activity ratio of acrylonitrile to acrylate with the Cu_2O–isonitrile catalyst was much higher than the ratios with the usual base catalysts such as sodium alcoholate and tertiary amine. The specific increase of the acrylonitrile reactivity in the copolymerization and in the addition by the copper catalyst may be due to the specific coordination of acrylonitrile to copper probably through the cyano group.

Experimental Section

Reagents. Vinyl monomers were commercial reagents, which were purified by usual procedures and distilled under nitrogen before use. DMF was a commercial reagent and was dried over CaH_2 and distilled under nitrogen. *t*-BuNC was prepared according to Ugi's procedure.[11] PPh_3 was a commercial reagent, which was used without purification. $P(OCH_3)_3$ was a commercial reagent and was distilled under nitrogen.

Isolation and Purification of Cyclopentadienylcopper Complexes. 1 was prepared from cyclopentadiene, Cu_2O, and *t*-BuNC according to our method[3g] and then purified by recrystallization using a combination of ether (solvent) and pentane (nonsolvent) at −20° followed by sublimation at 60° under a reduced nitrogen pressure of 0.3 mm. 2 was prepared from cyclopentadiene, *t*-BuOCu, and PPh_3 according to our method.[12]

Polymerization and Copolymerization. Polymerization was carried out under nitrogen in a sealed test tube. In the case of addition of CO or O_2, the test tube was equipped with a self-sealing cap, and gas was introduced through a syringe. After polymerization, the polymer solution was poured into a mixture of CH_3OH and aqueous HCl solution. The product polymer was filtered, washed with CH_3OH, and dried *in vacuo*. Molecular weight was determined in DMF by means of a Hitachi Perkin-Elmer 115. Copolymerization was stopped at conversions below 10%. Copolymer composition was determined by nmr spectroscopy in d_6-DMSO. In the spectra of the product polymers of the acrylonitrile–styrene copolymerization by the 1–*t*-BuNC system, no peak which would be attributed to the phenyl hydrogens of the styrene unit was observed. The composition of acrylonitrile–methyl methacrylate copolymer was determined based on the area ratio of the peak at τ 7.4 (the methoxy hydrogens of methacrylate unit) to the multiplet from τ 7.9 to 9.1 (total of the methine, methylene, and methyl hydrogens of both units).

Nmr Measurement. The nmr spectrum was measured using a 60-MHz Hitachi R-20B spectrometer.

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The Spontaneous Homopolymerization of Vinylidene Cyanide and Unsaturated Ethers on Mixing the Two Monomers, and the Formation of 1:1 Alternating Copolymers in the Presence of a Free Radical Initiator

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ABSTRACT: The reaction of vinylidene cyanide with the unsaturated ethers *p*-dioxene, dihydropyran, ethyl vinyl ether, isopropyl vinyl ether, and ketene diethyl acetal in a variety of solvents at 25° spontaneously afforded poly(vinylidene cyanide), the cycloaddition products 7,7-dicyano-2,5-dioxabicyclo[4.2.0]octane and 8,8-dicyano-2-oxabicyclo[4.2.0]octane, the 1,1-dicyano-2-alkoxycyclobutanes, and 1,1-diethoxy-2,2,4,4-tetracyanocyclohexane, respectively, and, with the exception of *p*-dioxene, homopolymers of the unsaturated ethers. In the presence of AIBN at 80°, alternating copolymers were obtained in addition to the homopolymers and the cycloaddition products, supporting the involvement of donor–acceptor complexes.

Studies of the polymerization of electron-donating vinyl monomers, especially *N*-vinylcarbazole[1] and vinyl ethers,[2] initiated by electron acceptors which are unable to undergo polymerization themselves, support a mechanism of initiation involving an initial donor–acceptor complex which generates a radical cation from the donor vinyl monomer and a radical anion from the acceptor molecule by a one-electron "T-class" reaction.[3] The radical ions have been implicated both in the formation of the 2 + 2 cycloaddition product and in the formation of a polymer from the donor vinyl monomer by a cationic propagation reaction. Only limited information on the reactions of electron-donating vinyl monomers with electron-accepting vinyl monomers, both of which can undergo polymerization, is available. The report[4] that mixing certain vinyl ethers with vinylidene cyanide gave homopolymers of each of these two types of monomers, and that these polymerizations were occurring by the simultaneous cationic polymerization of the vinyl ether and the anionic polymerization of the vinylidene cyanide, prompted the further investigation of this type of polymerization reaction. Vinylidene cyanide is a strong electron acceptor which homopolymerizes by anionic propagation, but polymerizes only very slowly in the presence of a radical initiator.[4,5] Alkyl vinyl ethers, dihydropyran, *p*-dioxene, and ketene diethyl acetal were chosen as the donor vinyl monomers to be used in this study. With

Table I
Reaction of Vinylidene Cyanide (1) with Vinyl Ethers at 25°[a]

	Mole ratio			% yield[b]			
Vinyl ether	1/vinyl ether	AIBN/1 (×10^3)	Solvent	Cycloadduct	6 (η_{sp}/c)[c]	Polyether (η_{sp}/c)[d]	Copolymer (η_{sp}/c)
2				**10**			**14**
	0.36		$C_6H_5CH_3$	38	21 (1.53)		
	1.01		$C_6H_5CH_3$	23	67 (1.83)		
	0.53		CH_2Cl_2	32	67 (1.02)		
	1.01		CH_2Cl_2	24	71 (1.36)		
	0.97	27	$C_6H_5CH_3$	5	22 (0.61)		60 (0.21)
	0.34	25	C_6H_6	12	12 (0.47)		73 (0.24)
	1.01	12	C_6H_6	9	24 (0.48)		69 (0.23)
	2.83	10	C_6H_6	18	66 (0.74)		53 (0.20)
3				**11**		**7**[e]	**15**
	1.11		C_6H_6	37	54 (0.57)		<5
	0.22		$C_6H_5CH_3$	31	33 (1.34)		
	1.11		$C_6H_5CH_3$	26	58 (0.80–1.09)		
	5.56		$C_6H_5CH_3$	27	58 (0.70)		
	1.11		$CHCl_3$	22	78 (1.18)		
	0.22		CH_2Cl_2	51	33 (0.77)		
	1.11		CH_2Cl_2	25	72 (1.16)		
	0.22		CH_3CN	49	25 (0.89)		
	1.11		CH_3CN	28	83 (>2.0)		
	0.37	23	C_6H_6	24	28 (0.63)		45 (0.17)
	1.11	8	C_6H_6	11	55 (0.70)		37 (0.17)
	3.33	6	C_6H_6	17	78 (0.68)		36 (0.21)
4a				**12a**		**8a**	**16a**
	0.30		$C_6H_5CH_3$	27	52 (1.05)	84 (0.091)	
	1.2		$C_6H_5CH_3$	17	75 (1.45)	69 (0.085)	
	4.0		$C_6H_5CH_3$	33	85 (1.75)	53 (0.073)	
	0.31	7.8	$C_6H_5CH_3$	Trace	Trace	83[f]	38 (1.42)
	1.20	2.4	$C_6H_5CH_3$	Trace	60 (0.61)	80[f]	30 (1.34)
	3.85	3.0	$C_6H_5CH_3$	Trace	72 (1.20)	58[f]	42 (1.57)
4b				**12b**		**8b**	
	0.52		$C_6H_5CH_3$	13	52 (1.13)	81 (0.10)	
	1.5		$C_6H_5CH_3$	9	71 (1.02)	67 (0.11)	
	4.1		$C_6H_5CH_3$	20	86 (0.87)	43 (0.11)	
5				**13**		**9**[f]	
	0.55		$C_6H_5CH_3$	22	Trace	43	
	0.66		$C_6H_5CH_3$	31	52 (0.37)	32	
	1.82		$C_6H_5CH_3$	34	64 (0.34)	28	
	4.97		$C_6H_5CH_3$	37	67 (0.52)	Trace	
	0.52		CH_2Cl_2	27	Trace	51	
	1.66		CH_2Cl_2	42	44 (0.30)	31	
	5.52		CH_2Cl_2	47	65 (0.29)	Trace	

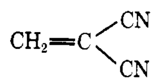
[a] The reaction time was 3 days in all cases. [b] Yields of cycloadducts and copolymers were calculated with respect to the monomer present in the smaller molar amount. [c] Reduced viscosities of **6** were taken in dimethylformamide with concentrations of 0.35 to 0.45 g/100 ml at 30°. [d] Reduced viscosities of the poly(alkyl vinyl ethers) (**8**) were taken in toluene at concentrations of 0.35 to 0.45 g/100 ml at 30°. [e] The yield of **7** was low (~ 1%) in all cases. [f] Low molecular weight methanol soluble polymer.

the exception of *p*-dioxene,[6] which does not homopolymerize, these monomers readily undergo homopolymerization by cationic catalysis, but do not polymerize in the presence of radical initiators.[7,8]

Results

Spontaneous Homopolymerization. The reactions of vinylidene cyanide (**1**) with the unsaturated ethers (**2–5**) at 25° in various solvents afforded, with the exception of *p*-dioxene, three types of products: high molecular weight poly(vinylidene cyanide) (**6**), the poly(vinyl ethers) (**7–9**), and cycloaddition products (**10–13**) (Table I). In each case, the reaction occurred without the observation of color and the poly(vinylidene cyanide) (**6**) precipitated immediately. In the case of *p*-dioxene (**2**), only the 2 + 2 cycloaddition product, 7,7-dicyano-2,5-dioxabicyclo[4.2.0]octane (**10**), and poly(vinylidene cyanide) (**6**) were produced; as expected, no polymer of *p*-dioxene (**2**) was obtained.

In general, the homopolymers of the unsaturated ethers were soluble in pentane, the cyclization products were insoluble in pentane, but soluble in toluene, and the poly(vinylidene cyanide) was soluble only in dimethylformamide. The structures of the homopolymers were assigned primarily on the basis of their elemental analyses, ^{13}C nmr spectra, and infrared spectra. Poly(ethyl vinyl ether) (**8a**) and poly(isopropyl vinyl ether) (**8b**) were assigned the head-



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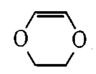

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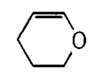

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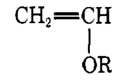
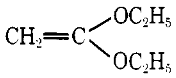


$\begin{array}{l} CH_2{=}CH \\ \quad | \\ \quad OR \end{array}$

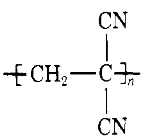
4a, R = C_2H_5

b, R = $i\text{-}C_3H_7$



$CH_2{=}C(OC_2H_5)_2$

5

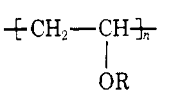


$-\!\!\!\!+CH_2-\overset{CN}{\underset{CN}{C}}+\!\!\!\!-_n$

6

$+C_5H_8O+_n$

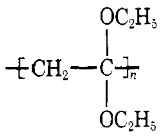
7



$-\!\!\!\!+CH_2-\underset{OR}{CH}+\!\!\!\!-_n$

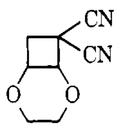
8a, R = C_2H_5

b, R = $i\text{-}C_3H_7$



$-\!\!\!\!+CH_2-\overset{OC_2H_5}{\underset{OC_2H_5}{C}}+\!\!\!\!-_n$

9



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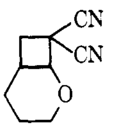

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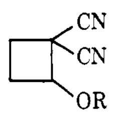
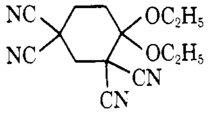


12a, R = C_2H_5

b, R = $i\text{-}C_3H_7$



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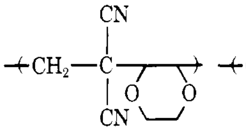

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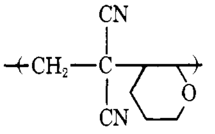

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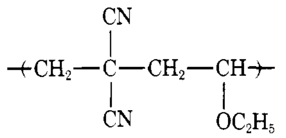


$-\!\!\!\!+CH_2-\overset{CN}{\underset{CN}{C}}-CH_2-\underset{OC_2H_5}{CH}+\!\!\!\!-$

16

to-tail structure from the agreement between the calculated and observed ^{13}C nmr chemical shifts (Table II). The infrared spectrum of poly(dihydropyran) (**7**) was superimposable with that of an authentic sample[8] obtained by a cationic polymerization. The appearance of the 5.8 μ carbonyl absorption indicated that both ring-opening polymerization and vinyl polymerization had occurred. Poly(ketene diethyl acetal) (**9**) was obtained as a methanol-soluble oligomer which had an infrared spectrum identical to that of an authentic sample.

Elemental analysis showed that the 7,7-dicyano-2,5-dioxabicyclo[4.2.0]octane (**10**) contained the 1:1 composition of vinylidene cyanide to *p*-dioxene, and the mass spectrum of the cycloadduct showed a parent peak at *m/e* 164. Both the ^1H nmr and the ^{13}C nmr were consistent with the assigned structure (Table II). The cycloadduct, 8,8-dicyano-2-oxobicyclo[4.2.0]octane (**11**) had the correct elemental analysis and the mass spectrum showed a small parent peak at *m/e* 162. The ^{13}C nmr chemical shifts of the cycloadduct (Table II) were in agreement with the calculated values, and an off-resonance decoupling study of the ^{13}C nmr spectrum of the cycloadduct showed a spin–spin splitting pattern which was consistent with the assigned structure. The ^1H nmr chemical shifts provided further support for the proposed structure. The chemical shift of H_a (δ 4.62) was similar to that of the corresponding methine proton (C_1–H, δ 4.98) of 7,7,8,8-tetracyano-2-oxabicyclo[4.2.0]octane, but the resonance of H_e (δ 2.86) was upfield from that of the corresponding methine proton (C_6–H, δ 3.78) of 7,7,8,8-tetracyano-2-oxabicyclo[4.2.0]octane. The assignment of the H_e resonance was confirmed by the fact that irradiation of the multiplet at δ 2.86 ppm caused the collapse of the H_a signal into a broad singlet.

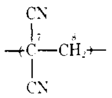
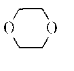
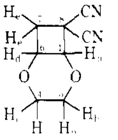
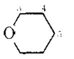
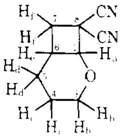
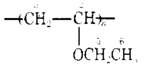
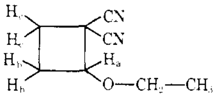
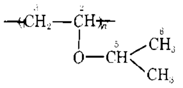
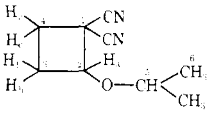
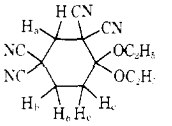
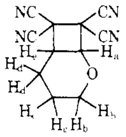
The structure of 1,1-dicyano-2-ethoxycyclobutane (**12a**) was assigned on the basis of its elemental analysis, mass spectrum (*m/e* 150 (M^+)), and ^1H nmr spectrum (Table II). The upfield resonance of H_b (δ 2.45) in comparison with that of the methylene proton (C_4–H, δ 3.20) of 1,1,2,2-tetracyano-3-ethoxycyclobutane[2] was in agreement with the head-to-head structure. The structure 1,1-dicyano-2-isopropoxycyclobutane (**12b**) was also assigned based on the elemental analysis, mass spectrum (*m/e* 164 (M^+)), ^{13}C nmr spectrum (Table II), and ^1H nmr spectrum. The chemical shift of each proton of 1,1-dicyano-2-isopropoxycyclobutane was similar to that of the corresponding proton in 1,1-dicyano-2-ethoxycyclobutane. The proximity of the asymmetric center C2 renders the two methyl groups diastereotopic and therefore magnetically nonequivalent. This nonequivalence manifests itself in two distinctly discernible absorptions (δ 1.28 and 1.20) in the ^1H nmr spectrum. 1,1-Diethoxy-2,2,4,4-tetracyanocyclohexane (**13**) was identified by its elemental analysis (2 to 1 stoichiometry of vinylidene cyanide and ketene diethyl acetal), mass spectrum (parent ion at *m/e* 272), and ^1H nmr spectrum (Table II). The broad singlet resonance at δ 2.29 ppm was resolved into a AA′BB′ multiplet, when the spectrum of the cycloadduct was taken in deuterated acetonitrile solution.

Several features of these reactions are 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. Poly(vinylidene cyanide) did not initiate the polymerization of the unsaturated ethers and conversely none of the poly(unsaturated ethers) initiated the polymerization of vinylidene cyanide under the reaction conditions. In addition, neither the homopolymerization of vinylidene cyanide nor that of the unsaturated ethers could be initiated by the respective cycloaddition products. It had been reported previously[4] that the addition of trihydroxyethylamine or phosphorous pentoxide to the vinylidene cyanide–vinyl ether mixtures inhibited the polymerizations of the vinyl ethers and vinylidene cyanide, respectively.

Radical Influenced Polymerization. The reaction of vinylidene cyanide (**1**) with the unsaturated ethers *p*-dioxene (**2**), dihydropyran (**3**), and ethyl vinyl ether (**4a**), in the presence of a free radical initiator, AIBN, at 80° produced 1:1 alternating copolymers in addition to those products which were obtained on mixing **1** with the unsaturated ethers in the absence of a free radical initiator (Table I). Contrary to a previous report,[4] the rapid ionic polymerization of these pairs in each other's presence did not preclude the possibility of free radical initiation, and the copolymer was formed in preference to the homopolymers and the cycloadducts. Each copolymer was characterized by solubility behavior, the conditions of the copolymerization reactions which produced the copolymer, elemental analysis, and the ^{13}C nmr spectrum. Copolymers **14–16a** were insoluble in toluene but soluble in acetonitrile. The homopolymers of the vinyl ethers were soluble in petroleum ether and toluene, while poly(vinylidene cyanide) was insoluble in any of the aforementioned solvents, but was soluble in dimethylformamide. The composition of the copolymers showed a 1:1 ratio of unsaturated ether to vinylidene cyanide regardless of the monomer feed ratio (Table V).

The microstructures of the copolymers were examined by the ^{13}C nmr spectra (Table III) and compared with the ^{13}C spectra of the corresponding homopolymers and cycloadducts (Table II). The assignment of each of the ab-

Table II
Nmr Spectra Cycloadducts and Homopolymers

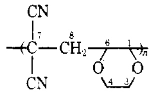
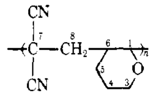
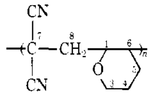
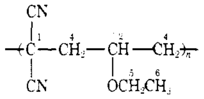
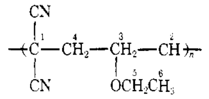
Compd	^1H chemical shifts (solvent)	$^{13}C^a$ chemical shift; obsd (calcd)^b Solvent	C1	C2	C3	C4	C5	C6	C7	C8	CN
		DMSO-d_6							30.2 (28.2)	66.0 (50.3)	113.6
		DMSO-d_6			66.9 (67.9)						
	(CD_3CN) 4.61 (d, 1, J = 4 Hz, H_a) 4.40 (m, 2, H_d + H_b) 3.73 (m, 3, H_b + $2H_c$) 2.53 (m, 2, $2H_e$)	$CDCl_3$	74.3 (85.2)		62.7 (67.1)^c	62.3 (67.1)^c		70.4 (66.8)	34.4 (37.7)	30.8 (27.7)	114.8 114.3
		DMSO-d_6			68.4 (67.7)	27.0 (29.4)	23.8 (27.5)				
	($CDCl_3$) 4.62 (m, 1, H_a) 4.18 & 3.54 (m, 2, $2H_b$) 2.86 (m, 3, H_e + H_f) 1.80 (m, 4, $2H_d$ + $2H_c$)	$CDCl_3$	75.9 (86.1)		64.9 (67.9)	22.7 (27.2)	31.3 (30.5)	24.5 (26.3)	34.1 (38.5)	30.5 (29.4)	115.2 115.6
		Off-resonance decoupling^d	d		t	t	t	d	t	s	
		$CDCl_3$		73.1 (71.4)	40.5 (38.4)		64.2 (60.3)	15.2 (13.4)			
	($CDCl_3$) 4.40 (m, 1, H_a) 3.70 (m, 2, $-OCH_2-$) 2.45 (m, 4, $2H_b$ + $2H_c$) 1.35 (t, 3, J = 7 Hz, CH_3)										
		$CDCl_3$		71.3 (71.4)	42.6 (38.4)		68.8 (68.5)	23.1 (21.6)			
	($CDCl_3$) 4.42 (m, 1, H_a) 3.81 (m, 1, OCH<) 2.39 (m, 4, $2H_b$ + $2H_c$) 1.28 (d, 3, J = 6 Hz, CH_3) 1.20 (d, 3, (J = 6 Hz, CH_3)	$CDCl_3$	28.9 (28.4)	77.6 (83.6)	25.0 (19.4)	35.2 (32.3)	73.0 (68.5)	21.6 (21.6)			115.2
	($CDCl_3$) 3.79 (m, 4, 2($-OCH_2-$)) 2.82 (s, 2, $2H_a$) 2.29 (s, 4, $2H_b$ + $2H_c$) 1.30 (t, 6, J = 7 Hz, 2(CH_3))										
	(CD_3COCD_3) 4.98 (d, 1, J = 6 Hz, H_a) 4.17 (m, 1, H_b) 3.78 (m, 2, H_b + H_e) 2.25 (m, 4, $2H_c$ + $2H_d$)										

[a] Taken on a Brucker HX-90E pulsed Fourier transform spectrometer. [b] For method of calculation, see ref 9. [c] The calculation model for C5 and C6 was $ROCH_2CH_2OR$; thus the calculated values are equal. [d] s = singlet, d = doublet, t = triplet.

sorptions was made on the basis of the calculated chemical shifts. The chemical shift of the methylene carbon (C8) of the copolymer of *p*-dioxene and vinylidene cyanide (**14**) was different than that of poly(vinylidene cyanide), thus verifying the absence of blocks of vinylidene cyanide. The absence of broad peaks and a multiplicity of absorptions other than those expected for one kind of copolymer, as well as good agreements between the observed chemical shifts for copolymer **14**, the cycloadduct **10**, and the calculated shifts, support the alternating structure.

The absence of a methylene peak at 66.02 ppm, characteristic of poly(vinylidene cyanide) (**6**) in the 1:1 copolymer of dihydropyran and vinylidene cyanide, showed the absence of poly(vinylidene cyanide) blocks. The calculated spectra for both the head-to-head and head-to-tail alternating structures agree well with the observed spectrum,

Table III
^{13}C Nmr Spectra of Copolymers[a]

Compd	Chemical shift; obsd (calcd)[b]								
	C1	C2	C3	C4	C5	C6	C7	C8	CN
	74.1 (85.2)		67.1 (67.1)	62.4 (67.1)		74.5 (66.8)	34.4 (27.7)	35.3 (37.7)	114.0
	76.3 (86.1)		67.8 (67.9)	23.0 (27.2)	33.2 (30.5)	21.3 (26.3)	34.4 (29.4)	*c* (38.5)	114.0
	76.3 (71.9)		67.8 (67.9)	23.0 (27.7)	21.3 (22.1)	*c* (40.1)	33.2 (31.1)	34.4 (39.2)	114.0
	31.8 (29.0)	73.1 (65.2)		32.0 (44.3)	65.2 (60.3)	14.3 (13.4)			115.7
	(28.4)	(32.4)	(19.4)	(83.6)	(60.3)	(13.4)			

[a] Taken on a Brucker HX-90E Fourier transform spectrometer. Solvent: DMSO-d_6. [b] For calculation method, see ref 9. [c] This peak may be buried under DMSO-d_6 peaks (37.2–42.0).

and no directional assignment could be made on this basis. Unfortunately, one peak was missing from either structure (head-to-head, C8, or head-to-tail, C6) and is evidently buried under the solvent peak. Since a suitable model compound for the head-to-tail structure was not available, neither of the two possible structures can be discounted. The shape and number of the absorptions preclude a sequence other than an alternating one, however. By analogy to the vinylidene cyanide–ethyl vinyl ether copolymer (**16**), however, a head-to-tail order, structure **15**, is expected.

In the ^{13}C spectrum of the copolymer of vinylidene cyanide and ethyl vinyl ether (**16**), the absence of absorbance for the methylene carbons of poly(vinylidene cyanide) (C8) and poly(ethyl vinyl ether) (C3) established the absence of blocks of either polymer. The absence in the copolymer spectrum of the calculated methylene absorption for the head-to-head structure (C3) supports the head-to-tail order. Again, the peak shape and the absence of multiple resonances other than those which could be calculated for the alternating copolymer rule out a random structure.

Thus the radical initiated mixture of *p*-dioxene (**2**) and vinylidene cyanide afforded a 1:1 copolymer (**14**) in addition to poly(vinylidene cyanide) (**6**) and cycloadduct **10.** Dihydropyran (**3**) and ethyl vinyl ether (**4a**) with vinylidene cyanide (**1**) gave, in addition to **6**, polyethers **7** (trace amounts) and **8a**, cycloadducts **11** and **12a**, and the two 1:1 alternating copolymers **15** and **16**, respectively. The copolymer was usually formed at the expense of the cycloadduct and, to some extent, the polymer formed from the monomer present in the smaller molar amount. The cycloadducts **10–12** were stable under the reaction conditions, and radical polymerization of the cycloadduct did not take place. Any ring-opening radical polymerization of the cycloadducts would be expected to give a head-to-head copolymer. The cycloadducts were not affected by anionic or cationic polymerization catalysts.

Discussion

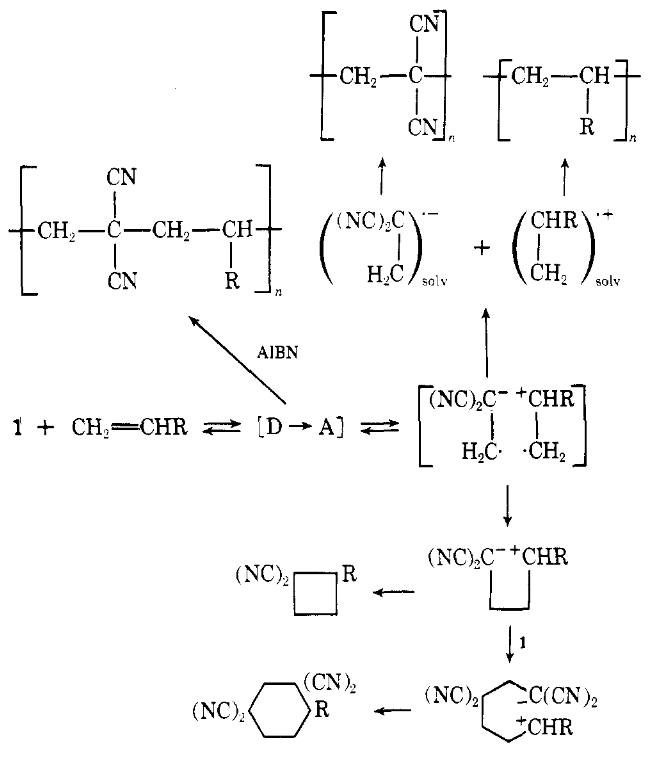
The results obtained from the study of the cycloaddition reaction of tetracyanoethylene with vinyl ethers[2] support a mechanism for this reaction which involves the sequential formation of a donor–acceptor complex, a radical-cation–radical-anion pair, and a zwitterion.[2,10–12] The transient color of the donor–acceptor complex is observed, yet in this reaction no polymerization of the vinyl ethers takes place. The absence of color when vinylidene cyanide is the acceptor molecule does not necessarily imply the absence of a donor–acceptor complex, since the complex could be present in low concentrations as a result of large differences in the relative rates of formation and disappearance of the complex. The observations that vinylidene cyanide and the unsaturated ether donor monomers afforded alternating head-to-tail copolymers in the presence of free radical initiators with the simultaneous formation of the cycloaddition products and homopolymers support the presence of the donor–acceptor complex. In all of these polymerizations, the precipitation of poly(vinylidene cyanide) was immediate, obscuring careful visual observation, and precluding uv studies. The inhibitory effects of trihydroxyethylamine and phosphorous pentoxide on the vinyl ether–vinylidene cyanide polymerization mixtures demonstrate that the poly(vinyl ethers) are a result of cationic polymerization while the poly(vinylidene cyanide) is a result of anionic polymerization.[4]

Two types of spontaneous polymerization can be observed as a result of donor–acceptor complex formation involving vinyl monomers: (1) the homopolymerization of the donor monomer by a cationic propagation and/or the homopolymerization of the acceptor monomer by an anionic propagation; (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 but do not spontaneously homopolymerize may form an alternating copolymer by a radical initiated propagation reaction. Which one of these types of polymerization reactions occurs has been postulated[13] to depend on the strength of the complex as measured by the equilibrium constant K_{eq} for the formation of the complex. When

$$\mathrm{D} + \mathrm{A} \overset{K_{eq}}{\rightleftarrows} [\mathrm{D}\rightarrow\mathrm{A}] \rightleftarrows [\mathrm{D}\cdot^{+}, \mathrm{A}\cdot^{-}] \rightleftarrows \mathrm{D}\cdot^{+}(\mathrm{solv}) + \mathrm{A}\cdot^{-}(\mathrm{solv})$$

$K_{eq} \simeq$ 1–5, spontaneous homopolymerization is observed; when $K_{eq} \simeq$ 0.1, spontaneous alternating copolymerization takes place. Estimated equilibrium constants for these complexes can be obtained from the ionization potentials of the donor vinyl monomers and a calculated electron affinity for vinylidene cyanide. A correlation of the equilibrium constants between chloranil and a series of donors[14] with the difference in the electron affinity of chloranil[15] and the ionization potential of the donors show generally a linear relationship. Although the electron affinity of vinylidene cyanide is not available, the observation[16] that a cyano group attached to a conjugated chain of an sp^2 hybridized carbon raises the electron affinity of the system by 12.7 kcal/mol allows the calculation of the electron affinity of vinylidene cyanide. Since the electron affinity of tetracyanoethylene is 2.89 eV, the electron affinity of vinylidene cyanide can be approximated to be 1.78 eV. The ionization potentials of styrene (9.00 eV)[16], dihydropyran (8.54 eV),[17] and ethyl vinyl ether (8.80 eV)[18] are known. It is reasonable to assume that the ionization potentials of ketene diethyl acetal and *p*-dioxene are smaller than those of ethyl vinyl ether or dihydropyran. From the difference between the ionization potentials of the donors and the estimated electron affinity of vinylidene cyanide, a K_{eq} of greater than 0.3 can be estimated for ethyl vinyl ether and vinylidene cyanide. The K_{eq} estimated for styrene and vinylidene cyanide is, however, less than 0.1. Styrene spontaneously gives an alternating copolymer with vinylidene cyanide, while the unsaturated ethers spontaneously polymerize to give homopolymers.

A polymerization mechanism involving donor–acceptor complexes which satisfactorily accounts for the cycloadduct and alternating copolymer in the presence of a radical initiator does not satisfactorily explain the details of the ionic homopolymerization, however. The fact that both cationic and anionic propagation reactions take place in the same reaction vessel, whether they take place simultaneously or not, is quite astounding.



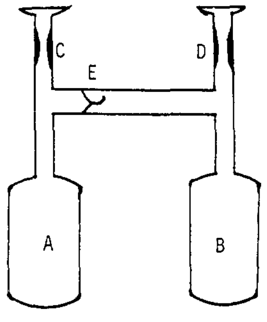
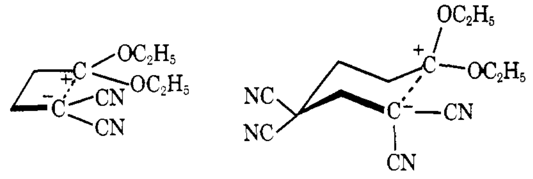


Figure 1. Reaction vessel.



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. When the vinyl ether is ketene diethyl acetal, for example, severe eclipsing takes place in the formation of the cyclobutane ring, whereas, this can be relieved in cyclohexane formation. This same behavior, the formation of the cyclohexane derivative, has been observed in the reaction of *N,N*-dimethylisobutenylamine with diethyl methylenemalonate[18] and in the reaction of styrene with vinylidene cyanide.[19]

Experimental Section

Materials. Vinylidene cyanide was prepared by the thermal decomposition of 1,1,3,3-tetracyanopropane,[4] bp 51° (10 mm) [lit[4] bp 50.5° (10 mm)], and purified by distillation and stored over phosphorus pentoxide. Ketene diethyl acetal was prepared by the dehydrobromination of 1-bromo-2,2-diethoxyethane,[20] bp 62° (30 mm). The product thus obtained was purified by spinning band distillation and stored under reduced pressure in an ampoule coated with a sodium mirror. Vinyl ethers were washed with water, dried over potassium hydride, distilled over metallic sodium, and stored inside an ampoule coated with metallic sodium after removing air by several freeze–thaw cycles under reduced pressure. Toluene and benzene were purified and dried by conventional methods and distilled from sodium metal; the center cut was stored in an ampoule coated with a sodium mirror under reduced pressure. Acetonitrile and dichloromethane were distilled from phosphorus pentoxide and stored over calcium hydride inside an ampoule after the removal of air by several freeze–thaw cycles under reduced pressure. 2,2′-Azobis(2-methyl propionitrile) (AIBN) was recrystallized from methanol and dried *in vacuo.*

General Procedure for the Reactions in the Absence of AIBN. Polymerization reactions were carried out under reduced pressure inside the Pyrex reaction vessel (Figure 1). Each of the purified monomers and solvents was transferred on a vacuum line by trap-to-trap distillation into the appropriate ampoule cooled in liquid nitrogen, and each ampoule was sealed under reduced pressure. The solutions were warmed to 25° and mixed inside one ampoule through the breakable seal E. After 3 days, the solvent was transferred to the empty ampoule which had been cooled with liquid nitrogen. The reaction vessel was then opened and the solid residue was fractionated into a petroleum ether soluble fraction, a toluene soluble fraction, and an insoluble solid. Ir spectra, elemental analyses, and nmr spectra of these fractions showed that the insoluble fraction was poly(vinylidene cyanide), the toluene soluble fraction was the cycloadduct of the vinylidene cyanide and unsaturated ether, and the petroleum ether soluble fraction was the poly(unsaturated ether) (Table II).

For the reactions of vinylidene cyanide and ethyl vinyl ether or isopropyl vinyl ether, both the cycloadducts and poly(vinyl ethers) were petroleum ether soluble. The cycloadducts were separated from poly(vinyl ethers) by distillation under reduced pressure.

The solution viscosities of the polymers were determined at 30°

Table IV
Analyses of Homopolymers and Cycloadducts

Compd	Elemental analysis						Mass spectrum, *m/e* (M⁺)
	Anal. Calcd			Found			
	C	H	N	C	H	N	
Poly(vinylidene cyanide) (6)	61.53	2.59	35.89	61.93	2.89	33.44	
Poly(dihydropyran) (7)	71.39	9.58		70.83	9.60	2.06	
Poly(ethyl vinyl ether) (8a)	66.63	11.18		66.24	11.08	1.63	
Poly(isopropyl vinyl ether) (8b)	69.72	11.70		69.14	11.81	2.55	
Poly(ketene diethyl acetal) (9)	62.04	10.42		61.83	9.47	5.23	
7,7-Dicyano-2,5-dioxabicyclo[4.2.0]octane (10)	58.53	4.91	17.07	58.63	4.96	17.23	164
8,8-Dicyano-2-oxabicyclo[4.2.0]octane (11)	66.64	6.21	17.28	66.77	6.27	17.09	162
1,1-Dicyano-2-ethoxycyclobutane (12a)	64.00	6.71	18.67	64.25	6.60	18.52	150
1,1-Dicyano-2-isopropylcyclobutane (12b)	65.82	7.37	17.06	65.92	7.35	17.26	164
1,1,4,4-Tetracyano-2,2-diethoxycyclohexane (13)	61.75	5.98	20.85	61.86	6.01	21.01	272

Table V
Elemental Analyses of Alternating Copolymers of Vinylidene Cyanide (1) and Vinyl Ethers

Vinyl ether	Molar ratio of 1:vinyl ether	*Anal.* Calcd			Found		
		C	H	N	C	H	N
p-Dioxene (2)	0.34	58.53	4.91	17.07	58.46	5.32	17.16
	0.36				58.62	5.16	16.81
	0.91				58.31	5.19	17.37
	1.01				58.76	5.43	16.79
	1.01				58.92	5.06	17.24
	2.83				58.23	4.76	17.19
Dihydropyran (3)	0.37	66.64	6.21	17.28	67.03	6.28	17.60
	1.11				66.00	6.68	17.63
	1.11				66.72	6.50	17.36
	3.33				66.30	6.57	17.62
Ethyl vinyl ether (4a)	0.31	64.00	6.71	18.67	63.92	6.62	18.74
	0.91				63.74	6.52	18.32
	1.20				64.16	6.71	18.76
	3.85				64.12	6.53	18.39

in toluene for the poly(vinyl ethers), and in dimethylformamide for poly(vinylidene cyanide).

The following procedure is illustrative. Into ampoule A, 2.4 g (2.5 ml, 28.5 mmol) of dihydropyran and 20 ml of degassed toluene were transferred by trap-to-trap distillation and the ampoule was sealed at constriction C under reduced pressure. Vinylidene cyanide (0.49 g, 0.5 ml, 6.3 mmol) and 15 ml of degassed toluene were distilled into ampoule B which was then sealed at constriction D under reduced pressure. The reaction solutions were warmed up to room temperature and mixed inside one ampoule through the breakable seal E. After 3 days, the solvent was transferred to the empty ampoule which had been cooled in liquid nitrogen. The ampoules were then opened. The residue was fractionated into three fractions by successive extractions with petroleum ether (60–70°) and toluene. The toluene insoluble fraction was identified as poly(vinylidene cyanide) (0.16 g) by ir comparison with an authentic sample.

Evaporation of solvent from the toluene soluble fraction yielded 0.31 g of 8,8-dicyano-2-oxabicyclo[4.2.0]octane: ^1H nmr ($CDCl_3$), see Table II.

Solvent removal from the petroleum ether soluble fraction gave 0.04 g of poly(dihydropyran). The compound had an ir spectrum identical to that of an authentic sample. See Table IV for analytical data.

***General Procedure for the Reactions in the Presence of* AIBN.** Polymerization reactions were carried out under reduced pressure in the Pyrex reaction vessel (Figure 1). 2,2′-Azobis(2-methyl propionitrile) was used as the radical initiator in all cases. Vinylidene cyanide and the solvent were transferred by trap-to-trap distillation into one of the ampoules which was sealed under reduced pressure. The unsaturated ether and the solvent were transferred into the other ampoule of the reaction vessel containing 2,2′-azobis(2-methyl propionitrile) and the ampoule was sealed under reduced pressure. The reaction solutions were allowed to mix inside one ampoule through the breakable seal E, and the mixture was heated to 80° immediately. After 3 days, the mixture was allowed to cool to room temperature. The solvent was transferred to the empty ampoule which had been cooled with liquid nitrogen. The ampoules were then opened. The residue was fractionated into four fractions by successive extractions with petroleum ether, toluene, and acetonitrile. Elemental analyses, ir spectra, and nmr spectra showed that the petroleum ether soluble fraction was predominately the poly(unsaturated ether), the toluene soluble fraction was the cycloadduct, the acetonitrile soluble fraction was the copolymer, and the insoluble fraction was essentially poly(vinylidene cyanide).

For the reaction of vinylidene cyanide and ethyl vinyl ether, both the cycloadduct and the poly(ethyl vinyl ether) were soluble in petroleum ether. The cycloadduct was separated from poly(ethyl vinyl ether) by distillation under reduced pressure.

The following procedure is illustrative. Dihydropyran (1.44 g, 1.5 ml, 17.9 mmol) and 15 ml of degassed benzene were distilled into ampoule A, which contained 24 mg (1.5×10^{-2} mmol) of 2,2′-azobis(2-methyl propionitrile), by trap-to-trap distillation and the ampoule was sealed at constriction C under reduced pressure. Similarly into ampoule B, 0.49 g (0.5 ml, 6.3 mmol) of vinylidene cyanide and 20 ml of degassed benzene were transferred and the ampoule was sealed at constriction D under reduced pressure. The solutions were warmed to room temperature and mixed inside one ampoule through the breakable seal E, then heated to 80° immediately. After 3 days, the solvent was transferred to the empty ampoule which had been cooled in liquid nitrogen. The ampoules were then opened. The residue was fractionated into four fractions by successive extractions with petroleum ether (bp 60–70°), toluene, and acetonitrile. The acetonitrile insoluble fraction (0.14 g) was identified as poly(vinylidene cyanide) by comparison of its ir spectrum with that of an authentic sample. The acetonitrile soluble fraction (0.68 g) was identified as a 1 to 1 alternating copolymer of dihydropyran and vinylidene cyanide (Table V). The toluene soluble fraction (0.25 g) was identified as 8,8-dicyano-2-oxobicyclo[4.2.0]octane, ^{1}H nmr, $CDCl_3$, see Table II. The petroleum ether soluble fraction (0.03 g) was identified as poly(dihydropyran) by comparison of its ir spectrum with that of an authentic sample.

Preparation of 7,7,8,8-Tetracyano-2-oxabicyclo[4.2.0]octane. A solution of 0.96 g (1.0 ml, 11.4 mmol) of dihydropyran in 3 ml of tetrahydrofuran was added to a solution of 0.65 g (5.1 mmol) of tetracyanoethylene in 20 ml of tetrahydrofuran. A red color developed immediately. After 6 hr, the color faded and the solvent was removed under reduced pressure. The white solid residue was washed with ether and recrystallized from acetonitrile–dichloromethane to yield 1 g (92%) of 7,7,8,8-tetracyano-2-oxobicyclo[4.2.0]octane: mp 169–170° (lit.[18] 173–176°); ^{1}H nmr data are reported in Table II. *Anal.* Calcd for $C_{11}H_8N_4O$: C, 62.26; H, 3.80; N, 26.40. Found: C, 62.12; H, 3.48; N, 26.42.

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References and Notes

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Poly(amine esters) Derived from Diethyl 1,4-Cyclohexanedione-2,5-dicarboxylate

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ABSTRACT: The reaction of diethyl 1,4-cyclohexanedione-2,5-dicarboxylate (SSE) with benzylamine was studied, and the product was fully characterized as diethyl 2,5-bis(benzylamino-3,6-dihydroterephthalate). This material was oxidized to the aromatic derivative under different conditions. The polycondensation of the title compound and several benzylic diamines to produce poly(aminodihydroterephthalates), and their subsequent oxidation, was investigated. The solubilities and thermal and spectroscopic properties of the polymers were studied.

The reaction between 1,4-cyclohexanedione-2,5-dicarboxylate (I) and amines to give diethyl 2,5-diamino-1,4-dihydroterephthalates was first reported by Baeyer,[1] in 1886, when he synthesized diethyl 2,5-diamino-1,4-dihydroterephthalate. In 1914, Liebermann[2] synthesized a number of N-substituted diaminodihydroterephthalates. This reaction has subsequently been applied to polymer synthesis. In 1968, Kimura[3] first synthesized aromatic poly(aminodihydroterephthalates) using I and *m*-phenylenediamine or 4,4′-diaminodiphenyl ether. These polymers were used as precursors for polyquinolones. Higashi, *et al.*,[4] later reacted I with aliphatic diamines to obtain polymers which formed tough films of higher molecular weight than those reported by Kimura.

Diethyl 1,4-cyclohexanedione-2,5-dicarboxylate and its tautomer, diethyl 2,5-dihydroxy-3,6-dihydroterephthalate, have four electrophilic sites, the two ethyl carboxylate carbons, and the two enol α carbons. Under mild reaction conditions, *e.g.*, 120°, in a polar solvent, reaction takes place exclusively at the enol sites.

Higashi, *et al.*,[4] have shown that the reaction between I and amines occurs in steps (Figure 1).

At room temperature, an unstable ammonium salt (II) is formed. Between 50 and 70°, the monoaminodihydroterephthalate ammonium salt, III, is formed. At temperatures greater than 100° II or III is converted to the diaminodihydroterephthalate, IV.

Oxidation of IV to the aromatic moiety, V, is easily accomplished with reagents such as pentachloronitrobenzene in potassium hydroxide,[5] chloranil,[6] air in glacial acetic acid,[2] and iodine dispersed in an organic solvent.[7]

When R (IV, V) is aryl, conversion to linear *trans*-quinacridones (VI, VII) is readily achieved. This transformation can be accomplished with aluminum chloride in trichlorobenzene,[8] polyphosphoric acid,[9] and phosphorous oxychloride in nitrobenzene,[10] at elevated temperatures. This conversion can also be effected thermally in a high boiling inert solvent such as Dowtherm A[11] (biphenyl–biphenyloxide, 23.5:76.5) (the Conrad–Limpach reaction).

It was hoped that the introduction of the benzylic group in the polymer chain would increase the flexibility of the system, enhancing solubility in organic solvents, and lead to high molecular weight aromatic polyamines. Furthermore, introduction of the benzylic group might inhibit cyclization (to produce a seven-membered ring) and result in a cross-linked network, formed by intermolecular acyla-