mathit{H}_2CH_3$), 3.26 (variable, broad singlet, –OH), 3.09 and 3.15 (two singlets, 3 H, $-OCH_3$), 2.65 (two doublets, 2 H, $-C\mathit{H}_2CH-$), 1.00 ppm (two overlapping triplets, 3 H, $-OCH_2C\mathit{H}_3$); ir (Nujol) 3315 (OH), 2240 and 2260 (CN), 1730 and 1710 (C=O, quinone), and 1115 cm^{-1} (alkoxy); uv λ_{max} (CH_3CN) 231, 270, 280, and 357 nm (ϵ 16,234, 10,992, 10,941, and 2798); mass spectrum (20 eV) *m/e* 332, 301, 287, 243, 227, 89, 61, and 41. Sample may have contained some excess hydroquinone. *Anal.* Calcd for $C_{13}H_{12}O_4N_2Cl_2$: C, 47.13; H, 3.62; N, 8.46. Found: C, 46.71; H, 2.63; N, 9.77.

Reaction of 1,1-Diphenylethylene with 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone. A solution of 1 g (4.4 × 10^{-3} mol) of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and 0.79 g (4.4 × 10^{-3} mol) of 1,1-diphenylethylene in 100 ml of acetonitrile was stirred at ambient temperature for 6 hr. After the addition of 20 ml of methyl alcohol, the solution was stirred for an additional 10 hr. The volatiles were then removed under reduced pressure and the tarry residue was triturated with Skelly B, producing a light brown solid product, **6**. This was recrystallized from benzene: mp 160–162° dec; nmr (CD_3CN) δ 7.3 (s, 10 H, C_6H_5), 5.0 (s, 2 H, CH_2), 3.2 (s, 3 H, OCH_3), and 2.9 ppm (variable broad s, OH); ir (Nujol) 3220 (OH) and 1250 cm^{-1} (CN); mass spectrum (70 eV) *m/e* 77, 105, 165, 178, 179, 180, 197 (most intense by 100 times), 228, 407 ± 2, and 599 ± 5. *Anal.* Calcd for $C_{23}H_{16}N_2O_3$: C, 62.88; H, 3.67; N, 6.38. Found: C, 62.44; H, 3.55; N, 6.31.

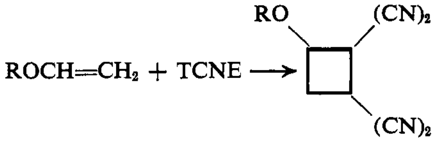
Reactions of Alkyl Vinyl Ethers with Tetracyanoethylene. Polymerization of Alkyl Vinyl Ethers with Tricyanoethenol in Tetracyanoethylene. Polymerization. The polymerizations were carried out as described in the general procedure employing 0.0128 g (10^{-4} mol) of tetracyanoethylene of various degrees of purity and 4.6 ml (3.4 g, 0.04 mole) of isopropyl vinyl ether, 3.8 ml (2.9 g, 0.04 mol) of ethyl vinyl ether, or 5.2 ml (4.0 g, 0.04 mol) of butyl vinyl ether. The results are shown in Table IV. Tetracyanoethylene purified by three recrystallizations from chlorobenzene followed by two sublimations at 1.0 mm was colorless, mp 200–202° (lit.[25] mp 200–202°), and did not initiate polymerization. However, if tetracyanoethylene was purified by one recrystallization from chlorobenzene followed by vacuum sublimation, mp 197–199°, it initiated the polymerization of isopropyl vinyl ether. Polymerization also occurred with catalyst that had been aged for 3 months at 25° in the atmosphere after purification or that was obtained from Aldrich Chemical Co., Inc., and used without further purification; light brown crystals, mp 193–196°.

Effect of Water. Into a Pyrex glass ampoule into which had been placed 0.0128 g (10^{-4} mol) of tetracyanoethylene and various amounts of distilled water was transferred 20 ml of dried acetonitrile by trap-to-trap distillation under reduced pressure. This mixture was aged at room temperature for various amounts of time (0–48 hr) and then degassed by several freeze–thaw cycles to remove any hydrogen cyanide which had been produced. Then 4.6 ml (3.4 g, 0.04 mol) of isopropyl vinyl ether was transferred into the polymerization ampoule and the general polymerization procedure was followed. Table V shows the mole ratios of tetracyanoethylene and water employed, the aging times, and the results of the various conditions on the polymerization.

Tricyanoethenol. To 100 ml of acetonitrile was added 1 g (0.008 mol) of tetracyanoethylene and 0.29 ml (0.016 mol) of water. This solution was placed in the dark at room temperature and after three days the volatiles were removed under reduced pressure. The residue was extracted with cold water and the water was immediately evaporated from the extract solution giving a brown oil. The brown oil was added to 20 ml of acetonitrile containing 1.357 g (0.008 mol) of tetramethylammonium bromide. Upon cooling this solution, 0.096 g (9.6%) of yellow needlelike crystals of tetramethylammonium salt of tricyanoethenol precipitated, mp 208–211 (lit.[16] mp 210–211°). The ir spectrum of this salt prepared in acetonitrile is the same as that prepared in water.[16] *Anal.* Calcd for $C_9H_{12}ON_4$: C, 56.2; H, 6.3; N, 29.2. Found: C, 57.2; H, 6.5; N, 29.9.

A water solution of tetramethylammonium tricyanoethenolate

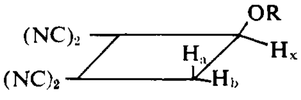
TABLE XI
3-ALKOXY-1,1,2,2-TETRACYANOCYCLOBUTANES



R	% yield	Mp, °C	Reaction time,[a] hr
C_2H_5	42.8	140.5–143[b]	12
$(CH_3)_2CH$	60.5	110–112.5	1.5
n-C_4H_9	52.7	90.5–91.5	72
tert-C_4H_9	63.9	120–122	0.25

[a] The times observed for the color of the charge-transfer complex to disappear when the reaction was carried out in the solvent toluene. [b] Lit.[7] 141–143.

TABLE XII
NMR SPECTRAL ANALYSIS OF
3-ALKOXY-1,1,2,2-TETRACYANOCYCLOBUTANES[a]



R	H_x	H_aH_b
C_2H_5[b]	Two doublets (4.89)	Eight peaks (centered about 3.25)
$(CH_3)_2CH$[c]	Two doublets (4.78)	Two doublets (3.13, 3.28)
$(CH_3)_3C$[c]	Two doublets (4.89)	Two doublets (3.12, 3.28)

[a] All values are given in ppm downfield from TMS; the spectra were run on a 60-MHz instrument. [b] The solvent used was hexadeuterioacetone; the values given agree well with those given in the literature for the ethoxycyclobutane.[7] [c] The solvent used was deuteriochloroform.

was passed through an acid ion-exchange column, Dowex 50-X8. The eluate was evaporated leaving a yellow oil, which became solid upon trituration with ethyl ether. Following the general polymerization procedure, 10 mg of this solid which had been dried at 68° under reduced pressure, initiated the polymerization of isobutyl vinyl ether in acetonitrile giving a 10.6% yield of polymer.

Cycloaddition of Alkyl Vinyl Ethers and Tetracyanoethylene. To a red solution of 0.500 g (3.90×10^{-3} mol) of tetracyanoethylene in 25 ml of toluene was added 1 ml of alkyl vinyl ether. The solution was shaken and placed in the dark for the duration of the reaction; the flask was periodically checked for the disappearance of color. When the reaction solution became colorless, it was poured into 150 ml of stirring petroleum ether (bp 60–70°). The white solid which precipitated was filtered and recrystallized from 1,2-dichloroethylene. Melting points and yields of the cyclobutane derivatives prepared appear in Table XI. The nmr chemical shifts for the ring protons are given in Table XII. *Anal.* Calcd for $C_{10}H_8N_4O$ (from ethyl vinyl ether): C, 60.00; H, 4.00; N, 28.00. Found: C, 59.57; H, 3.97; N, 29.05. Calcd for $C_{11}H_{10}N_4O$ (from isopropyl vinyl ether): C, 61.67; H, 4.70; N, 26.16. Found: C, 61.02; H, 5.07; N, 26.33. Calcd for $C_{12}H_{12}N_4O$ (from *tert*-butyl vinyl ether): C, 63.13; H, 5.30; N, 24.55. Found: C, 63.26; H, 5.16; N, 24.62. Found (from *n*-butyl vinyl ether): C, 62.70; H, 5.33; N, 24.33.

Electron Spin Resonance Studies. Tetracyanoquinodimethane. To an esr flat cell equipped with two side-arm reservoirs was added 0.5 mg (2.4×10^{-5} mol) of tetracyanoquinodimethane, and after this cell was attached to a high-vacuum system and evacuated, 1.15 ml (0.86 g, 0.01 mol) of isopropyl vinyl ether was added to the empty side arm and 5 ml of acetonitrile was added to the side arm containing the tetracyanoquinodimethane. The frozen acetonitrile solution was warmed to room temperature and poured into the esr cell while the isopropyl vinyl ether was kept frozen and isolated from the tetracyanoquinodimethane acetonitrile solution. The instrument was tuned and any small signal was recorded. The isopropyl vinyl ether was then thawed and mixed with the tetracyanoquinodimethane solution and this mixture was observed for 4 hr. No esr signal was observed under these conditions after several attempts. Cloudiness indicating polymer formation was observed each time within 20 min after mixing the reagents. Concurrent polymerizations under identical conditions but in a polymerization ampoule produced polymer in yields of 40–60%. Only trace amounts of polymer were isolated from the esr reaction mixture. Some leakage could be observed in the esr apparatus, and to obviate this the apparatus was filled with argon after the reagents had been added. The esr spectrum still showed no signal, but cloudiness occurred within 10 min and 0.287 g (34%) of polymer was isolated from the esr reaction mixture.

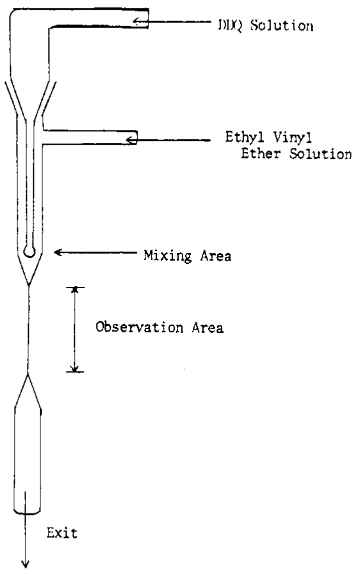


Figure 8. Modified esr cell for flow experiments.

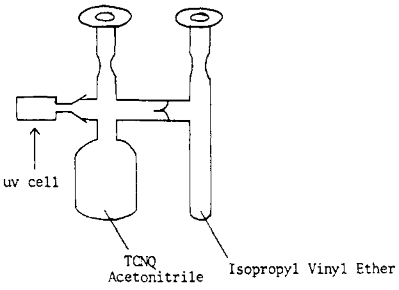


Figure 9. Apparatus for tetracyanoquinodimethane kinetic studies.

2,3-Dichloro-5,6-dicyano-*p*-benzoquinone. An esr flat cell was modified as shown in Figure 8. Solutions of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and ethyl vinyl ether, respectively, were flowed simultaneously into the cell at a constant rate and mixed just before entering the flat portion or observation area of the cell under an atmosphere of N_2. For a 1:1 molar ratio of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (0.05 *M*) and ethyl vinyl ether (0.05 *M*) in acetonitrile, an esr signal, similar in width to an authentic sample of the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone radical-anion lithium salt (Figure 3; modulation amplitude 1, signal level 8000) but unresolved, was observed during the flow of the two solutions (Figure 4; modulation amplitude 500, signal level 5000). Flow rates were varied from 1.5 to 3.0 ml/sec with similar results. When the flow was stopped the signal disappeared rapidly (15–30 sec). Within 30 min a similar and resolvable signal appeared and was stable for hours.

An esr signal was also observed for a 1:400 molar ratio of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (0.0025 *M*) and ethyl vinyl ether (1.0 *M*) in acetonitrile (Figure 4). This signal was also unresolvable and of approximately the same width as an authentic sample of the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone radical anion. No significant differences were observed in this signal by varying the flow rate from 1.5 to 3.0 ml/sec.

Kinetic Studies. The kinetic studies of the reaction of tetracyanoquinodimethane and isopropyl vinyl ether were carried out in the apparatus shown in Figure 9, by following the disappearance of the maximum absorbance of tetracyanoquinodimethane at 393.5 nm. After the tetracyanoquinodimethane spectrum was recorded, the reagents were mixed by opening the break seal. The various initial concentrations, temperatures, and kinetics are given in Table VII. The concentration of tetracyanoquinodimethane was found to be linear with absorption.

A Durram-Gibson stopped-flow spectrophotometer was employed in determining the kinetics of the charge-transfer complex disappearance to the cycloaddition product of tetracyanoethylene and alkyl vinyl ethers (Figure 6, Table X), in methylene chloride and acetonitrile. The charge-transfer complex formation was too rapid to follow by this technique. This instrument was also used to follow the kinetics of the free-radical intermediate 2,3-dichloro-5,6-dicyano-*p*-benzoquinone radical anion, in the reaction of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and alkyl vinyl ethers (Table IX).

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Polymerization of *N*-Vinylcarbazole with Zinc Bromide. I. Electroinitiated

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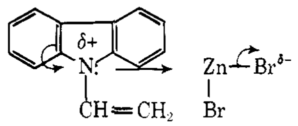
ABSTRACT: The electroinitiated polymerization of *N*-vinylcarbazole is described. The reaction medium consists of monomer dissolved in an acetone–zinc bromide solution. Elemental analysis and infrared and nuclear magnetic resonance spectroscopy identified the reaction product as poly(vinylcarbazole). Molecular weights were obtained from gel permeation chromatography and intrinsic viscosity measurements. Generally, polymer yield increased with increased applied current density. High polymer yields were obtained in short reaction times. Weight-average molecular weights were low and in the range 2000–5000. Molecular weight distributions were very narrow and always in the range 1–1.2.

Breitenbach, *et al.*,[1] studied the electroinitiated polymerization of *N*-vinylcarbazole (VCZ) using techniques not involving donor–acceptor mechanisms. Their studies involved the cationic polymerization of the monomer in nitrobenzene solution using supporting electrolytes such as tetraalkylammonium compounds and silver perchlorate. Good yields of low molecular weight polymers were obtained. However, the perchlorate systems lend themselves to some experimental criticism, since it is known that cationic polymerization can take place with perchlorate catalysts in systems containing trace amounts of water in the absence of electrolytic current.

Recently, several electroinitiated polymerizations have been studied in which donor–acceptor complexes are thought to be part of the reaction mechanism.[2-6] The results can be interpreted on the model proposed by Gaylord,[7] which was arrived at after observing experimental behavior on the copolymerization of pairs of polar monomers in the presence of suitable salts.

The postulate involves the interaction between an electron-donor monomer and an electron-acceptor monomer to form an equimolar charge-transfer complex. This complex formation is enhanced by a metal salt which acts as an electron acceptor. The formation of the complex is then followed by the spontaneous or radical-initiated polymerization to produce an alternating copolymer.

An extension of the Gaylord donor–acceptor theory may be applicable in the case of homopolymerization in the presence of a transition metal salt such as $ZnBr_2$. Such a mechanism was tentatively proposed by Gaylord for acrylonitrile polymerization utilizing $ZnCl_2$.[7] Since VCZ is a very basic monomer it will complex readily with Zn salts, thereby forming a complex in which the VCZ moiety has increased electrophilic character. The complexed VCZ–$ZnBr_2$ molecule (*i.e.*, the acceptor) under the influence of electrical current (electroexcitation) will be vulnerable to nucleophilic attack from a VCZ monomer (*i.e.*, the donor molecule), thereby initiating a cationic-type polymerization.



In electrochemical systems, polymerization of the donor–acceptor complexes is thought to be initiated by activation of these complexes at the electrode, with the rate of formation of the activated complex being dependent on the current. It is likely that elevated temperatures increase the reactivity of the donor–acceptor complexes. However, higher temperatures are also thought to decrease the concentration of the complexes, giving rise to a decrease in reaction rate. Electrochemical initiation offers a tool for investigation these

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