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The Role of Donor-Acceptor Complexes in the Initiation of Ionic Polymerization

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ABSTRACT

Work carried out in the past few years aimed at elucidating the mechanism of initiation of vinyl polymerization when a donor and an acceptor molecule, one or both of which may be vinyl monomers, is summarized. The emphasis of our investigation has been on polymerizable ether donors and strong electron acceptors which do not undergo polymerization, or the acceptor vinylidene cyanide. Alkyl vinyl ethers were polymerized in the presence of tetracyanoquinodimethane (TCNQ) and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) in polar solvents. Observation of the ESR spectrum of the DDQ radical anion and the isolation of a 1:1 addition product of DDQ and alkyl vinyl ether when the two are mixed in a 1:1 ratio and quenched in alcohol support an initiation mechanism involving a coupling reaction of the donor monomer (radical cation) and the acceptor initiator (radical anion). The reaction of vinylidene cyanide (VC) with the vinyl ethers p-dioxene, dihydropyran, ethyl vinyl ether, isopropyl vinyl ether, and ketene diethylacetal in a variety of solvents at 25°C spontaneously afforded poly(vinylidene cyanide), the cycloaddition products 7,7-dicyano-2,5-dioxo-bicyclo[4.2.0]octane, 8,8-dicyano-2-oxo-bicyclo[4.2.0]octane, the 1,1-dicyano-2-alkoxycyclobutanes, and 1,1-diethoxy-2,2,4,4-tetracyanohexane, respectively, and with the exception of p-dioxene, homopolymers of the vinyl ethers. In the presence of AIBN at 80°C, alternating copolymers were obtained in addition to the homopolymers and cycloaddition products, supporting the involvement of donor-acceptor complexes. The reaction of styrene with VC spontaneously formed an alternating copolymer in addition to the 1:2 head-to-head cycloaddition product, 1,1,3,3-tetracyano-4-phenylcyclohexane. Mixing VC with any one of the cyclic ethers tetrahydrofuran, oxetane, 2,2-dimethyloxirane, 2-chloromethyloxirane, and phenyloxirane resulted in the polymerization of both the VC and the cyclic ether to afford homopolymers of both. The cyclic ethers trioxane, 3,3-bis(chloromethyl)oxetane, and oxirane initiated the polymerization of VC, but did not undergo ring-opening polymerizations themselves. Other ethers such as 1,3-dioxolane, tetrahydropyran, and diethyl ether did not initiate the polymerization of VC. In these polymerizations, VC and the cyclic ethers polymerize via anionic and cationic propagation reactions, respectively.

INTRODUCTION

The reaction of an electron donor with an electron acceptor, one or both of which may be a vinyl monomer, often results in the polymerization of the donor, the acceptor, or both. Although donor-acceptor complexes as well as their intermediate reaction products, radical cations and radical anions, have been observed in these polymerizations, the initiation mechanisms are not well understood. Most proposed mechanisms invoke a "T-class" reaction of the complex in the first stages of the initiation step to give a radical cation and a radical anion:

$$\mathrm{D} + \mathrm{A} \overset{\mathrm{Ke}}{\rightleftharpoons} [\mathrm{D} \rightarrow \mathrm{A}] \rightleftharpoons \mathrm{D}^{\dot{+}},\mathrm{A}^{\dot{-}} \rightleftharpoons \mathrm{D}^{\dot{+}}\ (\mathrm{solv}) + \mathrm{A}^{\dot{-}}\ (\mathrm{solv})$$

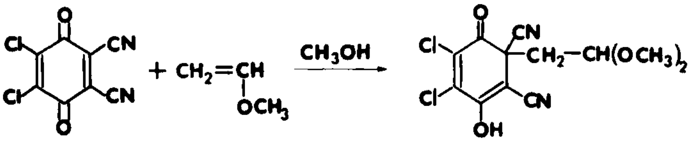
Two types of spontaneous polymerization have been observed; 1) the homopolymerization of the donor monomer by a cationic propagation and/or the homopolymerization of the acceptor monomer by an anionic propagation, and 2) the alternating copolymerization of the donor and acceptor monomers by a free radical propagation. In addition, donor and acceptor monomers which form a complex and do not spontaneously homopolymerize may form an alternating copolymer by a radical propagation reaction. Which one of these types of polymerization reactions occurs has been postulated [1] to depend on the strength of the complex as measured by the equilibrium constant, K_{eq}.

SPONTANEOUS HOMOPOLYMERIZATION

Donor Monomer Homopolymerization via Nonmonomer Acceptors [2-5]

Although in the presence of tetracyanoethylene (TCNE) vinyl ethers form intermediate donor-acceptor complexes that ultimately lead to cyclobutane 2 + 2 cycloaddition products, the ethers polymerize in the presence of the acceptors tetracyanoquinodimethane (TCNQ) and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), neither of which can undergo facile 2 + 2 cycloaddition.

High molecular weight polymers ($\overline{M}_n = 10^5$) are obtained from catalytic amounts of the acceptor via a cationic propagation mechanism. Immediately after mixing the vinyl ether and the TCNQ or DDQ acceptor, a color characteristic of the donor-acceptor complex was observed which eventually disappeared. The rate of initiation was dependent on the solvent, the temperature, and the vinyl ether; polar solvents and higher temperatures led to faster rates while the rates of initiation followed the order t-C_4H_9 > i-C_3H_7 > C_2H_5. The DDQ radical anion was observed by ESR using flow techniques. In certain cases the rates of formation and disappearance of the donor-acceptor complex as well as that of the radical anion could be obtained. When DDQ and methyl vinyl ether (1:1) were mixed in a flow system and then quenched in methanol, the 1:1 reaction product (1) was formed.



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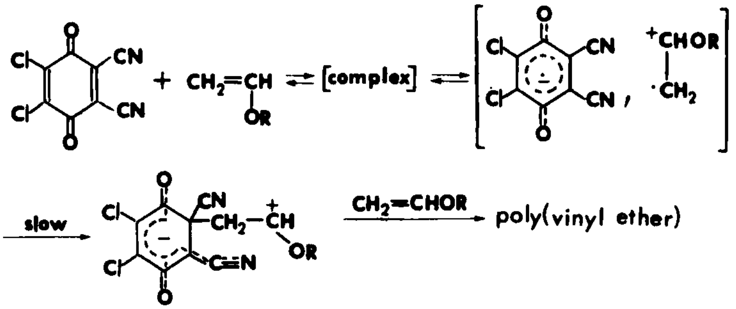
Thus the following mechanism of initiation was proposed, as illustrated with DDQ.



If this mechanism is correct, several important questions regarding it are unanswered. The role of the delocalized anion is not understood; whether it is destroyed early in the polymerization or serves as a counterion during propagation and ultimately is consumed, perhaps in an ion coupling termination reaction, is not known.

Quite unexpectedly, the highly polar electron donating monomer, ketene diethyl acetal, gives only low yields (<15%) of polymer in the presence of the electron acceptors TCNE, TCNQ, and DDQ. Contrary to earlier reports [6], polymer is obtained only in the polar solvent, acetonitrile, but not in toluene or methylene chloride. No pure cycloadduct could be isolated in the reaction with TCNE.

Why this monomer, which, with the same acceptors, forms a stronger donor-acceptor complex than the alkyl vinyl ethers, yet does not undergo polymerization, remains unexplained. The proposal [1] that monomers which form very strong complexes ($K_{eq} \geq 5$) do not undergo polymerization does not provide a satisfactory explanation.

Acceptor Monomer Homopolymerization via Nonmonomer Donor [5]

The polymerization of vinylidene cyanide (2), a strong electron acceptor monomer, takes place rapidly with an anionic catalyst, but only slowly in the presence of a radical initiator. Since p-dioxene (3) is an electron donor monomer that does not undergo homopolymerization, its reaction with vinylidene cyanide was studied.

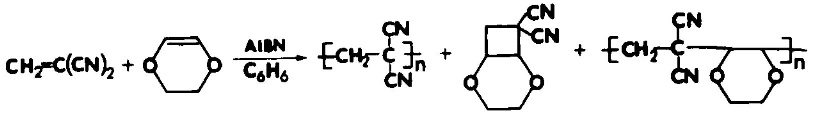
High molecular weight poly(vinylidene cyanide) (4) and the cycloaddition product, dicyano-2,5-dioxo-bicyclo[4.2.0]octane (5), were obtained. Equal molar amounts of reactants gave a 2:1 ratio of polymer to cycloaddition product. Although no color characteristic of a donor-acceptor complex could be observed, the presence of a radical initiator led to the formation of poly(vinylidene cyanide), cycloadduct 5, and a 1:1 head-to-tail alternating copolymer (6, $\eta_{inh} = 0.25$, Table 1). The cycloadduct, 5, neither initiates the polymerization of vinylidene cyanide nor polymerizes in the presence of a free radical initiator. The structure of the copolymer was established by its solubility characteristics, its 1:1 composition regardless of the monomer feed ratio, and its ^{13}C NMR spectrum.

An initiation mechanism similar to that postulated for the vinyl ethers in the presence of TCNQ or DDQ (vide supra) can be written, but in this case is much less satisfactory.

Acceptor Monomer-Donor Monomer Homopolymerization [5]

The reaction of vinylidene cyanide, an electron acceptor monomer with the electron donor monomers, the vinyl ethers [7], ketene

TABLE 1. Copolymerization of Vinylidene Cyanide and p-Dioxene

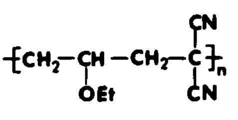


2	3	4	5	6
Mole ratios			% Yields	
1	2	12	12	73
1	1	24	9	69
2.8	1	66	18	53

diethyl acetal, and dihydropyran in each case afforded cycloadduct, poly(vinylidene cyanide), and the corresponding polyether (Table 2).

Several features of these reactions are mechanistically noteworthy. The presence of light had little effect either on the yields of homopolymers or on the yields of cycloadducts. In general, an increase in the molar ratio of one of the two monomers resulted in an increased yield of the corresponding homopolymer. In the polymerization reactions of vinylidene cyanide and dihydropyran, higher conversions of vinylidene cyanide to polymer were observed in the more polar solvents, particularly in acetonitrile. Further, higher yields of cycloadducts were produced in the more polar solvents, but in a given solvent the yield of cycloadduct was relatively constant, regardless of the mole ratio of the donor and acceptor charged.

Under the reaction conditions, poly(vinylidene cyanide) (4) would not initiate the polymerization of the vinyl ethers, the poly(vinyl ethers) would not initiate the polymerization of vinylidene cyanide, and the cycloadduct would not initiate the polymerization of either vinylidene cyanide or the ether monomers. The observations [7] that the addition of trihydroxyethylamine or phosphorus pentoxide to the vinylidene cyanide-vinyl ether mixtures inhibited the polymerizations of the vinyl ethers and vinylidene cyanide, respectively, suggest cationic and anionic propagation reactions of these monomers. Although no transient colors characteristic of the donor-acceptor complexes were observed, alternating copolymers 16 and 17 could be obtained from the reactions of vinylidene cyanide (2) and ethyl vinyl ether (7a) or dihydropyran (13), respectively, in the presence of a free radical initiator. Cycloadduct, 8 or 14, poly(vinylidene cyanide) (4), and poly(ethyl vinyl ether) (9a) were also produced along with the copolymer (Table 3). Neither cycloadduct 8 nor 14 polymerized in the presence of the free radical initiator, an anionic catalyst or a cationic catalyst.



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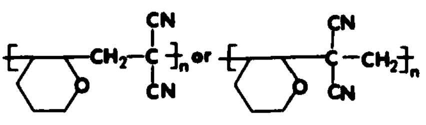

17

The structures of the alternating copolymers (16 and 17) were established by their solubility characteristics, their 1:1 compositions regardless of the monomer feed ratios, and their ^{13}C NMR spectra.

In the case of polymer 17, a head-to-tail or a head-to-head structure could not be conclusively established by the ^{13}C NMR spectrum.

SPONTANEOUS ALTERNATING COPOLYMERIZATION [5,7]

Surprisingly, the reaction of vinylidene cyanide with styrene in the absence of a free radical initiator gave both a head-to-tail alternating copolymer (18) and the head-to-head cycloadduct (19) (Table 4). No homopolymer of either monomer was obtained. The structure of the copolymer was established from its solubility, its 1:1 composition regardless of monomer feed ratio, and its ^{13}C NMR spectrum.

The mechanisms of initiation of the polymerizations which take place when vinylidene cyanide and the vinyl ether donor monomers p-dioxene (3), ethyl vinyl ether (7a), i-propyl vinyl ether (7b), ketene diethyl acetal (10), and dihydropyran (13) are mixed in an inert solvent are certainly open to speculation. Tetracyanoethylene reacts with these monomers to give transient colors characteristic of the donor-acceptor complexes, yet in all cases only the cycloadduct is obtained* and no polymerization of the donor monomer is observed. The absence of color when vinylidene cyanide is the acceptor molecule does not necessarily imply the absence of a donor-acceptor complex, since it could be present in low concentrations as a result of a large difference in its relative rates of formation and disappearance. The observations that vinylidene cyanide and the vinyl ether donor monomers afforded alternating head-to-tail copolymers in the presence of free radical initiators implicates the presence of the donor-acceptor complex.

This series of reactions of vinylidene cyanide with donor vinyl monomers provides examples of the two modes of spontaneous polymerizations. The proposal [1] that spontaneous homopolymerization is observed when $K_{eq} \simeq 1$ to 5 and spontaneous alternating copolymerization occurs when $K_{eq} \simeq 0.1$ is generally observed. The estimated equilibrium constants for these complexes as obtained from the ionization potentials of the donor vinyl monomers and a calculated electron affinity for vinylidene cyanide show that a $K_{eq} \simeq 0.1$ gives the alternating copolymer (styrene, vinylidene

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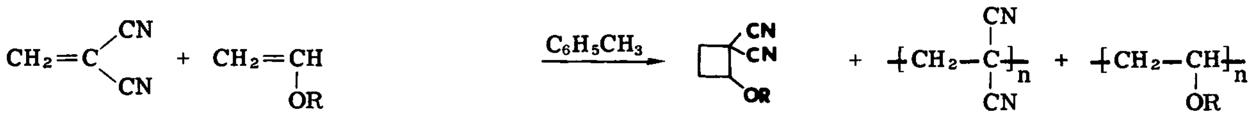
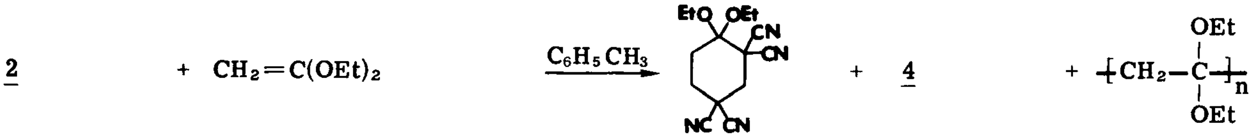
*The exception is ketene diethyl acetal, in which case only an impure unstable product is isolated.

TABLE 2. Vinylidene Cyanide-Vinyl Ether*

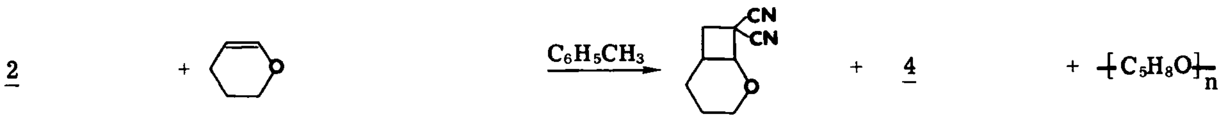


R = (a) C_2H_5; (b) iC_3H_7

2	7		8	4	9
1	3.3	a	27	52	84
1	2	b	13	52	81
1.2	1	a	17	75	69
1.5	1	b	9	71	67
4	1	a	33	85	53
4.1	1	b	20	86	43



2	10	11	4	12
1	1.8	22	Trace	43
1.7	1	32	58	30

5	1	37	67	Trace
				
	13	14		15
1	4.5	31	33	
1	1	26	52	Trace
5.6	1	27	58	

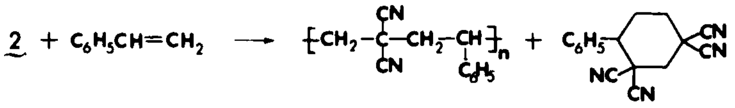
*Yield % with respect to reactant present in smaller molar amount.

TABLE 3. Copolymerization of Vinylidene Cyanide and Donor Monomers

Mole ratio			Product yield (%)[a]			
2	:	7a	8	4	9	16
1		3.3	Trace	Trace	83	38
1.2		1	Trace	60	80	30
3.85		1	Trace	72	58	42
2	:	13	14	4	-	17
1		2.7	12	12		73
1		1	9	24		69
3.3		1	18	66		53

[a] Based on the monomer present in the smaller mole ratio.

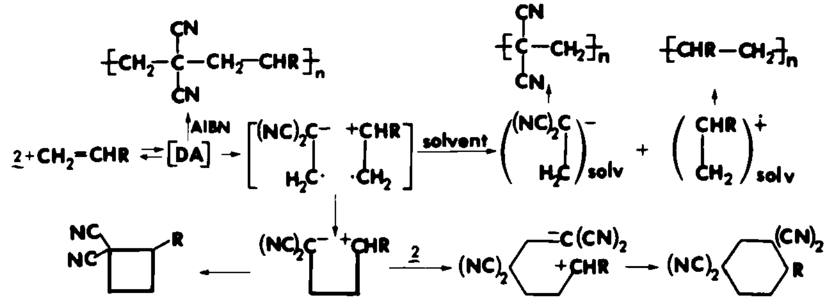
TABLE 4. Copolymerization of Vinylidene Cyanide and Styrene



Mole ratio		% Yield	
		18	19
1	1.37	49	33
1.45	1	53	23
2.17	1	78	20

cyanide) and a $K_{eq} \simeq 0.3$ affords homopolymer (ethyl vinyl ether, vinylidene cyanide).

A polymerization mechanism involving donor-acceptor complexes which satisfactorily accounts for the formation of cycloadduct and alternating copolymer in the presence of radical initiators does not satisfactorily explain or provide the details of the ionic homopolymerizations, however. The fact that both cationic and anionic propagation reactions take place in the same pot, whether they take place simultaneously or not, is quite astounding. Whether a four- or a six-membered cycloaddition product is obtained may depend either on steric factors which prevent the closure to a four-membered ring or on the ability of the cation to be sufficiently delocalized, thus allowing insertion of a second vinylidene cyanide before closure.



VINYLIDENE CYANIDE POLYMERIZATION BY CYCLIC ETHERS [8]

These extraordinary results prompted us to explore the possibility that other monomers such as cyclic ethers, which are both electron donors and are susceptible to polymerization via cationic mechanisms, would also lead to the formation of homopolymers of each type of monomer (vinylidene cyanide and cyclic ether) when the two are mixed.

The reaction of vinylidene cyanide with certain polymerizable cyclic ethers in bulk or in toluene gave poly(vinylidene cyanide) (Table 5). The ethers which were studied can be divided into three categories: 1) those which induced the polymerization of vinylidene cyanide and polymerized themselves—tetrahydrofuran, oxetane, 2,2-dimethyloxirane, epichlorohydrin, and styrene oxide; 2) those which induced the polymerization of vinylidene cyanide but do not polymerize themselves—trioxane, 3,3-bischloromethyloxetane, and oxirane; and 3) those which do not polymerize vinylidene cyanide—1,3-dioxolane, tetrahydropyran, and diethyl ether.

TABLE 5. Polymerization of Vinylidene Cyanide (2) and Cyclic Ethers at 25°[a]

Cyclic ether	Mole ratio 2:Ether	Solvent	Insoluble fraction			Soluble fraction		
			% 4	% Conversion	$[\eta]^d$	% Ether	% Conversion[a]	$[\eta]^e$
Trioxane	1:1	CH_2Cl_2[b]	86	62			0	
	5:1	CH_2Cl_2[b]	86	32			0	
Tetrahydrofuran	1:10	Bulk[c]		Trace		86	25	1.28
	1:1	Bulk[c]	92	54	0.85	93	65	0.74
	5:1	Bulk[c]	93	36	1.36	95	100	0.27
Oxetane	1:5	Toluene	68	37	0.12	97	79	1.22
	1:1	Toluene	78	64	0.40	95	100	0.24
	5:1	Toluene	90	33	0.52	94	100	0.10
3,3-Bis(chloromethyl) oxetane	1:5	Toluene	86	34			0	
	1:1	Toluene	86	56			0	
	1:1	Acetonitrile	88	56			0	
2,2-Dimethyloxirane	1:5	Toluene	87	100	0.21	90	3	2.10
	1:1	Toluene	90	84	0.77	88	7	0.90
	5:1	Toluene	85	61	1.39	70	44	0.14

2-Chloromethyloxirane (epichlorohydrin)	1:10	Toluene	86	73		2
	1:1	Toluene	92	94	80	69
	10:1	Toluene	94	79		4
2-Phenyloxirane (styrene oxide)	1:5	Toluene	79	100	91	3[f]
	1:1	Toluene	87	100	83	45[f]
	5:1	Toluene	99	54	80	67[f]
Oxirane (ethylene oxide)	1:5	Toluene	87	16		1[g]
	1:1.5	Toluene	93	100		5[g]
	2.5:1	Toluene	92	84		2.5[g]
	1:10	Bulk	82	90	51[h]	1.5[g]

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[a] Polymerizations were carried out for 96 hr, except with tetrahydrofuran, in which case the polymerizations were allowed to continue for 168 hr. Conversions are calculated on the basis of the respective monomer charged.

[b] Cyclic ether is insoluble in toluene.

[c] Polymerization of cyclic ether in toluene takes place only very slowly.

[d] Measured in dimethylformamide at 25°.

[e] Measured in benzene at 25°.

[f] A mixture of two diphenyl-1,4-dioxane isomers was obtained in each example.

[g] In each case, 1,4-dioxane was obtained from the reaction.

[h] Block copolymer as evidenced by its NMR spectrum and solubility in toluene. The NMR spectrum was identical with that of the two homopolymers.

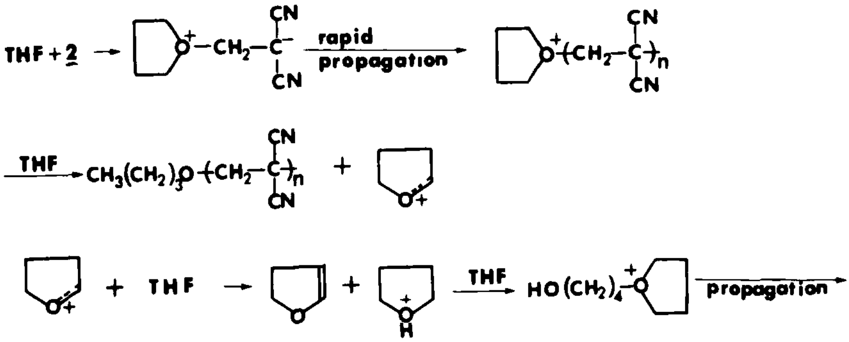
Styrene oxide and ethylene oxide are the only two cyclic ethers in this series which also are known to afford polymer by anionic initiation and propagation mechanisms, and therefore the poly(ethylene oxide) and poly(styrene oxide) could have been produced anionically. In both cases, however, dioxane derivatives were isolated from the polymerization mixture containing polyether and poly(vinylidene cyanide); dioxane was obtained from the ethylene oxide polymerization and two of the diphenyl dioxanes (cis- and trans-2,5-diphenyl-1,4-dioxane) were obtained from the styrene oxide polymerization. These products are characteristic of the cationic polymerization of these monomers, and are not produced during the course of anionic polymerization.

When phosphorus pentoxide was present in the tetrahydrofuran or oxetane polymerizations, vinylidene cyanide did not polymerize; when pyridine was present, no polyethers were obtained. Kinetic studies showed a rapid rate of vinylidene cyanide polymerization ($K_2/K_{THF} \simeq 10^2$).

In these polymerizations of vinylidene cyanide with the cyclic ethers, weak donors and a strong electron acceptor are involved, but no color, however transient, was observed. Attempts to initiate the polymerization of oxetane or tetrahydrofuran with the stronger electron acceptors, DDQ, TCNE, and TCNQ, produced only traces of polyethers. Thus a donor-acceptor mechanism is not consistent with these observations.

The observations that the rates of disappearance of the vinylidene cyanide in these polymerizations increased by increasing the amount of tetrahydrofuran initially charged, and that the molecular weight of each polymer increased as the ratio of the other monomer was decreased, indicate mutual initiation by the two monomers. Thus the initiator in the polymerization of vinylidene cyanide is either a cyclic ether or perhaps a complex of a cyclic ether. Clearly, anionic propagation in the polymerization of vinylidene cyanide and cationic propagation in the polymerization of the cyclic ethers are taking place. The studies of the rates of polymerization indicate, however, that the polymerization of vinylidene cyanide is rapid, and that significant polymerization of cyclic ethers does not take place until the propagation of vinylidene cyanide chains has ceased. Since the poly(vinylidene cyanide) precipitates in the early stages of the polymerization, the anion end may be buried in the polymer chain, fed by vinylidene cyanide monomer, and inaccessable to any terminating species such as a cationically propagating polyether.

A polar mechanism may be responsible for the initiation of polymerization. This mechanism relies on the rapid rate of propagation of vinylidene cyanide compared to the cyclization of the zwitterion.



Models show that cyclization of the dimer is not sterically possible, but cyclization could be accomplished after a second monomer addition. Cyclization at this stage may be precluded both by the rapid propagation rate and the fact that the anionic charge is delocalized over the nitrile, providing resonance stability and a diffuse charge. After the addition of subsequent vinylidene cyanide monomers, cyclization to ring sizes greater than nine becomes relatively more difficult. When the polymerization gets past the oligomer stage, the polymer precipitates, is immobile, and cannot cyclize readily. After precipitation, the chain end can be fed by vinylidene cyanide monomer by diffusion.

The steric bulk surrounding the oxonium ion end could effectively prevent attack of THF at carbon in a propagation step. Hydride transfer from monomer generates the free oxonium ion which is known to decompose to dihydrofuran and provide a proton initiator.

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