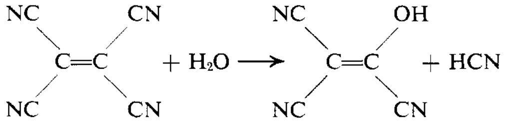
TABLE II
EFFECT OF WATER ON THE POLYEMRIZATION OF ISOPROPYL VINYL ETHER WITH HIGHLY PURIFIED TCNE IN ACETONITRILE[a,b]

$[H_2O]/[TCNE]$	Aging time, hr	Induction period, min	Yield, %	η_{sp}/C^c
1/1	0		0	
1/1	4.5		0	
1/1	24	60	26.8	0.06
1/2	24	30	30.8	0.13
2/1	24		0	

[a] Conditions were the same as those described in Table I. [b] The aging solutions were degassed before polymerization to remove the HCN produced. [c] See corresponding footnote, Table I.

transfer reaction would be long-lived enough to continue the polymerization after 30 min. Highly purified TCNE showed the transient color characteristic of the charge-transfer complex, but did not effect polymerization.

Highly purified TCNE could be converted to an active catalyst by addition of water to its acetonitrile solution (Table II). Equal molar or less than equimolar amounts of water reacted with TCNE for 24 hr provided a polymerization catalyst. Unreacted water inhibits polymerization at higher water concentrations. TCNE is known[8] 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 TCNE and water in acetonitrile. Therefore it



appears that the true catalyst in polymerizations involving incompletely purified TCNE is tricyanoethenol. A prepared sample of tricyanoethenol[9] was found to initiate the polymerization of isobutyl vinyl ether. The charge-transfer complex evidently does not play a part in the polymerization reaction by generating a cationic species, but is responsible only for cyclobutane formation.

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Polymerization of Alkyl Vinyl Ethers Catalyzed by Tetracyanoquinodimethan

In the preceding publication,[1] the role of acidic impurities in the acceptor molecule in the polymerization reactions of donor alkyl vinyl ether monomers was described. From this study, it was clear that even though an acceptor molecule forms a charge-transfer complex with a donor monomer, this complex need not be responsible ultimately for producing a cationic species which initiates the polymerization. Although tetracyanoethylene (TCNE) undergoes a 2 + 2 cycloaddition reaction with vinyl ethers,[2] presumably through a charge-transfer intermediate, tetracyanoquinodimethan (TCNQ) generally undergoes 1,6 addition. For example, TCNE gives 2 + 2 and 2 + 4 cycloaddition reactions with conjugated dienes[3] but TCNQ gives polymeric products with cyclopentadiene and 2,3-dimethylbutadiene[4] in which a 1,6 addition across TCNQ has taken place. For this reason, the reaction of TCNQ with vinyl ethers would not be expected to form a cycloadduct, and its role in a reaction with a donor vinyl monomer would be expected to provide cationic initiation for the donor vinyl monomer *via* a charge-transfer complex. TCNQ has been shown to initiate the polymerization of N-vinylcarbazole[5] and ketene diethyl acetal.[6]

TCNQ, purified by various methods, was employed in catalytic amounts as an initiator for the polymerization of *n*-butyl vinyl ether in acetonitrile. In every case the polymer yields and molecular weights were the same (Table I). The polymerization of a series of alkyl vinyl ethers initiated by TCNQ was also attempted in a variety of solvents. Polymerization took place

TABLE I
POLYMERIZATION OF *n*-BUTYL VINYL ETHER CATALYZED BY TCNQ IN ACETONITRILE[a]

TCNQ[b]	Induction period, min	Polymer yield, %	η_{sp}/C^c
A	90	19.5	0.12
B	25	22.4	0.15
C	70	17.1	0.12
D	40	21.1	0.17
E	80	18.7	0.11

[a] Conditions: $[BVE] = 2.0\ M$, $[TCNQ] = 5 \times 10^{-3}\ M$ at 25° for 20 hr. Polymerizations were carried out in sealed ampoules from a vacuum line. [b] A, recrystallized from ethyl acetate, mp 298–302°; B, recrystallized from ethyl acetate, mp 302–304°; C, chromatographed with ethyl acetate on calcium carbonate, mp 300–301°; E, recrystallized from ethyl acetate with active carbon, mp 299–301°; E, D was mixed with active carbon and sublimed under reduced pressure, mp 298–301°. [c] Determined in benzene at 30° ($C = 0.5$ g/dl).

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TABLE II
POLYMERIZATION OF ALKYL VINYL ETHERS CATALYZED BY TCNQ[a]

$ROCH{=}CH_2$ R	Solvent	Polymer yield, %	η_{sp}/C[c]
C_2H_5	CH_3CN	22.2	0.19
	CH_3NO_2	35.6	0.24
i-C_3H_7	CH_3CN	69.5	0.05
	CH_3NO_2	90.0	0.07
n-C_4H_9	CH_3CN	23.1	0.13
	CH_3NO_2	20.1	0.13
i-C_4H_9	CH_3CN	32.1[b]	0.28
	CH_3NO_2	23.6[b]	0.19
t-C_4H_9	CH_3CN	Trace	
	CH_3NO_2	11.6	0.08

[a] Conditions: $[ROCH{=}CH_2] = 2.0\ M$, $[TCNQ] = 5 \times 10^{-3}\ M$ at 25°, 20 hr. [b] The ir spectrum of this polymer did not reveal maxima characteristic of CN, and indicated that the structure was amorphous [see K. Iwasaki, *J. Polym. Sci.*, **56**, 27 (1962)]. [c] See corresponding footnote, Table I.

in the polar solvents acetonitrile and nitromethane (Table II), but did not take place in ethylene dichloride or toluene. Acetonitrile or nitromethane alone were not initiators for the polymerization, although it has been shown[7] that nitromethane initiates the polymerization of N-vinylcarbazole at higher temperatures. These results are in agreement with the observations that a "T-class" reaction,[8] in which a complete one electron transfer from donor to acceptor takes place thermally, is promoted by polar solvents. In general, the rate of cationic polymerization is increased by solvents with high dielectric constants.[9] Irradiation of the polymerization by ultraviolet light not only retarded the polymerization but also lowered the molecular weight of the polymer.

In these polymerizations (Table II) the initial yellow color produced on mixing the reagents slowly changed to yellow-green and ultimately faded, except in the case of t-butyl vinyl ether. In this case, the precipitation of the polymer and the appearance of a green color were observed almost immediately after mixing the reagents, and the polymerization was complete in a few minutes. From the induction periods of the polymerizations in acetonitrile, the relative reactivities of the alkyl vinyl ethers were n-butyl (1–2 hr) < isopropyl (10 min) < t-butyl (<1 min). This order is that which would be expected from a consideration of the electron-donating ability of the alkyl group as observed in cationic homo-[10] and copolymerizations.[11,12] At higher temperatures the induction period decreased. Since the polymer yields did not vary with a change in temperature or longer reaction times, there appears to be a limit of conversion in these polymerizations. The fact that conversion depends on the catalyst ratio indicates that a termination reaction is deactivating the catalyst.[13]

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