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# Oxonium–Carbanion Zwitterions as the Initiating Species in the Reactions of Oxacycles with Electrophilic Olefins

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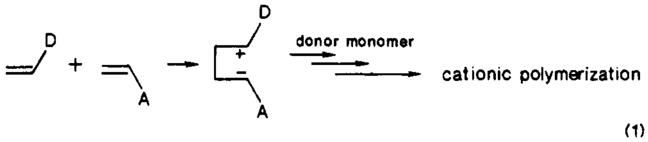
ABSTRACT: Polymerization reactions of representative oxacycle monomers with four electrophilic olefins were examined. Methyl $\beta,\beta$-dicyanoacrylate (1) and dimethyl cyanofumarate (2) slowly oligomerized cyclohexene oxide, and 1 and 2 themselves oligomerized anionically. Tetracyanoethylene (3) slowly polymerized cyclohexene oxide. It reversibly cyclotrimerized aldehydes to 1,3,5-trialkyltrioxanes and gave a cyclopolymer from glutaraldehyde. The reluctance of unsubstituted 1,3,5-trioxane to take part in these reactions was ascribed to the lesser stability of its intermediate oxacarbenium ions. Cleaner cationic initiations were observed with $\beta,\beta$-dicyanovinyl chloride, but they were still slow, and chloride ion was found to compete nucleophilically with the rather weakly nucleophilic monomers. These results delineate the requirements that must be met in the design of effective olefin initiators for cationic polymerization.

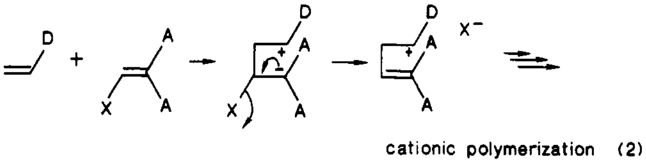
## Introduction

We have extensively investigated the reactions of nucleophilic olefins, $\pi$ donors, with electrophilic olefins. Our bond-forming initiation theory[1] implicates a tetramethylene intermediate in the observed cycloadditions and polymerizations. Strong donor and strong acceptor substituents lead to zwitterionic tetramethylenes, which can initiate the cationic homopolymerization of the donor olefin.[2]



D, donor substituent (alkoxy, *p*-methoxyphenyl, *N*-carbazolyl, etc.)
A, three or four acceptor substituents (CN or COOCH$_3$)

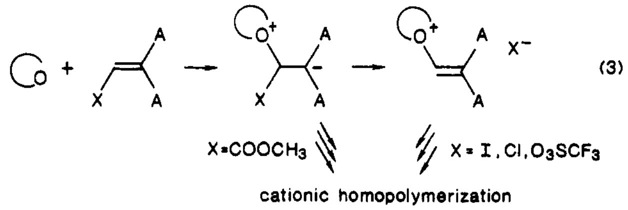
Increased initiating ability of a tetramethylene zwitterion can be achieved by a $\beta$-leaving group in the acceptor olefin. Expulsion of the leaving group from the tetramethylene zwitterion results in a more efficient carbenium ion initiator.[3,4]



X, strong leaving group (Cl, I, O$_3$SCF$_3$, etc.)

Correspondingly, if the electrophilic olefin is very susceptible to anionic polymerization, such polymerizations will be initiated by the anionic terminus of the tetramethylene zwitterion. This has been observed for nitroethylene,[5] vinylidene cyanide,[6] methyl $\alpha$-cyanoacrylate,[7] and methyl $\beta,\beta$-dicyanoacrylate.[8]

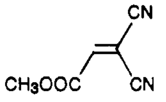
We now extend our studies from $\pi$-donor nucleophilic vinyl monomers to n-donor oxacycle monomers. We propose that in this case the initiation should again involve bond formation between the nucleophilic monomer and the electrophilic olefin



Stille and his colleagues[6] have investigated the reactions of various oxacycles with the electrophilic olefin vinylidene cyanide. Reaction of epoxides with vinylidene cyanide led to homopolymers of several of the donor components. Anionic polymerization of the vinylidene cyanide also occurred, consuming it. Trioxane polymerized vinylidene cyanide, but did not polymerize itself, while mixing dioxolane with vinylidene cyanide did not polymerize the former. These reaction mixtures often became heterogeneous because of the insolubility of poly(vinylidene cyanide).

Recently Okamoto and Zama[9] investigated the copolymerization reaction of tetracyanoethylene and tetrahydrofuran in equivalent concentration under high pressure.

We wanted to know if representative electrophilic olefins 1–4 offered advantages as initiators of these ring-opening polymerizations. This series has two compounds without



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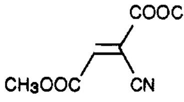

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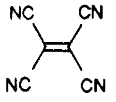

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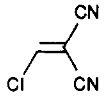

4

$\beta$-leaving groups, methyl $\beta,\beta$-dicyanoacrylate (1)[10] and dimethyl cyanofumarate (2),[11] one compound with the weak leaving group CN, tetracyanoethylene (3), and one with the strong leaving group Cl, $\beta,\beta$-dicyanovinyl chloride (4).[7]

## Results

**Methyl $\beta,\beta$-Dicyanoacrylate (1) and Dimethyl Cyanofumarate (2).** The electrophilic trisubstituted olefins 1[9] and 2[10] were studied with typical oxacyclic monomers. Reactions in general were slow.

Methyl $\beta,\beta$-dicyanoacrylate (1) is slow to react with cyclohexene oxide. At a 14:1 ratio, respectively, and 92 h at 90 °C, only 16% conversion is obtained. Even of this, only half is low molecular weight polycyclohexene oxide (MW = 3300). The remaining material is a mixture of a hexane-insoluble fraction rich in the electron-poor olefin and a hexane-soluble fraction rich in cyclohexene oxide. Similar results are obtained in solution at 82 °C for 140 h or at room temperature for 38 days. These reaction mixtures became heterogeneous.

Cyclohexene oxide with dimethyl cyanofumarate (2) in a 20:1 ratio at 90 °C in bulk resulted in the isolation of oligomer of 2 but no polymer of cyclohexene oxide.

Triethyl orthoformate, tetramethyl orthocarbonate, and trimethyl orthoformate, used as model acyclic alkoxy-containing molecules, were reacted with 1 (Table I). In

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**Table I**
**Reactions of Orthoesters with Electrophilic Olefins**

| oxygen nucleophile | amt, mmol | electro-phile olefin | amt, mmol | temp, °C | time, h | product | yield, % |
|---|---|---|---|---|---|---|---|
| $HC(OC_2H_5)_3$ | 3.0 | 1 | 1.38 | 86[a] | 244 | oligomer[d] | 66.3 |
| $C(OCH_3)_4$ | 3.76 | 1 | 1.49 | 86[a] | 69 | oligomer[d] | 97.5 |
| $HC(OCH_3)_3$ | 4.57 | 1 | 1.63 | 86[a] | 244 | oligomer[d] | 12 |
| $HC(OC_2H_5)_3$ | 3.0 | 3 | 0.1 | 58[b] | 168 | $(C_2H_5O)(NC)C{=}C(CN)_2$[e,f] | 81[c] |
|  | 6 | 3 | 3.5 | 70[b] | 168 | same | 58 |
|  | 6 | 3 | 3.5 | 120[b] | 1 | same | 38 |
|  | 6 | 4 | 1.1 | 86[b] | 137 | $(C_2H_5O)HC{=}C(CN)_2$[g] | 72 |
|  | 1 | 4 | 1 | 78[c] | 21 | same | 13 |
|  | 1 | 4 | 1 | 86[c] | 374 | same | 87 |
| $HC(OCH_3)_3$ | 9.14 | 4 | 1.0 | 86[b] | 137 | $(CH_3O)HC{=}C(CN)_2$ | 91 |
|  | 1 | 4 | 1 | 86[b] | 334 | same | 50 |
| $C(OCH_3)_4$ | 7.51 | 4 | 1.03 | 86[b] | 137 | same | 86 |
|  | 1 | 4 | 1 | 86[b] | 362 | same | 57 |

[a] In bulk in air. [b] In bulk in nitrogen atmosphere. [c] In 0.5 mL of $CDCl_3$ in air. [d] Oligomeric methyl β,β-dicyanoacrylate (1) according to chemical analysis: molecular weights are about 600. [e] After elution through silica gel. [f] Reference 12. [g] References 13 and 14.

**Table II**
**Cyclotrimerization of Aliphatic Aldehydes[a]**

| aldehyde | amt, mmol | electron-poor olefin | amt, mmol | time | % yield trimer | reactn product[e] from electrophile |
|---|---|---|---|---|---|---|
| $CH_3CH_2CHO$ | 6.9 | 1 | 0.31 | 144 h | 67 | 100% oligomer |
| $CH_3CH_2CHO$ | 6.9 | 2 | 0.1 | 115 h | 24 | 100% oligomer |
| $CH_3CH_2CHO$ | 6.9 | 3 | 0.19 | 4 h | 93 |  |
| $(CH_3)_3CCHO$ | 4.6 | 3 | 0.21 | 140 h | >90[b] |  |
| $CH_3CH_2CHO$ | 6.9 | 4 | 0.12 | 7 days | 50 |  |
| $(CH_3)_3CCHO$ | 4.6 | 4 | 0.74 | 47 h | >90[b] |  |

[a] Reactions in bulk at 28 °C. [b] Crystalline.

**Table III**
**Cyclohexene Oxide with TCNE 3[a]**

| amt, mmol |  |  |  |  |  |  | chem anal. |  |  | ratio[e] CHO/ |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CHO | TCNE | temp, °C | time, h | convrsn CHO[b] | % yield polymer[c] | MW[d] | C | H | N | TCNE | calcd MW[f] |
| 2 | 2 | 56 | 116 | 50 | 50 | 8600 | 71.03 | 9.43 | 4.13 | 13 | 1300 |
| 20 | 1 | 56 | 116 | 17 | 17 | 15000 | 72.96 | 10.26 | 0.99 | 57 | 5600 |
| 1 | 1 | 90 | 21 | 54 | 69 | 3000 | 69.16 | 8.39 | 7.80 | 7 | 700 |
| 20 | 1 | 90 | 21 | 14 | 13 | 6200 |  |  |  |  |  |
| 20 | 1 | 90 | 45 | 54 | 21 | 13500 |  |  |  |  |  |
| 20 | 1 | 90 | 52 | 73 | 21 | 17000 |  |  |  |  |  |
| 20 | 1 | 90 | 69 | 50 | 26 | 11000 |  |  |  |  |  |
| 20 | 1 | 90 | 76 | 92 | 42 | 1700 |  |  |  |  |  |
| 20 | 1 | 90 | 90 | 96 | 5 | 4600 | 72.34 | 10.45 | 2.30 | 25 | 2450 |
|  |  |  |  |  | 59[g] |  | 71.82 | 9.52 | 3.84 | 14 |  |
| 10 | 0.25 | 90 | 21 | 8 | 10 | 13800 | 72.60 | 9.99 | 1.07 | 51 | 5000 |

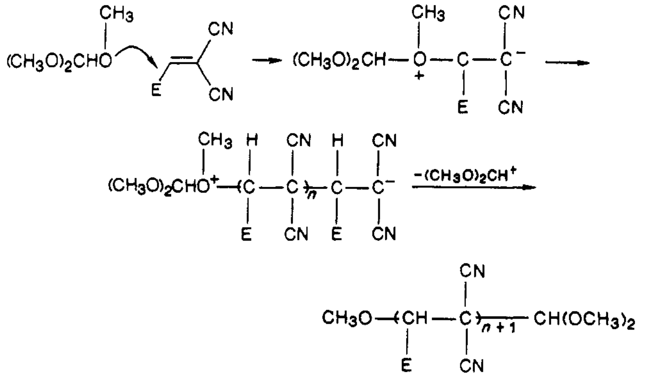
[a] Reactions run under nitrogen atmosphere in bulk. [b] Overall yield of cyclohexene oxide, excluding TCNE. [c] Percent yield of dichloromethane-soluble, methanol-insoluble polymer. [d] Molecular weight determined by SEC vs. polystyrene standards. [e] Ratio of CHO/TCNE in polymer calculated from chemical analysis. [f] Molecular weight calculated from chemical analysis. [g] Insoluble polymer.

bulk at 86 °C, these compounds caused anionic oligomerization of 1. This demonstrates reaction of neutral oxygen-containing nucleophiles with electrophilic olefin 1 leading to a zwitterion, which then initiates the anionic oligomerization (Scheme I).

Greater reactivity was found for aldehyde monomers (Table II). Bulk propionaldehyde in the presence of 1 at 28 °C for 144 h was converted to cyclic trimer in 67% yield, while 1 was completely oligomerized. Dimethyl cyanofumarate 2 gave a 24% yield of trimer in 115 h, 2 again completely oligomerizing in the process. Pivalaldehyde gave similar results, giving its trimer, 2,4,6-tri-*tert*-butyl-1,3,5-trioxane. No polyaldehydes were formed because these reactions at room temperature were carried out far above the ceiling temperature for polymerization.[15] When mixed at −50 °C, below the ceiling temperature, no polymers were formed.

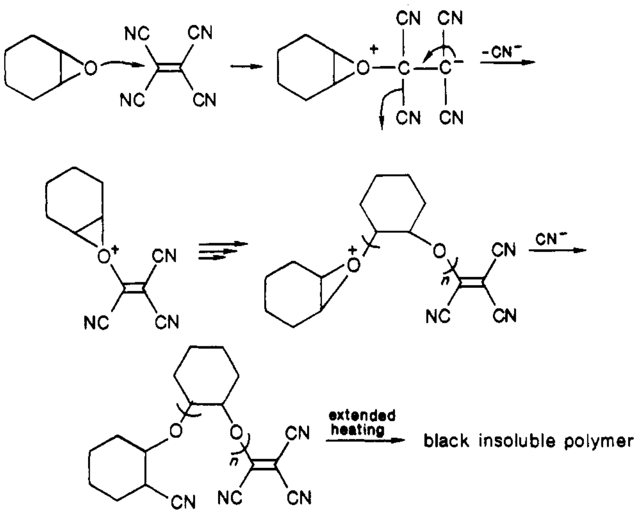
Electrophilic olefins 1 and 2, then, offer no advantages as initiators over the vinylidene cyanide studied earlier.[6]

**Scheme I**
**Oligomerization of Methyl β,β-Dicyanoacrylate (1)**

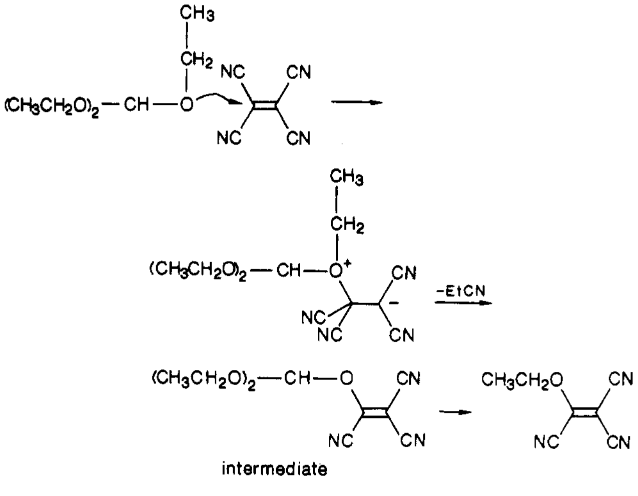


**Tetracyanoethylene (3).** Electrophilic olefin 3 functioned as a moderately reactive initiator for cyclohexene

Scheme II
Reaction of Cyclohexene Oxide with TCNE



Scheme III
Reaction of Triethyl Orthoformate with TCNE



oxide CHO (Table III), forming polymers of reasonable molecular weight. Reaction at 56 °C was rather slow, but at 90 °C modest conversions to polymer were obtained. At a 1:1 feed ratio, a 69% yield of polymer (MW 3000) formed, indicating a chain reaction. When the ratio of monomer to initiator was 20, the reaction was slower, giving a 26% yield of polymer (MW 11 000) after 69 h. This polymer was tan, soluble in dichloromethane, and insoluble in methanol. Here again a nucleophilic attack of the oxygen of cyclohexene oxide on **3** is proposed for the initiation (Scheme II). Attempts to increase the conversion by longer heating led to a decline first in molecular weight and then in the yield of soluble polymer. High conversions to a black intractable material took place. This black meterial no longer analyzed correctly for a copolymer, so a deep-seated decomposition occurred. It is proposed that the end group of poly(cyclohexene oxide) can expel HCN, yielding a vinyl ether, which can then again react with **3** or with a tricyanovinyl head group of another polymer chain, leading to extended cross-linking.

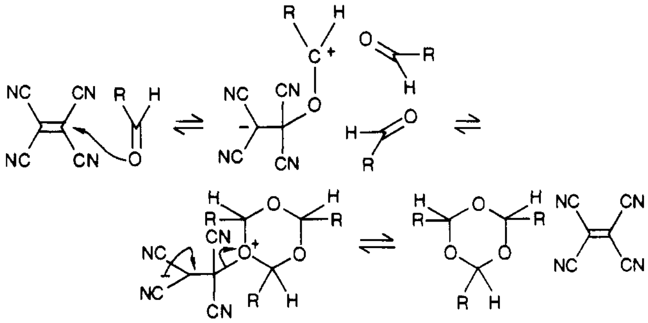
In model studies tetracyanoethylene (**3**) reacted with triethyl orthoformate: the intermediate could be seen by NMR. (Table I, Scheme III). When this intermediate was eluted through silica gel, it gave rise to ethoxytricyanoethylene. These reactions demonstrate slow reaction of **3** with neutral oxygen-containing molecules and also demonstrate replacement of the β-cyano group in these reactions.

Table IV
Cycloreversion of 2,4,6-Trialkyl-1,3,5-trioxanes to Aldehydes in the Presence of Electrophilic Olefins[a]

| 2,4,6-$R_3$-1,3,5-trioxane | amt, mmol | electron-poor olefin | amt, mmol | time | % yield aldehyde |
|---|---|---|---|---|---|
| R = $CH_3CH_2$ | 2.3 | **3** | 0.19 | 5 days | 94 |
| R = *tert*-butyl | 1.5 | **3** | 0.21 | 94 h | 72 |
| R = *tert*-butyl | 1.5 | **4** | 0.74 | 96 h | 93 |

[a] Reactions in $CDCl_3$ at 28 °C in NMR tube.

Scheme IV
Aldehydes ⇄ Trioxanes



With TCNE (**3**), aldehyde monomers were again the most reactive. Electrophile **3** at 28 °C caused cyclotrimerization of bulk propionaldehyde or pivalaldehyde to the corresponding 2,4,6-trialkyl-1,3,5-trioxanes in yields of 90% or more (Table II). These reactions are reversible, at least under conditions in which no oligomerization of the electrophilic olefin occurs. The reactions starting from the trioxanes went to the same equilibrium position as from the aldehydes.

Trifluoroacetic acid, a reference electrophile, catalyzed the above formations in an identical fashion.

Trioxane did not react with our electrophilic olefins even at 70 °C over 1 mo. To probe further this remarkable reactivity difference from the 2,4,6-trialkyl-1,3,5-trioxanes, we attempted the equilibration of aldehydes with trioxane under the action of trifluoroacetic acid.

Cotrimerization of propionaldehyde and pivalaldehyde in bulk in the presence of trifluoroacetic acid gave a mixture of four trimers as expected. However mixtures of trioxane with propionaldehyde or pivalaldehyde gave only the respective trimers of the latter.

The proposed mechanism of these transformations is shown in Scheme IV. A zwitterionic intermediate is the key intermediate in these transformations.

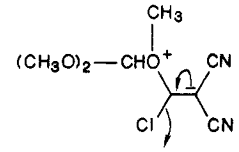
We explain the reluctance of trioxane to participate in exchange reactions in terms of the stability of the intermediate oxacarbenium ions. That from trioxane (R = H) lacks the additional stabilization conferred by the alkyl group when R = $C_2H_5$ or $t$-$C_4H_9$, and so does not readily form.

$$-OCH_2^+ \ll -OCH^+R$$

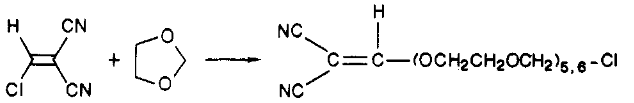
To work with a readily polymerizable aldehyde, we turned to cyclopolymerization.[16] Glutaraldehyde in the presence of TCNE (**3**) polymerized in bulk and in solution. Here the ceiling temperature is above room temperature, making it easier to demonstrate polymerization. In bulk the reaction is complete; after 30 h a quantitative yield of glassy polymer is obtained. When the polymerization is conducted in $CH_2Cl_2$ or toluene, viscous solutions are obtained after a few hours. The polymer showed cyclic units and aldehyde pendant units, with more of the former (ratio ~ 20/1). The polymer is not cross-linked, is soluble in dichloromethane, and has a rather low molecular weight (2000–5000). No polymer is obtained if the electrophile is omitted.

**$\beta,\beta$-Dicyanovinyl Chloride (4).** Finally, we studied electrophilic olefin 4, possessing the better leaving group, Cl, to enhance initiation efficiency (eq 2). Reactions were slow. A low yield of homopolymer (12%) of low MW (4200) is obtained if cyclohexene oxide is mixed with $\beta,\beta$-dicyanovinyl chloride 4 in a 20/1 ratio in bulk at 82 °C for 140 h. At a 1/1 ratio at the same temperature only a trace of polymer is obtained. The rest is oligomer, but the head and end groups in this low MW oligomer can be observed in the NMR spectrum (see Experimental Section).

Trimethyl orthoformate, triethyl orthoformate, and tetramethyl orthocarbonate reacted with $\beta,\beta$-dicyanovinyl chloride (4) at 86 °C for 137 h to give high yields of the corresponding $\beta,\beta$-dicyano-1-alkoxyethylenes (Table I). Yields range from 72% to 91%. In solution the same reactions occur more slowly. This demonstrates the expulsion of chloride ion from the initially formed tetramethylene zwitterion.



1,3-Dioxolane was oligomerized by 4 at 75 °C. No reaction occurred at 28 °C. The structure of the oligomeric oil is based on NMR and IR spectra, and here too the head and end groups can be observed (see Experimental Section).



This demonstrates that chloride ion competes with the weakly nucleophilic monomer for the growing chain. Accordingly 4 is not an optimal initiator either.

## Discussion

The results presented show that our concept of an oxonium–carbanion zwitterion is valid for the reactions of oxacycles with electrophilic olefins as shown in eq 3. The zwitterionic intermediates initiate chain cationic ring-opening polymerizations. However, the three initiators of the present study are not optimal for the rather slowly reacting oxacyclic monomers.

The trisubstituted electrophilic olefins 1 and 2 undergo anionic oligomerization. This type of electrophilic olefin (di- or trisubstituted, possessing no leaving group) is not satisfactory because (1) the electron-poor initiator may be consumed by anionic oligomerization before it can build up a high concentration of oxonium zwitterion to initiate the cationic polymerization and (2) the insolubility of this oligomer may bury the oxonium site.[6]

TCNE (3) also reacted quite slowly. Side reactions, in particular the loss of cyanide, occurred at an undetermined rate. TCNE is modestly effective as an initiator for cyclohexene oxide polymerization.

When $\beta,\beta$-dicyanovinyl chloride (4) is used as initiator, the readily expelled chloride ion is nucleophilic and competes with the rather weakly nucleophilic monomers to terminate polymerization.

These results point the way to new properly designed initiators. It appears that stable new trisubstituted initiators, possessing $\beta$-leaving groups that are nonnucleophilic, should be useful initiators. The $p$-toluenesulfonate group appears optimal for this purpose. Such initiators are now under study.[17]

## Experimental Section

**Methods.** NMR spectra are recorded with an EM-360 Varian 60-MHz nuclear magnetic resonance spectrometer. The infrared data are obtained from a Perkin-Elmer Model 983 spectrometer. Melting points are measured with a Thomas–Hoover capillary melting point apparatus without any correction. Chemical analyses are performed by Micanal, Tucson, AZ.

Size-exclusion chromatography was carried out with three columns, Du Pont Zorbax PSM 300S, PSM 60S and IBM GPC/SEC pore type A columns, calibrated with polystyrene standards, and with chloroform as eluent and a Spectra Physics detector at 254 nm.

**Materials.** Methyl $\beta,\beta$-dicyanoacrylate (1) is synthesized as follows (modified procedure): In a round-bottom flask (100 mL), equipped with a Soxhlet extraction containing activated molecular sieves, are placed methyl glyoxylate methyl hemiacetal (24 g, 0.2 mol, distilled) and malononitrile (6.6 g, 0.1 mol) in acetonitrile (50 mL). The reaction mixture is refluxed for 3 h, the solvent is evaporated, and the oil is distilled at 62–63 °C/(0.1 mmHg):[9] yield, 6 g (45%). The product is stored under nitrogen in the dark at –50 °C. NMR ($CDCl_3$) $\delta$ 3.94 (s, 3 H), 7.2 (s, 1 H). Anal. Calcd: C, 52.94; H, 2.94; N, 20.58. Found: C, 52.09; H, 2.87; N, 19.82.

Dimethyl cyanofumarate (2) was prepared according to literature procedure.[11]

Tetracyanoethylene (3) was purchased from Fluka, recrystallized from 1,2-dichloroethane, sublimed twice through a layer of activated carbon black, and stored at –10 °C (mp 198–200 °C).

$\beta,\beta$-Dicyanovinyl chloride (4) is synthesized according to literature procedure, distilled, and stored under nitrogen in the dark at –50 °C.

Cyclohexene oxide is dried with calcium sulfate and then over sodium hydroxide, distilled twice from calcium hydride, and stored under nitrogen at 0 °C.

1,3-Dioxolane is dried with sodium hydroxide, distilled from sodium, and stored under nitrogen at 0 °C.

Propionaldehyde is dried over calcium sulfate and fractionally distilled in the presence of hydroquinone twice.

Glutaraldehyde[19] was purified as follows: The aqueous solution is stirred repeatedly, with activated charcoal, freeze-dried to get rid of water, fractionally distilled under reduced pressure, dried over molecular sieves, treated with charcoal again, redistilled, and stored under argon in the dark at –45 °C.

Other chemicals were obtained from Aldrich and used without purification.

1,2-Dichloroethane is treated with sulfuric acid, washed with water, 5% aqueous sodium carbonate, and water, dried over magnesium sulfate, distilled from calcium hydride, and stored under nitrogen in the presence of molecular sieves.

**Cyclohexene Oxide Polymerization.** In a polymerization tube, the electron-poor olefin and cyclohexene oxide are mixed and cooled to –78 °C. A vacuum is applied and the tube is then filled with nitrogen gas. The procedure is repeated. The tube is then placed at the desired temperature. After the reaction is complete, unreacted monomer is removed under vacuum, and the residue is checked by NMR. The homopolymer is precipitated in methanol, dissolved and stirred in acetone, and reprecipitated into methanol. The polymer is identified by NMR, IR, chemical analysis and SEC. Poly(cyclohexene oxide): NMR ($CDCl_3$) $\delta$ 0.8–2.2 (br, 8 H), 3.0–3.6 (br, 2 H). IR (KBr) 2930, 2858, 1446, 1086 $cm^{-1}$. The insoluble polymer obtained from TCNE reactions also has absorptions at 2661 and 2222 $cm^{-1}$ in IR.

From the reaction of 6.9 mmol of cyclohexene oxide and 0.5 mmol of 1 at 90 °C for 92 h, we obtained (1) oligo(cyclohexene oxide), 4%; (2) methanol-soluble, hexane-insoluble cooligomer rich in 1, 6%; and (3) methanol-soluble, hexane-soluble cooligomer rich in CHO, 5%.

From the reaction of excess cyclohexene oxide and 2 for 112 h at 90 °C, oligo 2 is obtained: NMR ($CDCl_3$) $\delta$ 3.8 (broad); IR (KBr) 2950, 1743 $cm^{-1}$.

From the reaction of cyclohexene oxide and **4** in a 1/1 ratio (1,2-dichloroethane, $^1/_4$ h, 82 °C) only a trace of polymer is obtained. The rest is oligomer. In the NMR spectrum of this oligomer, the head[8] and end groups can be observed. NMR ($CDCl_3$) $\delta$ 0.7–2.5 (br, $CH_2$), 3.1–3.6 (br, $C\mathit{H}O$), 3.6–4.2 (br, $C\mathit{H}Cl$), 7.83 (s, $O\mathit{CH}{=}ClCN)_2$).

**Orthoester and Orthocarbonate Reactions.** The reactions are run in NMR tubes and followed by NMR spectroscopy.

1,1-Dicyano-2-ethoxyethylene: NMR ($CDCl_3$) $\delta$ 1.4 ($CH_3O$), 4.2–4.4 ($CH_2O$), 7.68 ($CH{=}C$).

1,1-Dicyano-2-methoxyethylene: NMR ($CDCl_3$) $\delta$ 4.2–4.4 ($CH_3O$), 7.6–7.7 ($HC{=}C$). IR absorptions at 2235 (sh) and 1614 $cm^{-1}$ (s) were observed.

The intermediate in the triethyl orthoformate–tetracyanoethylene reaction had new NMR absorptions at $\delta$ 1.45 (t, 6 H, $CH_3$), 4.68 (q, 4 H, $CH_2$), 5.30 (s, 1 H, CH). Ethoxytricyanoethylene had absorptions at $\delta$ 1.52 (t, 3 H, $CH_2$), 4.60 (q, 2 H, $CH_2$); IR: 2990 (w), 2239 (sh), 1584 $cm^{-1}$ (s).

**Aldehyde Trimerizations.** Trimethylacetaldehyde or propionaldehyde is placed in the presence of an electron-poor olefin in an NMR tube, and the reaction is followed by NMR. The cyclotrimer is compared to authentic material, synthesized by using trifluoroacetic acid. Trimer of $CH_3CH_2CHO$: NMR ($CDCl_3$) $\delta$ 1.0 (t, 9 H, $CH_3$), 1.6 (m, 6 H, $CH_2$), 4.8 (t, 3 H, -OCHO). Trimer of $(CH_3)_3CCHO$: NMR ($CDCl_3$) $\delta$ 1.10 (t, 27 H, $CH_3$), 4.4 (s, 3 H, CH).

**Attempted Aldehyde–Trioxane Reactions.** The reagents, in comparable millimolar amounts, were mixed at room temperature, and 25 $\mu$L (~1%) of trifluoroacetic acid was added by syringe. After 1 week at 28 °C, 75 $\mu$L of triethylamine was added to neutralize the catalyst, and the mixtures were analyzed by gas chromatography.

**Glutaraldehyde.** TCNE was placed into one arm of a Y polymerization tube containing a magnetic stirrer. Glutaraldehyde was syringed into the other arm. After two freeze–thaw cycles, the glutaraldehyde was added to TCNE with stirring in the dark. The polymer is stabilized by treatment with acetic anhydride and (dimethylamino)pyridine. NMR ($CDCl_3$) $\delta$ 1.0–2.8 (m, broad, $CH_2$), 4.6–5.48 (m, broad, OCHO), 9.8 (s, $CH{=}O$). IR 2951, 1744 (s), 1651, 1547, 1240, 1111 $cm^{-1}$.

**1,3-Dioxolane.** 2-Chloro-1,1-dicyanoethylene (**4**) (0.318 g, 2.83 mmol) is weighed in a vial. 1,3-Dioxolane (0.53 g, 7.7 mmol) is added at room temperature and then the solution is transferred to a polymerization tube using a syringe. The tube is placed in dry ice–acetone bath, full vacuum is applied, the tube is filled with $N_2$, and the process is repeated. The reaction mixture is warmed to room temperature and then placed in an oil bath at 75 °C for 96 h. When the reaction is finished, the mixture is dissolved in $CDCl_3$ and observed by NMR. The solvent is rotary evaporated and the oil is placed under full vacuum at 50 °C to remove any unreacted starting material. Polymer weighed 0.227 g (43%), MW by SEC < 666. Oligomer (when freshly synthesized): NMR ($CDCl_3$) $\delta$ 3.7–3.8 ($OCH_2CH_2O$), 4.3–4.8 ($OCH_2O$), 5.5 (s, $OCH_2Cl$), 7.82 (s, $CH{=}C$). IR (neat) 3036 (m), 2938 (s), 2233 (sharp), 1722 (weak), 1682 (w), 1682 (w), 1610 (s), 1038 (s), 842 (s), 642 $cm^{-1}$ (s).

The end groups are characteristic. The olefinic proton shows a peak at 7.82 ppm compared to the olefin **4** at 8 ppm. The unit $OCH_2Cl$ shows a peak at 5.5 ppm, distinct from 4.3–4.8 ppm for $OCH_2O$. The IR shows sharp CN absorption at 2233 $cm^{-1}$ and strong absorption at 842 and 642 $cm^{-1}$ characteristic of CCl.

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**Registry No.** **1**, 82849-50-1; **1** (homopolymer), 107516-16-5; **2**, 54797-29-4; **2** (homopolymer), 107516-15-4; **3**, 670-54-2; **4**, 10472-09-0; $CH(OC_2H_5)_3$, 122-51-0; $C(OCH_3)_4$, 1850-14-2; $CH(OCH_3)_3$, 149-73-5; $C_2H_5CHO$, 123-38-6; $(H_3C)_3CCHO$, 630-19-3; $F_3CCO_2H$, 76-05-1; $OHC(CH_2)_3CHO$, 111-30-8; $C_2H_5OC(CN){=}C(CN)_2$, 69155-32-4; $C_2H_5OCH{=}C(CN)_2$, 123-06-8; $H_3COCH{=}C(CN)_2$, 672-81-1; cyclohexene oxide, 286-20-4; poly(cyclohexene oxide), 25702-20-9; 2,4,6-triethyl-1,3,5-trioxane, 2396-42-1; 2,4,6-tri-*tert*-butyl-1,3,5-trioxane, 53607-03-7; poly(glutaraldehyde), 29257-65-6; $\beta,\beta$-dicyanovinyl chloride·dioxolane cotelomer, 107516-18-7.

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