2. As the size of the globule increases the rate of polymerization decreases (because the monomer must diffuse through the polymer), and the temperature of the outer surface of the globule is reduced to a point where crystallization can occur.
3. Crystallization occurs at the apex of the globule in the form of folded-chain lamellae. As more polymer is formed at the base of the globule further crystallization forms additional lamellae which are pushed out in the form of stacks of rather uniform diameter platelets. The center of each lamella will contain highly crystalline polymer, while the upper and lower surfaces will contain the amorphous polymer associated with the chain folds and chain ends. The difference in density of the two regions could account for the striations visible in the electron micrographs and illustrated in Figure 3a.

The uniformity in size of the globular base of the fibrils suggests that their size is controlled by competition between the rate of nucleation of crystallization and the rate of diffusion of monomer through the globule. Both of these processes might be expected to depend only on the dimensions of the globule. The absolute rate of growth of the fibril, which is clearly different at different locations on the catalyst surface (Figure 1), may depend on the number or activity of the catalyst sites located at the base of the fibril.

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Polymerization of Alkyl Vinyl Ethers by Tricyanoethenol in Tetracyanoethylene

Vinyl monomers containing electron-donating substituents are known to polymerize in the presence of an organic electron acceptor *via* a charge-transfer mechanism of initiation. Tetracyanoethylene (TCNE) is a strong electron acceptor[1] which has been reported to initiate the polymerization of N-vinylcarbazole[2,3] and ketene diethyl acetal.[4] TCNE also affords cyclobutane derivatives in reactions with N-vinylcarbazole[3,5] and alkyl vinyl ethers.[5]

Both the initiation of the polymerization of N-vinylcarbazole and the formation of the cyclobutane derivative have been postulated to take place through a charge-transfer complex of the N-vinylcarbazole donor with an acceptor such as TCNE[3] or acrylonitrile.[6] Both 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 solvent, impurities, etc.

When the reaction of an alkyl vinyl ether with TCNE (2:1) was carried out at 25°, the cycloaddition product was obtained. The red-orange color of the charge-transfer complex appeared immediately and, from the rate of disappearance of the color, it was observed that the rate of cyclobutane formation followed the order $C_2H_5\text{–} < (CH_3)_2CH\text{–} < t\text{-}C_4H_9\text{–}$. The reaction in a polar solvent, acetonitrile, was faster than in a nonpolar solvent, toluene.

TABLE I
POLYMERIZATION OF ISOPROPYL VINYL ETHER BY TCNE[a]

TCNE source[b]	Solvent	Polymer yield, %	η_{sp}/C^c
A	$(CH_2)_2Cl_2$	63.4	0.31
A	CH_3CN	85.1	0.10
A	CH_3NO_2	70.0	0.11
B	CH_3CN	42.2	
B	CH_3NO_2	39.7	
C	$(CH_2)_2Cl_2$	0	
C	CH_3CN	10.8	
C	CH_3NO_2	4.5	

[a] $[C_3H_7OC_2H_3] = 2.0$ mol/l., $[TCNE] = 5 \times 10^{-3}$ mol/l., 25°, 20 hr. Polymerizations were carried out in an ampoule using a vacuum line and employing carefully purified monomer and solvents. TCNE purified by three recrystallizations from chlorobenzene followed by two sublimations at 1.0 mm was colorless, mp 205–206°, and did not initiate polymerization of the monomer. [b] A, purified by one recrystallization from chlorobenzene followed by vacuum sublimation, pale yellow crystals, mp 201–203°; B, A after 3 months aging at 25° in the atmosphere; C, obtained from Aldrich Chemical Co. Inc., and used without further purification, light brown crystals, mp 197–200°. [c] Determined in benzene at 30° ($C = 0.5$ g/dl).

Highly purified TCNE would not initiate polymerization, even in polar solvents such as acetonitrile and nitromethane. However, when a catalytic amount of TCNE which was incompletely purified was added ([TCNE]/[alkyl vinyl ether] = 1:400) polymerization took place, depending on the solvent and purity of the TCNE. The polymerization of isopropyl vinyl ether, as well as *n*-butyl, isobutyl, and *t*-butyl vinyl ethers in polar solvents, was found to be initiated by incompletely purified TCNE. The results of polymerization of isopropyl vinyl ether are given in Table I.

This effect of impurities on the polymerization is similar to that found for the polymerization of N-vinylcarbazole initiated by *p*-chloranil. In this case, the initiator was found to be an acidic impurity, 3,5,6-trichloro-2-hydroxy-1,4-benzoquinone, in the chloranil.[7]

In these polymerizations, the red-orange color of the charge-transfer complex did appear immediately on mixing the TCNE and isopropyl 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 appears that the charge-transfer complex is not responsible for polymerization, since the color of the complex is not present throughout the polymerization, and it is unlikely that any cationic species formed *via* the charge-

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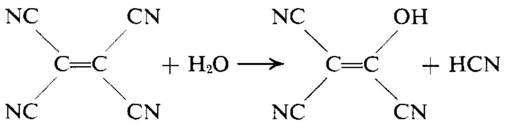
TABLE II
EFFECT OF WATER ON THE POLYEMRIZATION OF ISOPROPYL VINYL ETHER WITH HIGHLY PURIFIED TCNE IN ACETONITRILE[a,b]

$[H_2O]/[TCNE]$	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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