Order Number 9010485

Synthesis and polymerization of highly electrophilic monomers

Ramezanian, Merrikh Sabahi, Ph.D.

The University of Arizona, 1989

U·M·I

300 N. Zeeb Rd.
Ann Arbor, MI 48106

SYNTHESIS AND POLYMERIZATION OF HIGHLY ELECTROPHILIC MONOMERS

by

Merrikh Sabahi Ramezanian

A Dissertation Submitted to the Faculty of the

DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY

In the Graduate College

THE UNIVERSITY OF ARIZONA

1 9 8 9

THE UNIVERSITY OF ARIZONA
GRADUATE COLLEGE

As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Merrikh Sabahi Ramezanian

entitled SYNTHESIS AND POLYMERIZATION OF HIGHLY ELECTROPHILIC MONOMERS

and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Docter of Philosophy.

H K Hall Jr.	Sept. 13 1989
Prof. H. K. Hall Jr.	Date
J. E. Mulvaney	9/13/89
Prof. J. E. Mulvanev	Date
R. B. Bates	9-13-'89
Prof. R. B. Bates	Date
David Ehrlich	13 Sept 89
Prof. D. Wigly	Date
Prof. P. C. Keller	Date

Final approval and acceptance of this dissertation is contingent upon the candidate's submission of the final copy of the dissertation to the Graduate College.

I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

Prof. H. K. Hall Jr. H K Hall Jr.	Sept 13 1989
Dissertation Director	Date

STATEMENT BY AUTHOR

This dissertation has been submitted in partial fulfillment of requirements for an advanced degree at the University of Arizona and is deposited in the Library to be made available to borrowers under rules of the Library.

Brief quotations from this dissertation are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript is whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his or her judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: Mehrdad Ramezanian

ACKNOWLEDGEMENTS

The author wishes to thank Dr. H. K. Hall Jr. for his inspiration, guidance, and support throughout my graduate work. I would also like to thank Dr. J. E. Mulvaney and Dr. A. B. Padias for their invaluable input and assistance. Finally I would like to express my deepest gratitude to my husband Dr. M. Sabahi whose unending guidance and support gave me the opportunity to pursue this work.

TABLE OF CONTENTS

TABLE OF CONTENTS Continued

TABLE OF CONTENTS Continued

TABLE OF CONTENTS Continued

LIST OF TABLES

LIST OF ILLUSTRATIONS

ABSTRACT

The experimental results of the current work have two parts. First the synthesis, characterization, and spontanouse copolymerization of two highly electrophilic imines, tricyanomethanimine and methyl 3-aza-α,ß-dicyanoacrylate. 1,1-Dichloro-2,2-dicyanoethylene or methyl 3,3-dichloro-2-cyanoacrylate reacted with excess sodium azide to give the corresponding diazides, which smoothly underwent thermolysis in solution to give a solution of the novel tricyanomethanimine or methyl 3-aza-α,ß-dicyanoacrylate. Attempted isolation gave only oligomers, but reactions using solution of these imines succeeded. Cyclopentadiene and 2,3-dimethyl-1,3-butadiene afforded hetero Diels-Alder reactions. N,N-Dimethylaniline with tricyanomethanimine gave a p-substituted derivative, but with methyl 3-aza-α,ß-dicyanoacrylate only a charge transfer complex was formed. Imines - p-methoxystyrene copolymers were obtained. These imines are as reactive as TCNE, but in contrast can also polymerize. Second, a new unsymmetricaly substituted quinodimethane was synthesized, characterized, and copolymerized with electron donating monomers. Oxidation of the 1-cyano-1-phenylmethylene-4-cyano-4-ethoxycarbonylmethylene with MnO_2 gave mostly poly-7,8-dicyano-7-

ethoxycarbonyl-8-phenylquinodimethane(DCEPQ), but depolymerization by sublimation yielded 45% of DCEPQ. This compound was a mixture of cis and trans isomers. It was homopolymerized by anionic initiation. High molecular weight copolymers of DCEPQ-styrene, DCEPQ-p-methylstyrene and DCEPQ-p-methoxystyrene(p-MeOSt) were formed spontaneously in 1,2-dichloroethane. All polymerizations occurred by a radical mechanism. High molecular weight polymers formed at low conversion. DCEPQ - p-MeOSt copolymerizations yielded alternating copolymers. From spontaneous polymerization of DCEPQ with NVC no copolymer was obtained. All of these polymerizations begin with a bond forming mechanism and propagate by polyaddition.

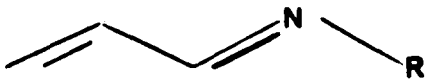
CHAPTER 1

INTRODUCTION

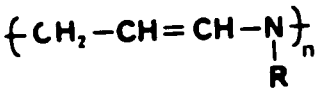
a) Synthesis and polymerization of highly electrophilic imines.

Although a great deal is known about the polymerization of C=C and C=O compounds, very little is known about the polymerization of C=N compounds. Imines often give cyclic trimers, indicating a tendency to polymerize. [1] However, no well-defined polymers have been reported.

From the study of various 1-substituted 1-azabutadienes:



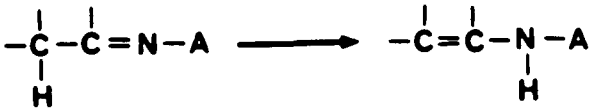
it was found that acceptor groups with anionic initiators gave high yields of high polymer with a 4,1- structure:[2]



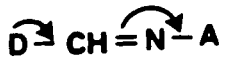
This implies that the C=N unit can be polymerized.

The positive results obtained with 1-azabutadiene showed that the preferred strategy for polymerization of azaethylene would be anionic polymerization of monomers with an acceptor group (i.e., -CN, SO2R, and NO2) on the nitrogen. The ester (COOR) group has been avoided because of self dimerization of monomer by hetero-Diels-Alder reaction.[3]

The nature of the substituents on the carbon atom of the imine group has an important effect on the reaction too. I) Imines with two hydrogens on carbon will be too reactive. II) Alkyl group substituents with ß-hydrogen will be unstable because of tautomerization to enamides:



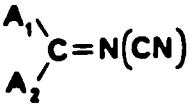
III) Donor substituents can stabilize the -C=N- acceptor:



2-Phenyl- and 2-t-butyl-N-cyanoazaethylene have been synthesized by Kim. Under anionic polymerization conditions a polymer of 2-phenyl-N-cyanoazaethylene was obtained. [4]

With these considerations in mind we can design monomers with the proper combination of stability and ability to polymerize.

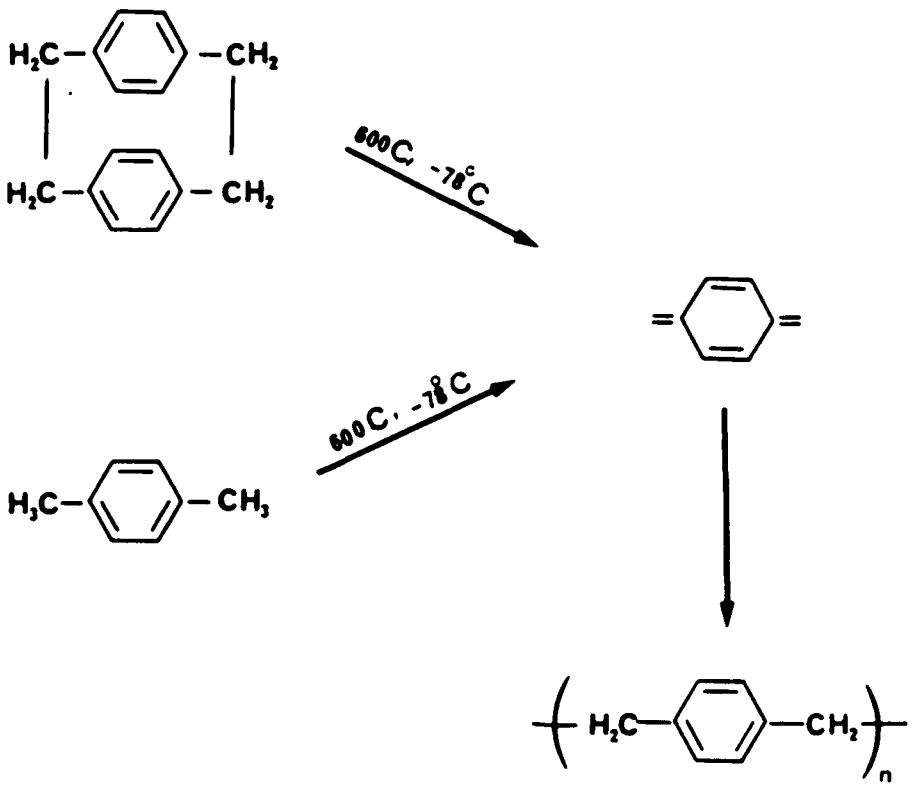
We chose to study the synthesis and polymerization of highly electrophilic imines with a cyano group attached to N and electron deficient groups on the carbon:



b) Synthesis and polymerization of unsymmetrical quinodimethane (QDM) monomer.

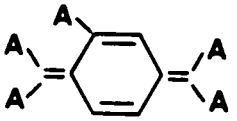
Quinodimethane monomers may be thought of as "aromatic olefin monomers". That is, both quinodimethane and olefin polymerizations occur by cleavage of carbon-carbon pi bond and formation of carbon-carbon sigma bonds. Quinodimethanes are "broken aromatic" olefins in the sense that their polymerization results in ring aromatization as well as bond formation:

p-Quinodimethane (see below) was isolated and characterized in 1947.[5] p-Quinodimethane polymerizes spontaneously in the condensed phase at low temperature. Poly-p-quinodimethane was isolated as an insoluble, crystalline solid. In one experiment the molecular weight of the polymer was determined to be greater than 2×10^5.[6]



In contrast, most acceptor group substituted quinodimethanes are stable, allowing them to be isolated and controllably homopolymerized and copolymerized.[7,8,9,10]

Exocyclic Substituted



Exocyclic and Ring Substituted

The latest group of acceptor substituted quinodimethanes are those heterosubstituted at each of the exocyclic positions.[11,12,13]

7,8,7,8-Heterosubstituted Quinodimethane

These 7,8,7,8-substituted quinodimethanes provide a means of introducing highly functionalized chiral centers into polymer backbone. These chiral centers increase the solubility of the homo- and copolymers of quinodimethane.

Mechanistic studies on the polymerization of quinodimethane have indicated that propagation is occurring by chain addition which predicts the production of high molecular weight polymer at low conversion.[14]

The incomplete understanding of the chemistry and propagation mechanism of polymerization of quinodimethane has led our group to synthesize and polymerize unsymmetrical quinodimethanes. Recently Itoh prepared the unsymmetrical quinodimethane 7,7,8-tricyano-8-phenylquinodimethane in our labs which did not polymerize. So we decided to synthesize and polymerize the unsymmetrical quinodimethane 7,8-dicyano-7-ethoxycarbonyl-8-phenylquinodimethane.

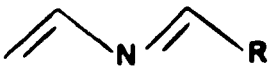
CHAPTER 2

SYNTHESIS AND POLYMERIZATION OF HIGHLY ELECTROPHILIC IMINES

BACKGROUND

The study of polymerization of conjugated imines, namely 1-aza-1,3-butadiene 1 and 2-aza-1,3-butadienes 2 have been carried out in our laboratories.[2,15]

1

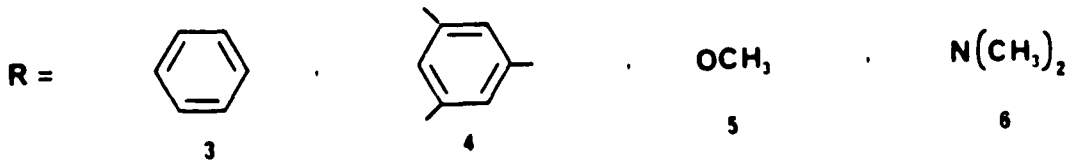


2

It has been suggested that the vinyl group would act as a "handle" for polymerization of the C=N group.[16]

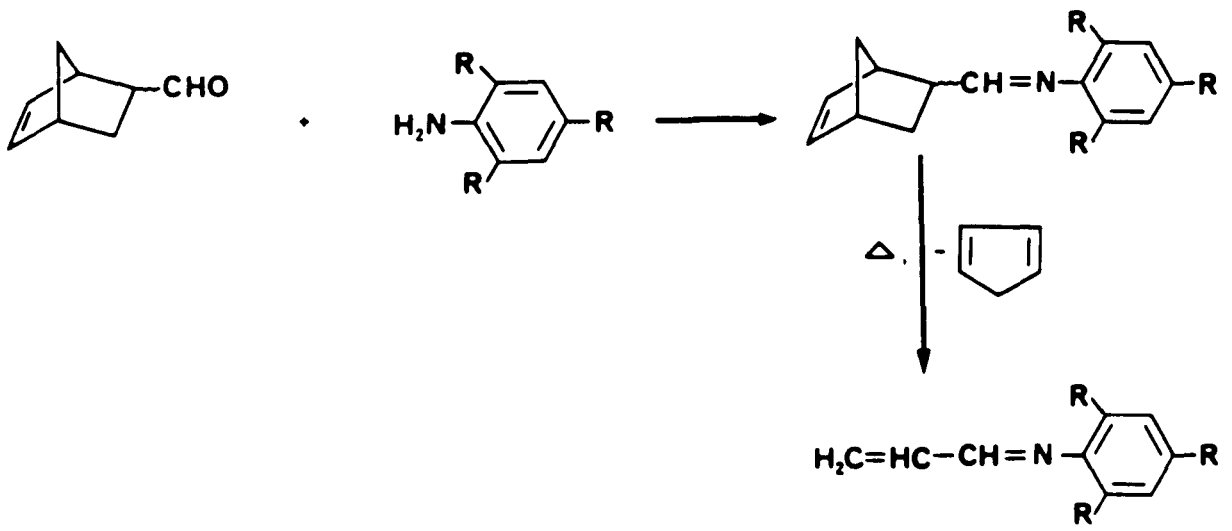
Although the 1-aza-1,3-butadiene system is not uncommon, only two reports have been published on its polymerization. Soto and Tsuruta [17] reported that three N-alkyl-3-methyl-1-aza-1,3-butadienes and N-alkyl-1-aza-1,3-butadienes polymerized through 4,3-vinyl-type polymerization by anionic initiators. Smith and co-workers [18] found that N-alkyl-1-aza-1,3-butadienes did not polymerize with peroxides or boron trifluoride etherate.

1-Azabutadienes with a variety of substituents on nitrogen (compounds 3 to 6) were synthesized and subjected to anionic, cationic and radical initiation .



Direct synthesis of the 1-aryl derivatives by a dehydration reaction between an arylamine and acrolein or methacrolein was not successful, owing to competitive Michael additions and condensations. However, the norbornene precursors were easily synthesized from the commercially available aldehyde and amines, which on subsequent thermolysis afforded the desired compound, (Scheme 1).

Scheme 1:



N-Methoxy-1-aza-1,3-butadiene, 5, and N-(dimethyl-amino)-3-methyl-1-aza-1,3-butadiene, 6, were synthesized directly from acrolein and methacroleine.[19,20]

Anionic polymerization was the most effective method for 1-aza-1,3-butadiene monomers. Monomers 3 and 4 gave polymers with anionic initiators such as butyllithium (BuLi) and tert-butylmagnesium chloride (t-BuMgCl) in toluene. The results are summarized in Table 1. Polymerization of 3 by BuLi in tetrahydrofuran (THF) failed, but 4 gave polymer in similar yields in both toluene and THF. Polymerization at 0°C in toluene gave a better yield and higher molecular weight polymer than at -78°C. Molecular weights ranged from 1000 to 7000 (by SEC).

Monomers 3 and 4 could be polymerized by cationic initiators such as BF_3OEt_2 and CF_3COOH to give slightly yellow powdery polymer, but the molecular weights were rather low.

Attempted radical homopolymerization and copolymerization of 3 or 4 with methyl methacrylate were unsuccessful. Similar observations were reported for N-cyclohexyl-1-aza-1,3-butadiene.[17]

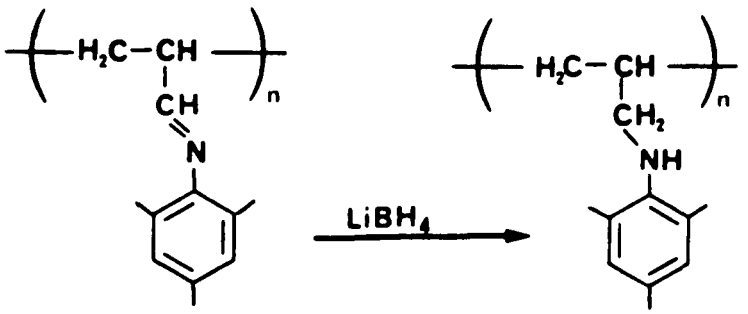
In the IR spectrum of the polymer 4, prepared using BuLi, a strong C=N stretching vibration band at 1657 cm^{-1} was observed. The ^{1}H-NMR spectrum of reduced poly-4 showed that the CH=N group was completely gone. In the IR spectrum

Table I
Polymerization of 1-Aryl-1-aza-1,3-butadienes[a]

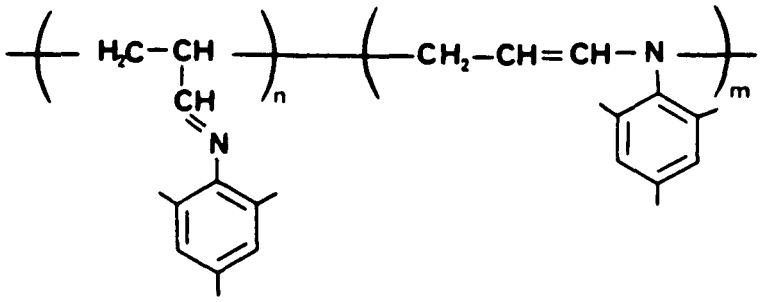
monomer	mmol	initiator	μmol	solvent	temp, °C	time, h	precipitant	yield, %	color	MW (SEC)	softening pt, °C
1	0.5 mL	BuLi	80	tol[f]	−78	24	*b*	23.6	white	2100	160
	(3.7 mmol)	BuLi	80	tol	0	24	*b*	89.3	white	7200	210
		BuLi	125	THF	−78	30	*b*	0			
		t-BuMgCl	80	tol	−78	30	*b*	8.7	white	1600	140
		BF_3OEt_2	74	DCM[g]	−78	30	*c*	19.2	lt brown	960	160
		CF_3CO_2H	74	DCM	−78	30	*c*	34.5	lt brown	1900	
2	1 mL	BuLi	110	tol	−78	24	*d*	38.8	white	4800	100
	(5.45 mmol)	BuLi	110	tol	0	24	*d*	58.0	white	3200	100
		BuLi	110	THF	−78	24	*d*	30.8	white	1000	
		BuLi	110	THF	0	24	*d*	63.7	white	1000	
		t-BuMgCl	120	tol	−78	24	*d*	5.5	yellow-white	2400	90
		BF_3OEt_2	110	DCM	−78	24	*e*	60.6	yellow-white	1500	130
		CF_3CO_2H	110	DCM	−78	24	*e*	~9.9	yellow-white	1100	150

[a] Polymerizations were carried out in Y-shaped tubes with vacuum valve. Catalysts were added by syringe. Five milliliters of solvent was used. [b] One-hundred milliliters of hexane. [c] Washed with Na_2CO_3 (aq), dried over K_2CO_3, and poured into hexane. [d] One-hundred milliliters of methanol. [e] One-hundred milliliters of methanol plus 5 mL of concentrated ammonium hydroxide. [f] Toluene. [g] Dichloromethane.

of reduced poly 4, the C=N band at 1657 cm^{-1} disappeared. The above results indicate that BuLi initiated poly-4 is formed through 4,3-addition (vinyl) polymerization and has the structure shown below.



In the NMR spectrum of poly-4 prepared using boron-trifluoride etherate, a broadened but distinguishable signal around 7.5 ppm was assigned to an imine proton. However, the intensity for the signal is low and corresponds to only 0.54 protons. On the other hand a new broad signal was observed at 5.6 ppm whose intensity corresponded to 0.41 protons. The latter signal was ascribed to a vinyl proton. The IR spectrum of the polymer showed a strong C=N stretching band at 1651 cm^{-1} similar to BuLi-initiated poly-4. These data indicate that the polymer contains at least two types of repeating units in the chain, which form through 4,3- and 4,1-addition:



The spectroscopic data for poly-3 prepared with BuLi at -78°C, showed that poly-3 contains both 4,1- and 4,3-structural units. Poly-3 prepared with BuLi at 0°C, showed an even weaker C=N band at 1644 cm^{-1}.

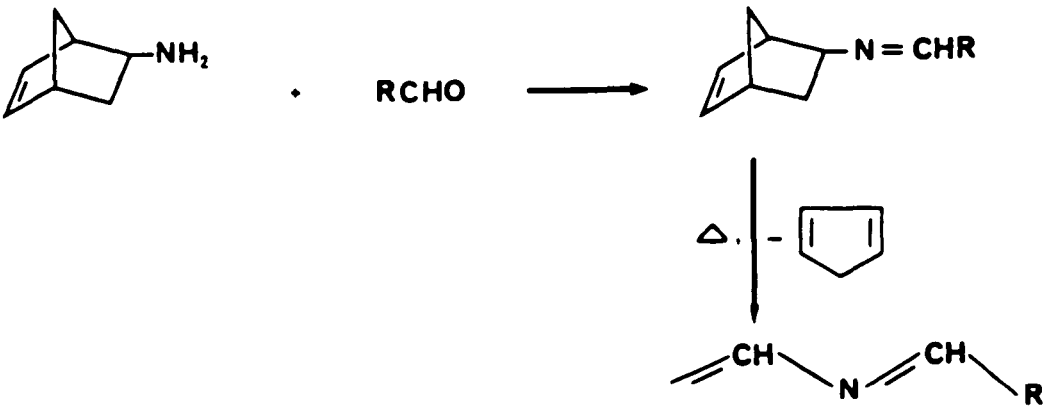
For monomer **4**, cationic polymerization proceeded by both 4,1- and 4,3-addition, which means that stabilization of the cation at nitrogen by the aromatic substituent overcomes the steric hindrance. Greater stabilization for the cation is due to the electron-donating character of the 2,4,6-trimethylphenyl group.

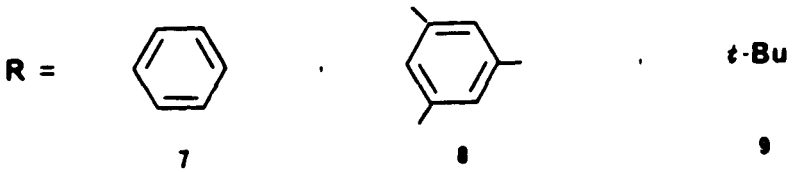
The strong electron-donor substituents, methoxy (**5**) and dimethylamino (**6**), prevented polymerization. Anionic polymerization was suppressed, possibly due to electron repulsion between the electron pairs of the substituent and the anionic propagating species. On the cationic side, the strong donor substituents, methoxy (**5**) and dimethylamino (**6**), rendered the system too basic/nucleophilic. A similar

situation allows only oligomer formation under cationic initiation.

1-Substituted 2-aza-1,3-butadienes (7, 8, and 9) were prepared from 5-aminonorborn-2-ene (Scheme 2).

Scheme 2:

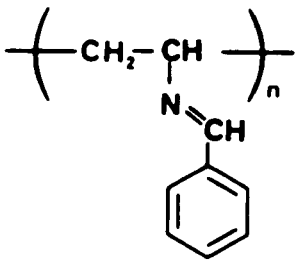




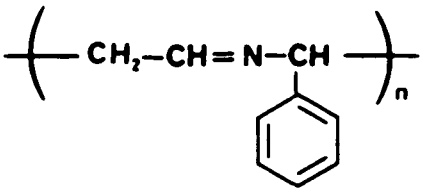
7 8 9

Polymerization of all three 2-azabutadiene monomers (7 to 9) was attempted using anionic initiators (butyllithium in toluene or tetrahyrofuran at 0 and -78°C), cationic initiators (borontrifluoride etherate or trifluoroacetic acid in dichloromethane at -78 and -10°C) and a radical initiator (AIBN in toluene at -78°C). Anionic

polymerization of monomer 7 using butyllithium in toluene at 0°C or in tetrahydrofuran at -78 or 0°C led to high yields of a very low molecular weight polymer (less than 5000). Trifluoroacetic acid led to a low yield of low molecular weight polymer at -10°C in dichloromethane as did AIBN at -70°C. Monomers 8 and 9 did not yield any polymer under any of the above conditions. The infrared spectrum of poly-7 from anionic polymerization does not show any residual terminal vinyl groups, but does show a peak for C=N around 1660 cm^{-1}. This indicates that the polymerization occurred in either a 4,3- fashion, leading to units with structure A (see below), or in a 4,1- fashion, yielding units with structure B, or a mixture of both.



A



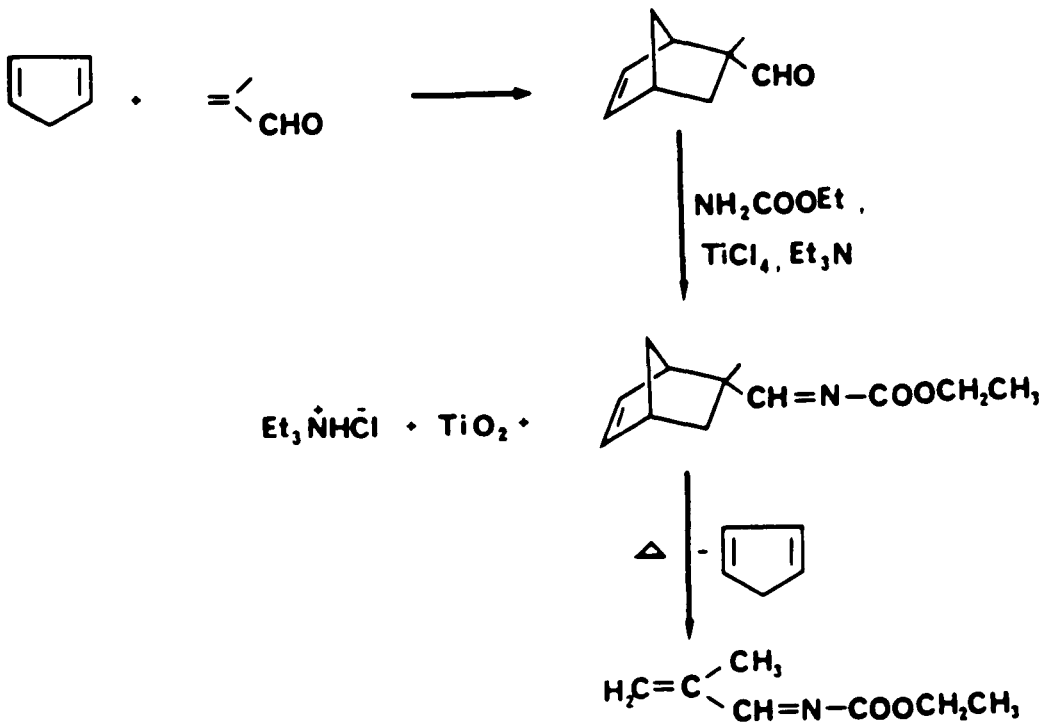
B

From the study of 1- and 2-azabutadiene we can conclude that 1-azabutadienes are much more efficient monomers than 2-azabutadienes. The positive results obtained from 1-azabutadiene showed that the electron

accepting groups on the nitrogen are effective substituents for anionic polymerizatin.

The monomer N-carboethoxy-3-methyl-1-aza-1,3-butadiene, CEMAB 10, was synthesized as shown in Scheme 3.[17]

Scheme 3:



10

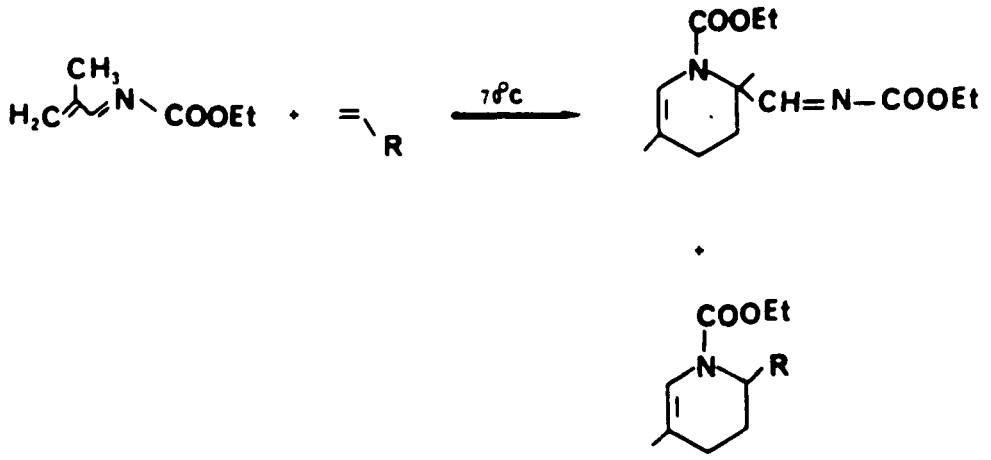
Diels-Alder cycloaddition of methacrolein to cyclopentadiene proceeds readily in good yield. The resulting-methyl-carboxaldehyde condensed with ethyl carbamate in the presence of titanium tetrachloride in triethylamine under absolutely dry conditions. The pyrolysis of the precursor and purification gave the desired compound.

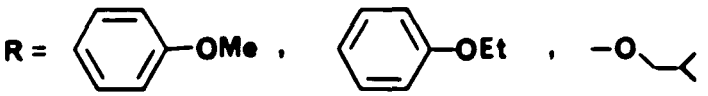
This method was not successful for acrolein because the intermediate imine underwent a tautomeric CH-NH shift to form the enamide:

11

Polymerization of 10 was carried out by radical and anionic initiators.[21] Anionic polymerization, especially when initiated by weak nucleophiles such as triethylamine or cyanide anion, gave moderate yields of polymers with rather low molecular weight (1200-2000 by SEC). The structures obtained corresponded almost completely to C=N bond opening (4,1- type predominant over the 1,2-type). Polymer obtained with KCN in DMF showed essentially only the 4,1-addition structure. Though most radical initiators effectively polymerize CEMAB, the conversions were low and found to be restricted by competitive dimerization by hetero-Diels Alder reaction of the monomer. The resulting structures showed mixed polymerization modes (4,1-, 2,1, and 4,3-type). Attempts to copolymerize CEMAB with electron rich olefins both with and without radical initiators were unsuccessful giving only the inverse Diels-Alder cycloaddition products

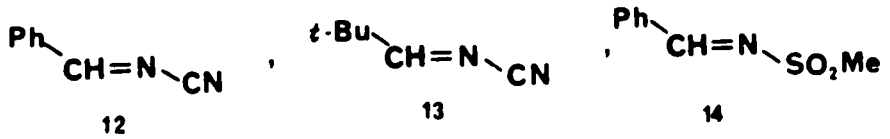
of CEMAB with olefins (see below).



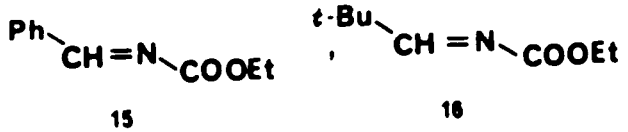


This cycloaddition reaction is a typical inverse Diels-Alder reaction of α,β-unsaturated imines, and is considered to be the major factor contributing to the absence of copolymerization. The cyclic dimerization of CEMAB progressed slowly at room temperature, but the reaction was faster at higher temperatures and the conversion reached 70% within two days at 70°C. Thermal dimerization was complete within five days in $CDCl_3$ and no other side reactions were found during the dimerization. The cycloadditions of CEMAB with electron-rich olefins were somewhat faster than the self-dimerization of CEMAB.

These observations indicated that the best strategy for polymerization of azaethylene would be anionic polymerization of monomers with an acceptor group on nitrogen. The best candidates for these experiments were: benzylidene cyanamide 12, pivalidene cynamide 13, N-methylsulfonylbenzylidene amine 14, N-carboethoxybenzylidene amine 15, and N-carboethoxypivalidene amine 16.[4]



12 13 14

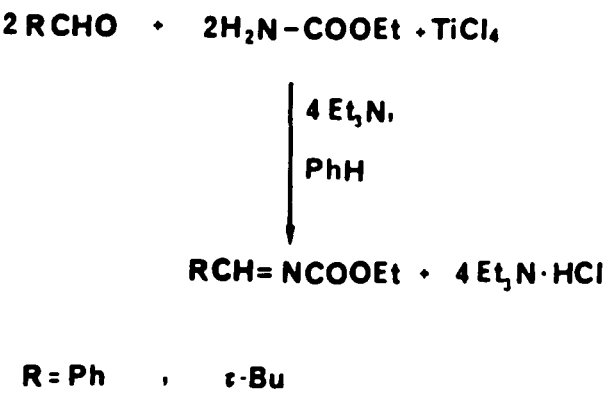


15 16

The N-cyanoimines 12 and 13 were easily synthesized from the reaction of the corresponding aldehydes with silylated compounds in the presence of a catalytic amount of titanium tetrachloride as shown below. This method is analogous to an enamine synthesis.[22]

R = Ph , *t*-Bu

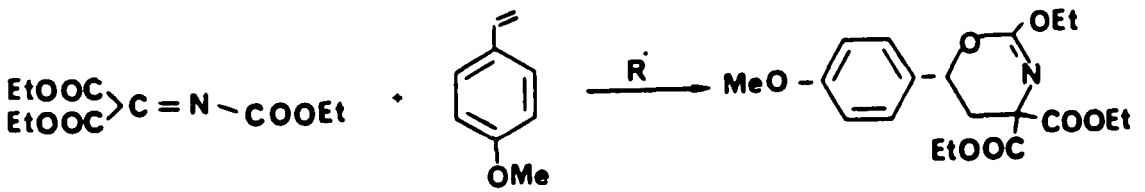
The N-carbethoxyimines 15 and 16 were prepared from the corresponding aldehyde and ethyl carbamate using an equivalent amount of $TiCl_4$:



The imine monomers 12-16 were treated with initiators for free radical and anionic polymerizations.[4] All polymerizations were very slow. Benzylidene cyanamide 12 is the best monomer, polymerizing with high yields after two days with a variety of anionic initiators, but the polymer had a very low molecular weight. Monomer 16 did not polymerize with any of the anionic initiators. Only the two N-cyanoimine monomers 12 and 13 polymerized under free radical conditions with 12 giving high yields of a low molecular weight polymer and 13 a low yield. Spontaneous reactions take place during work-up and polymer continues to precipitate. Monomers 14, 15, and 16 do not polymerize under free radical conditions.

The structures of the polymers of N-cyanoimines 12 and 13 are rather complicated. The NMR and IR spectra indicate that numerous side reactions occur, but the main reaction was at the C=N bond. On the other hand, the spectra for N-carboethoxyimines 15 and 16 are very clean.

Attempted polymerization of triethyl methane-tricarboxylate, 17, was not successful.[3] Even with p-methoxystyrene it underwent inverse Diels-Alder reaction by with C=N-C=O moiety as diene:



17

In summary we can make the following conclusions:

a) The cyano group on the nitrogen atom of the imine drives the molecule towards polymerization through C=N position better than any other electron-accepting substituent.

b) The presence of electron-releasing groups on the carbon atom of the C=N moiety stabilizes the monomer.

c) Two hydrogens on the carbon of the C=N moiety make it extremely reactive, polymerizing below -100°C.

d) Phenyl substituents on carbon result in low molecular weight polymers.

Armed with these data we carried out the synthesis and polymerization of monomer imines with a cyano group attached to N and two electron withdrawing groups attached to carbon:

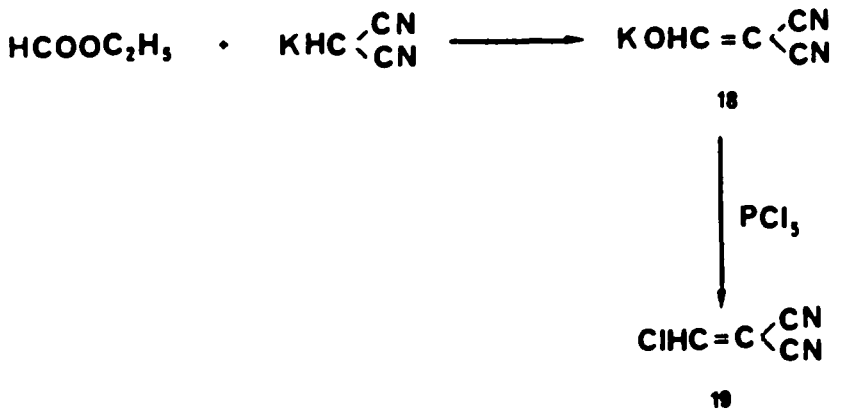
$$\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!\rangle C = N(CN) \qquad \begin{matrix} R_1, R_2 = CN \\ R_1 = CN \ , \ R_2 = COOMe \\ R_1, R_2 = COOMe \end{matrix}$$

RESULTS AND DISCUSSION

Synthesis of Tricyanomethanimine, 26.

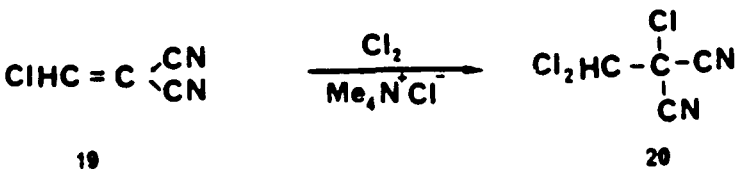
Reaction of potassium ethoxide with malononitrile and ethyl formate in absolute ethanol gave the potassium salt 18.[23]

Scheme 4:



Reaction of the dry potassium salt with phosphorus pentachloride in dry dichloromethane produced 1-chloro-2,2-dicyanoethene, 19. ^{1}H-NMR spectroscopy showed one peak at 7.8 ppm for the vinylic proton. Chlorine gas was bubbled through a solution of 1-chloro-2,2-dicyanoethylene, 19, in dry dichloromethane with a catalytic amount of triethylamine to form 1,1,2-trichloro-2,2-dicyanoethane, 20, as the addition product. ^{1}H-NMR spectroscopy showed a singlet at

6.0 ppm, and the IR spectrum showed the characteristic C-H band at 3000 cm^{-1} and CN band at 2257 cm^{-1}.



19 20

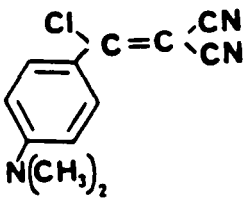
The elimination reaction was carried out by adding triethylamine to a solution of 1,1,2-trichloro-2,2-dicyanoethane, 20, in ether:

20 21

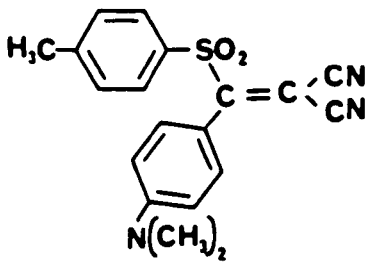
The IR spectrum of 21 showed the characteristic bands for CN at 2240 cm^{-1} and at 1597 cm^{-1} for C=C.

This literature method for preparation of 1,1-dichloro-2,dicyanoethylene, 21, is more convenient than a second one used previously.[24] Like the chlorination of tricyanoethylene [25a] and tetracyanoethylene, [25b] the chlorination of 1-chloro-2,2-dicyanoethylene, 19, is strongly catalyzed by tetramethylammonium chloride. It is probable here, as in the former cases, that chlorination of the strong acid proceeds by initial attack of the nucleophilic catalyst (chloride ion or amine) on the double bond.

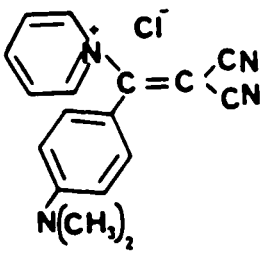
It is of interest that the chlorine atom of 21 can be replaced in good yield by a variety of nucleophilic groups. When a solution of 21 was treated with N,N-dimethylaniline, 1-chloro-1-(4-dimethylaminophenyl)-2,2-dicyanoethylene, 22, was formed. From the reaction of 22 with sodium p-toluenesulfinate, 1-(4-dimethylaminophenyl-1-(p-toluenesulfonyl)-2,2-dicyanoethylene, 23, was obtained and with pyridine the quaternary salt N-[1-(4-dimethylamino-phenyl)-2,2-dicyanovinyl]pyridinium chloride, 24, was obtanied.[23]



22



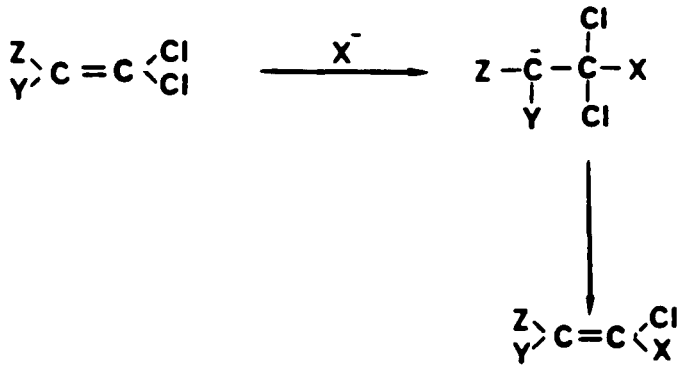
23



24

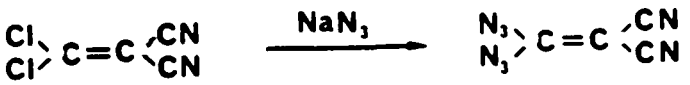
Ordinary vinylic halides are generally unreactive in S_N1 reactions. The first step of the general mechanism for an S_N1 reaction is:

Vinylic cations are highly unstable and this explains the difficulty in forming them in S_N1 reactions. The electrons of the π-bond repel an approaching nucleophilic group. But substitution is generally enhanced in substrates of the type $ZYC{=}CCl_2$, where Z and Y are electron-withdrawing groups such as HCO-, RCO-, EtOOC-, ArSO2-, NC-, -F, because of the stabilization of the intermediate carbanions by these groups:



A nucleophilic substitution reaction analogous to that of Saalfrank occurred from the reaction of 1,1-dichloro-2,2-dicyanoethylene with sodium azide in aqueous acetone to

produce 1,1-diazido-2,2-dicyanoethylene, 25.[27] The IR spectrum showed the characteristic $-N_3$ band at 2160 cm^{-1}.



21 25

1,1-Diazido-2,2-dicyanoethylene, 25, is a colorless liquid which changes to deep red in air at room temperature. Efforts, with great caution, towards the solidification and purification of 25 failed.[27]

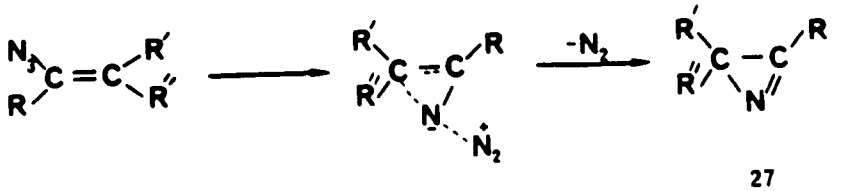
Addition of the freshly prepared azide 25 to warm (55-65°C) benzene, toluene, or 1,2-dichloroethane and subsequent analysis of the reaction mixture by spectroscopic methods showed the formation of the novel imine 26.

25 26

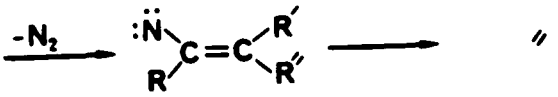
Evaporation of the solvent under reduced pressure resulted in the rapid formation of a light yellow solid whose IR spectrum does not show the characteristic C=N stretching. Our efforts towards the isolation of 26 were frustrated by its rapid polymerization as evidenced by the absence of the C=N stretching and the presence of the CN

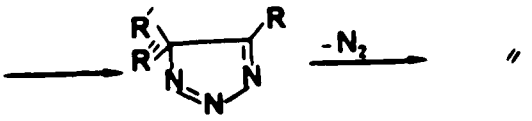
stretchings at 2216 and 2151 cm^{-1}. A solution of **26** in benzene remains unchanged for two days at 5-10°C, and indefinitely in toluene at -45°C as evidenced by its IR spectrum. The IR spectrum of this solution shows the characteristic C=N stretching at 1714 cm^{-1} and -CN stretching at 2323, 2246, and 2240 cm^{-1}. No azide absorption at 2160 cm^{-1} was present. The ^{13}C NMR spectrum of a dilute solution of **26** in deuterated benzene showed three peaks at 107.5, 109.3, and 110.1 ppm characteristic of the three nitrile groups.

Although thermolysis and photolysis of vinyl azides to azirines **27** are well established and synthetically useful,[28,29] their mechanistic pathway has not yet been clearly established. Three major pathways have been proposed for these transformations:[30] a) loss of nitrogen occurring concertedly with ring formation; b) the intermediacy of a vinyl nitrene (presumably a singlet) which can undergo symmetry-allowed electrocyclic ring closure; c) intramolecular [3+2] cycloaddition of the azido group to the double bond followed by loss of N_2 from an intermediate triazole:

a) 

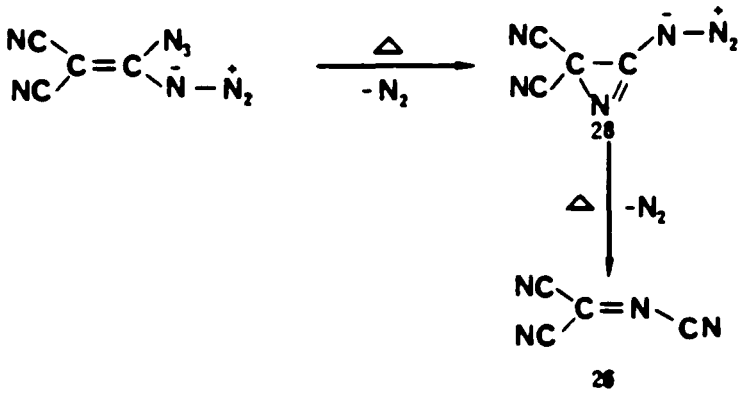
27

b) // 

c) // 

We assume (without evidence) that on heating 25 initially undergoes a 3,5-ring closure with elimination of nitrogen. The resulting azido azirine 28 then undergoes further loss of a nitrogen molecule and rearranges to form the imine 26 (Scheme 5).

Scheme 5:



28

26

Cyclic voltammetry of a $5x10^{-4}$ M benzene solution of 26 showed an irreversible peak at -0.16 V in 0.1 M tetrabutylammonium tetrafluoroborate in dichloromethane using Ag/0.1 M AgNO3 in acetonitrile as a reference electrode and an scan rate of 100 mV/sec. For comparison, under the same conditions TCNE showed a reversible peak at -0.11 V.

AM1 molecular orbital calculation [31](Table 2) found that the lowest unoccupied molecular orbital (LUMO) level for 26 (-2.19 eV) lies at higher energy than the LUMO for tetracyanoethylene (TCNE, -2.52 eV) which is consistent with the electrochemical results. On the other hand, the highest occupied molecular orbital (HOMO) for 26 lies -0.8 eV lower in energy than the HOMO of TCNE. The heat of formation of 26 is 135.3 Kcal/mole, and it is thermodynamically more stable than TCNE by 17 Kcal/mole.

Synthesis of Methyl 3-Aza-α,ß-dicyanoacrylate, 39.

At first we attempted the synthesis of 39 via a precursor similar to 1,1-dichloro-2,2-dicyanoethylene, 21, namely 3,3-dichloro-2-cyanoacrylate, 31. But all of our efforts failed. Then we used the literature method.[32,33]

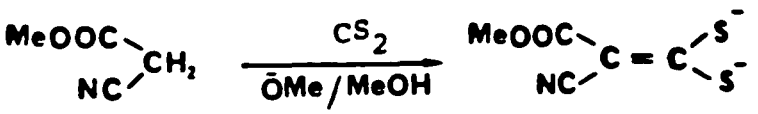
From the reaction of methyl cyanoacetate with carbon disulfide in the presence of sodium methoxide in methanol,

TABLE 2

AM1 Molecular Orbital Calculation

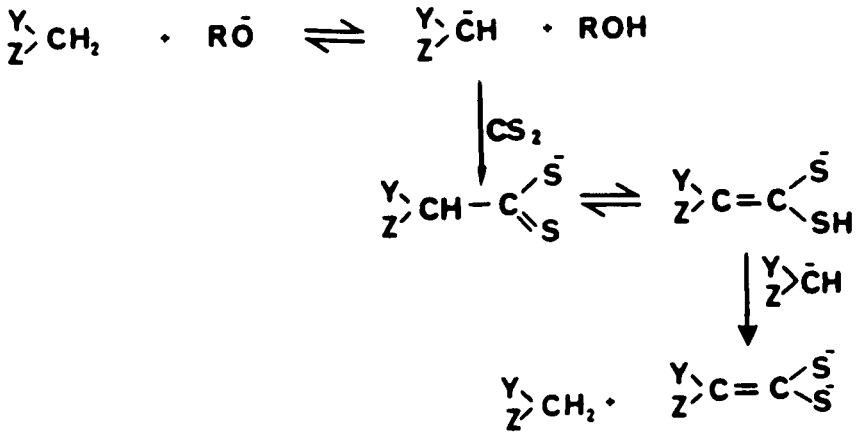
Compound	E_{HOMO} eV	E_{LUMO} eV	Heat of Formation Kcal/mole
26	-12.32	-2.19	135.2
39(cis)	-11.36	-1.71	-0.8
39(trans)	-11.86	-2.02	21.2
45	-11.58	-1.56	-94.7
TCNE	-11.52	-2.52	152.4

methyl disodium 2,2-dithiolato-1-cyanoacrylate, 29, was obtained.



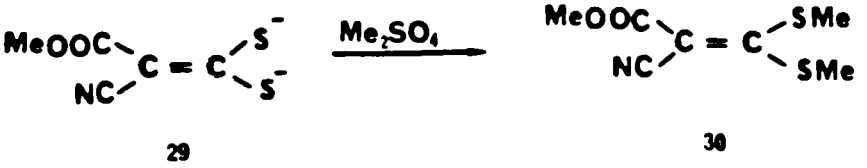
29

The suggested mechanism by Gompper and Topfl[32] is the formation of the enolate and its subsequent nucleophilic attack on carbon disulfide to form the thiol-thiolate intermediate which then undergoes an acid-base reaction with the original enolate to generate the disulfide 29.



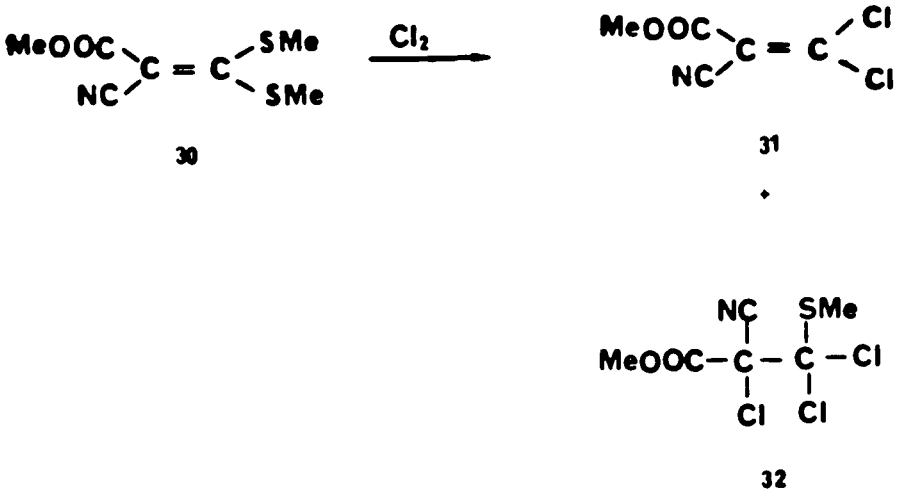
Y = COOMe , Z = CN , R = CH_3

Disulfide 29 was reacted with dimethyl sulfate to form the corresponding thioether 30.



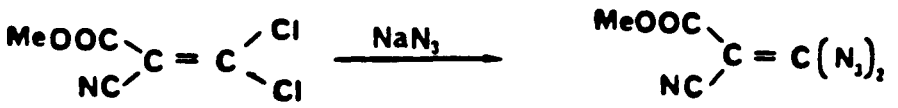
29 30

Chlorination of 30 in glacial acetic acid produced a mixture of substitution and addition products, 31 and 32, respectively, which were separated by distillation under reduced pressure.[33]



30 31 32

Reaction of sodium azide with 31 in aqueous acetone afforded methyl 3,3-diazido-2-cyanoacrylate 33.



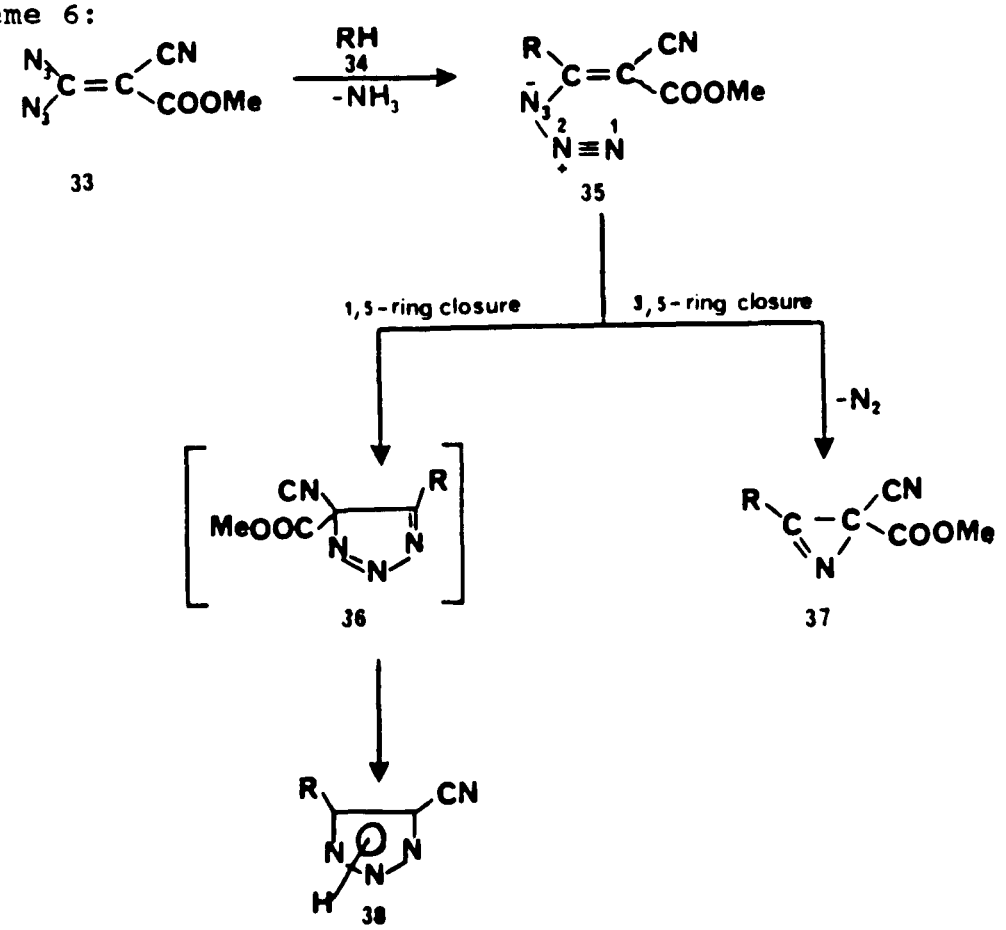
31 33

The IR spectrum showed the characteristic -CN and $-N_3$ bands at 2180 and 2160 cm^{-1}, respectively, and the C=O band at 1710 cm^{-1}. The ^1H NMR showed a singlet at 3.87 ppm for the -OMe group.

Pure methyl 3,3-diazido-2-cyanoacrylate 33 is a white crystalline solid which changes to lemon yellow immediately in the air. However, it is more stable than 1,1-diazido-2,2-dicyanoethylene, 25. Methyl 3,3-diazido-2-cyano-acrylate, 33, remains unchanged at room temperature for two days while 25 decomposes rapidly as judged by their IR and NMR spectra. Thus we recommend the preparation and immediate use of 25 in the subsequent reaction.

Reaction of methyl 3,3-diazido-2-cyanoacrylate 33 with amines 34 primarily leads to some remarkably stable donor substituted vinyl azides 35.[28] These undergo a 1,5-cyclization reaction and form 1,2,3-triazoles 38 via 4H-1,2,3-triazole 36. In the special case of a 3,5-cyclization the intermediate 35 gives 2H-azirines 37 (Scheme 6).

Scheme 6:



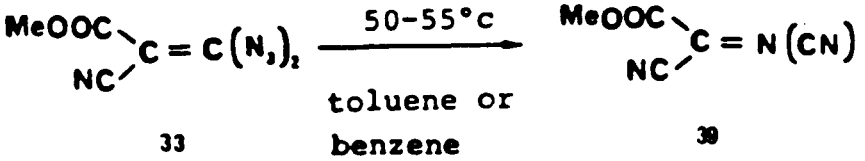
a, R=1-Adamantylamino e, R=Diethylamino

b, R=Pyrrolidino f, R=Thiomorpholino

c, R=Piperidino g, R=4-Methyl-1-piperazinyl

d, R=Morpholine h, R=4-Benzyl-1-piperazinyl

Thermolysis of vinylazide 33 in benzene or toluene formed methyl 3-aza-α,ß-dicyanoacrylate 39 in the solution. Again, we were unable to isolate 39 due to its high reactivity so we studied it in solution.



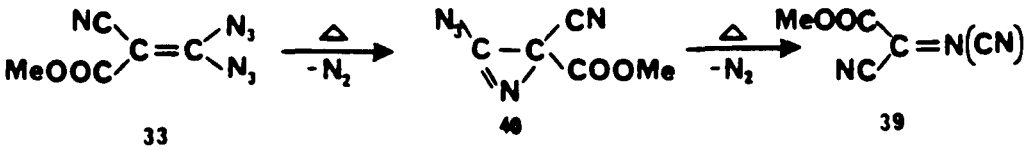
33 39

The ^{1}H NMR spectrum of 39 in d_6-benzene (fig 1) shows two methyl resonances at 2.9 and 3.1 ppm with a ratio of 43:57%. This is an indication of the presence of cis and trans isomers for this compound:

This geometric isomerism is better manifested in the ^{13}C NMR spectrum of 39 in which in addition to two resonances for the two distinct methyl groups at 53.5 and 54.0 ppm there are four well separated peaks for the nitrile groups at 109.0, 109.4, 110.5, and 112.0 ppm and two peaks for the carbonyl groups of the two isomers at 149.0 and 150.6 ppm. Coindidently, there is only one peak for the carbon of the imino group at 152.5 ppm.

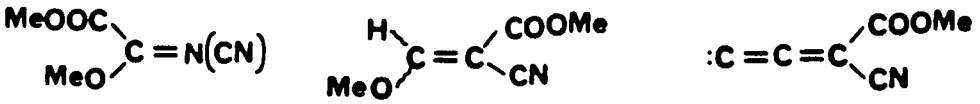
A probable mechanism for the formation of 39 is the loss of a mole of nitrogen and subsequent formation of an azidoazirine 40 which on heating loses another molecule of nitrogen and rearranges to 39 (Scheme 7).

Scheme 7:



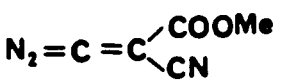
33 40 39

Saalfrank and coworkers[26,28] have shown that irradiation of 33 in methanol at -30°C results in the formation of methyl 2-(N-cyanimino)-2-methoxyacetate 41 in 70% yield along with photoproduct 42 (30%). They suggested that 42 results from insertion of the intermediate alkylidene carbene 43 into the H-O bond of methanol.



41 42 43

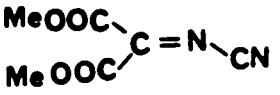
It is still unclear, however, which other intermediates are involved in the formation of 42. A further possible route to the vinyl ether 42 is the addition of methanol to the diazoethane 44 which results in the formation of the corresponding vinyldiazonium methoxide, followed by decomposition.



44

AM1 molecular orbital calculation,[31] (Table 2) showed that the lowest unoccupied molecular orbital (LUMO) of 39 (cis, -1.71 eV ; trans, -2.02 eV) lies at higher energy than the LUMO of TCNE and tricyanomethaneimine 26. On the other hand, the highest occupied molecular orbital of cis-39 (-11.36 eV) lies higher than the HOMO for TCNE and tricyanomethanimine 26. The highest occupied molecular orbital of trans-39 (11.86 eV) lies higher than that of 26. The heat of formation of cis-39 is -0.8 Kcal/mole and 21.2 Kcal/mole for trans-39 and it is thermodynamically much more stable than the tricyanomethanimine 26 by 135.2 Kcal/mole.

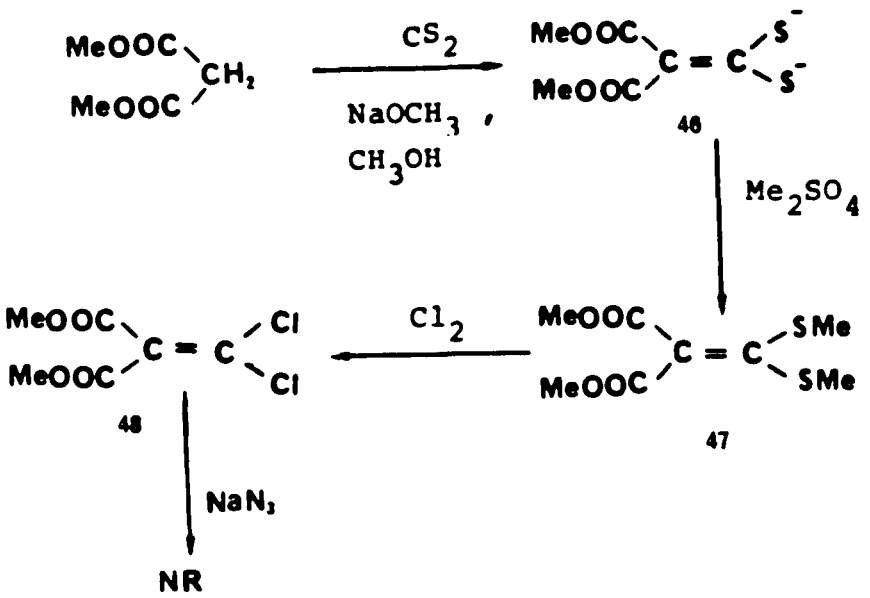
The results of these calculations indicate that the exchange of a nitrile group of tricyanomethanimine 26 with a methoxycarbonyl, 39, stabilized it by 136 Kcal/mole. When these computations were extended to compound 45 (not yet synthesized) in which two nitrile groups of 26 are exchanged with two methoxycarbonyl functionalities, it was found that the LUMO of 45 (-1.56 eV) lies even at higher energy than the LUMO's of TCNE, tricyanomethanimine 26, and methyl 3-aza-α,ß-dicyanoacrylate 39, Table 2.



45

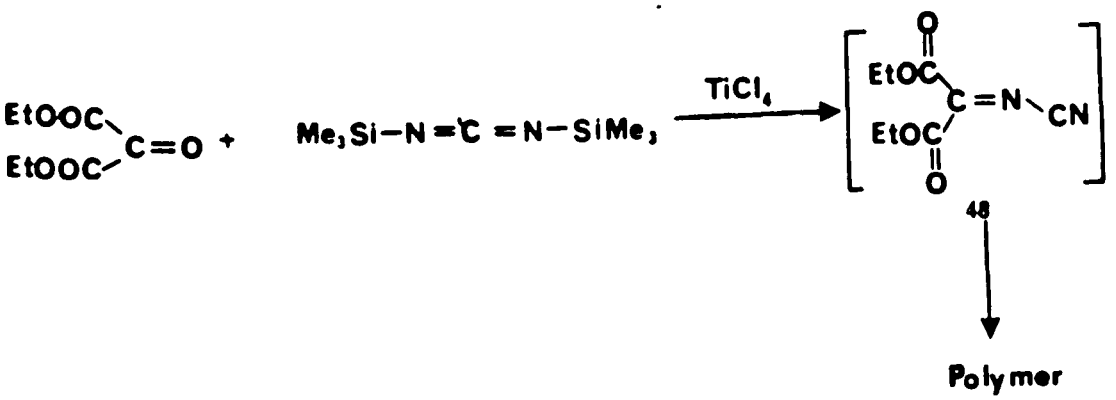
The HOMO of 45 (-11.58 eV) is close to TCNE. The heat of formation of 45 is -94.71 Kcal/mole. These theoretical calculations show that compound 45 is expected to be thermodynamically more stable than the others. Encouraged by these results we set out to synthesize the novel imine 45. Based on our successful experience in the synthesis of 39 we planned on the synthesis shown in Scheme 8.

Scheme 8:



The synthesis of 1,1-dichloro-2,2-dimethoxycarbonyl ethylene, 48, was accomplished in 61% yield.[32,33] However, we were surprised to find that this dichloride, in contrast to its analogs 21 and 31, does not react with sodium azide even

at temperatures as high as ambient temperature. It appears that at least one cyano group is required for sufficient activation. At this stage we decided to change our synthetic approach by reacting the commercially available diethyl ketomalonate with bis(trimethylsilyl)carbodiimide[35] to generate the ethyl ester analog of 49.[36] The infrared spectrum of the dilute solution indicated the presence of C=N in the molecule but again efforts towards the isolation of the imine were frustrated by its rapid polymerization.

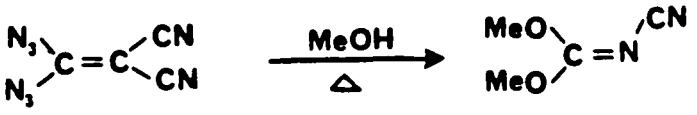


None of the N-cyanomethanimines synthesized in this study could not be isolated. They all polymerize (oligomerized) when the solvent was removed even in the presence of radical inhibitors or acid. This instability could be due to the high electrophilic character of these compounds which makes them very susceptible to anionic and/or free radical polymerization.

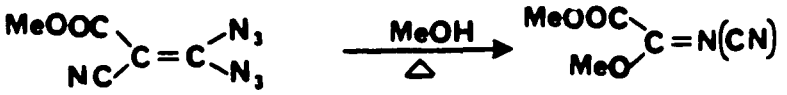
REACTIONS

Methanolysis:

Addition of azido compounds 1,1-diazido-2,2-dicyanoethylene 25, and methyl 3,3-diazido-2-cyanoacrylate 33 to methanol at 50- 55°C resulted in the formation of the white crystalline dimethyl N-cyanoimidocarbonate 50 (^{1}H NMR and MS) and methyl 2-(N-cyanimino)-2-methoxyacetate 41.



25 50



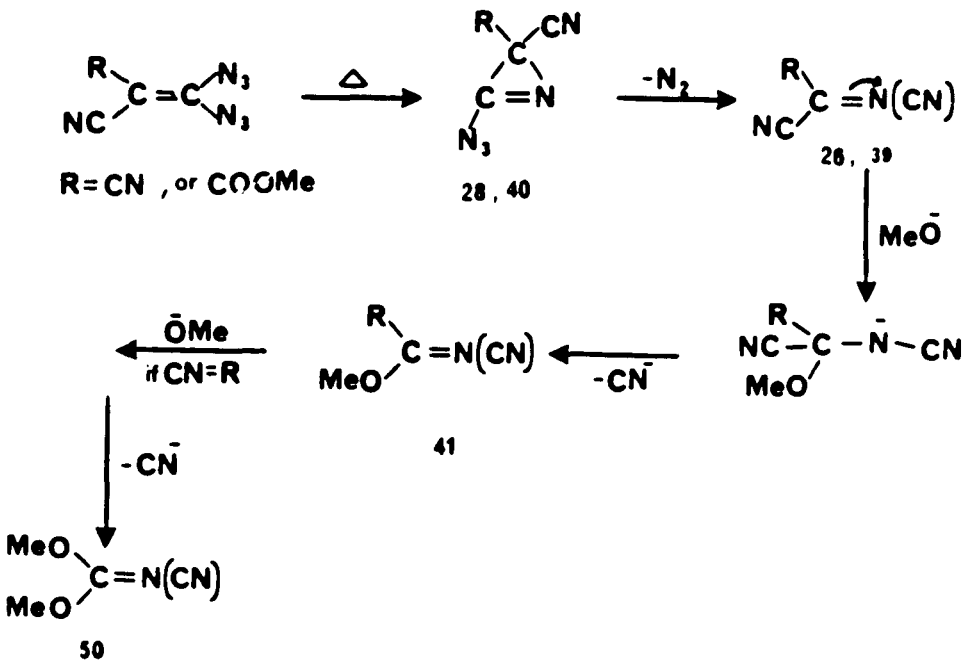
33 41

A synthesis of 50 patented by Jenko and coworkers[37] involves the reaction of sodium cyanamide in NaOH-MeOH-H_2O at 0°C with chlorine and the successive treatment of the reaction mixture with HCl to pH 7, CH_2Cl_2, $NCNH_2$ in H_2O and HCl, and heating to 15°C to give 50 in 90% yield. No spectroscopic data were reported for this compound.

The structure of methyl 2-(N-cyanimino)-2-methoxyacetate, 41, was confirmed by comparison with the data reported by Saalfrank and coworkers.[26,28]

The mechanism of these reactions (Scheme 9) are similar to what was discussed before involving thermolysis of a vinylazide and S_N1 reaction of the intermediate vinyl halide. It appears that aziridines 28 and 40 undergo loss of nitrogen followed by rearrangement to form the imines 26 and 39. Addition of one or two moles of methanol to the intermediate imine and elimination of hydrogen cyanide affords dimethylcarbonate N-cyanoimide 50, and methyl 2-(N-cyanimino)-2-methyoxyacetate 41.

Scheme 9:



This is supported by the following experiment. When a toluene solution of 39 was reacted with methanol at room temperature 41 was formed as an isomeric mixture.

Cycloaddition Reactions:

Reaction of a benzene solution of **26** or **39** with 2,3-dimethyl-1,3-butadiene or cyclopentadiene at room temperature under argon pressure afforded the corresponding adducts **51-54** as crystalline solids (Scheme 10). These adducts were characterized by spectroscopic methods and elemental analysis.

Scheme 10:

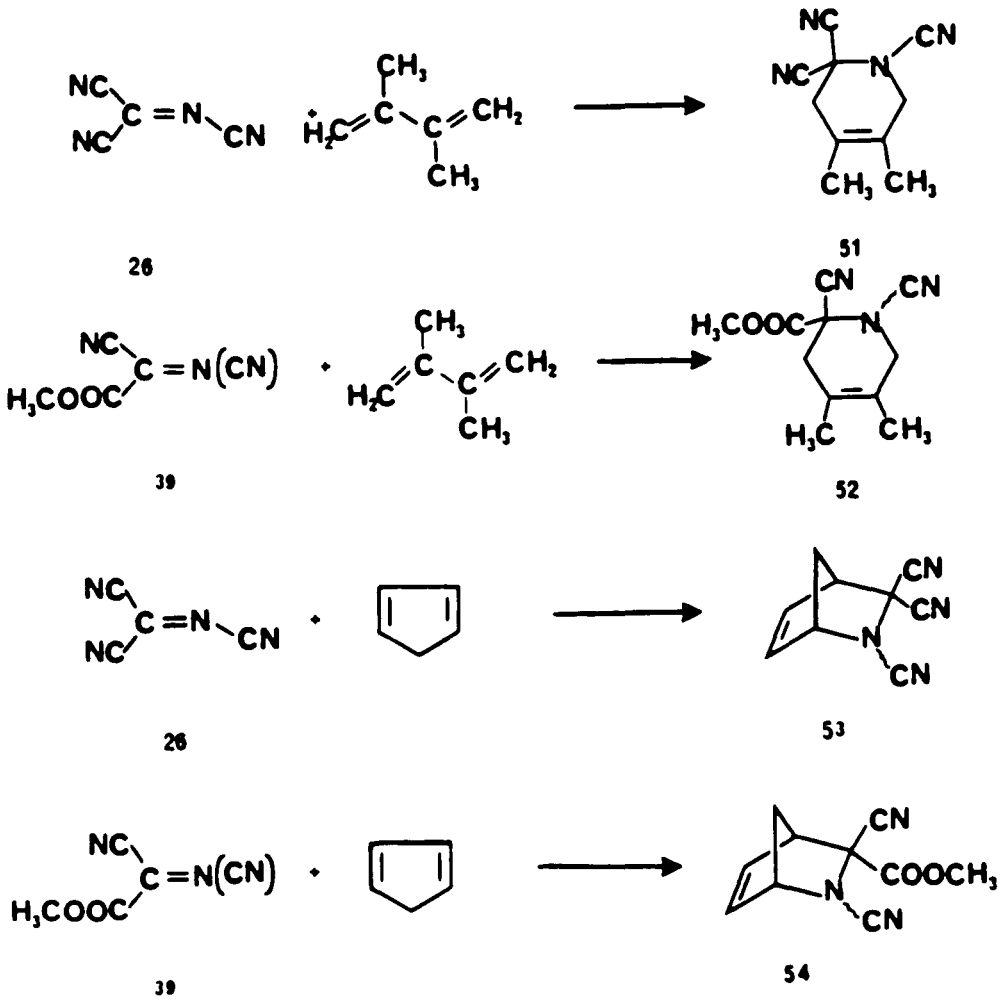
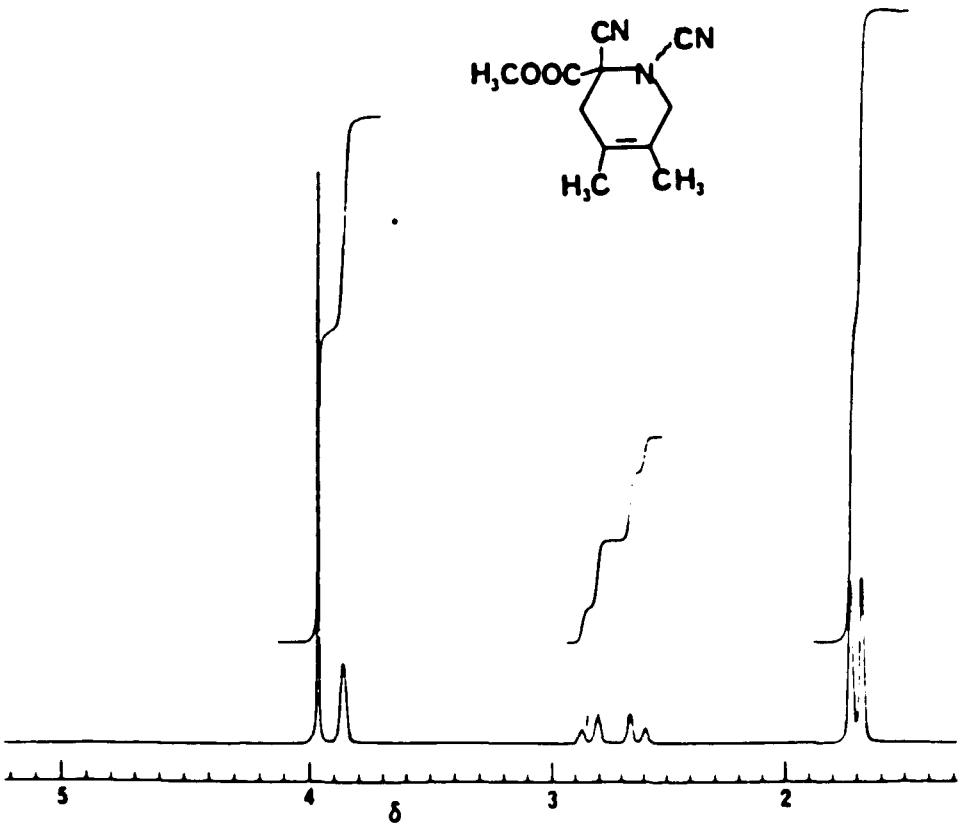
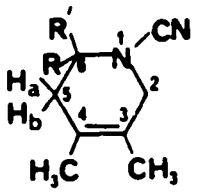


FIGURE 1 ^{1}H NMR Spectrum of 52

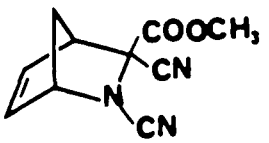


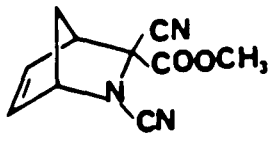
The ^1H NMR spectra of adducts 51 and 52 are similar to each other. The methylene protons adjacent to nitrogen absorb at lower field than the others. The allylic protons of the two methyl groups absorb at slightly different positions (δ ~0.05 ppm). The allylic hydrogens H_{5a} and H_{5b} in the tricyanomethanimine adduct 51 give a broad singlet which is an indication of the rapid interconversion of the two conformations at room temperature. However, in methyl 3-aza-α,ß-dicyanoacrylate adduct 52 these two protons are coupled to each other with a geminal coupling constant of 17.7 Hz. (Fig. 1). This is expected since they are α to a chiral center.



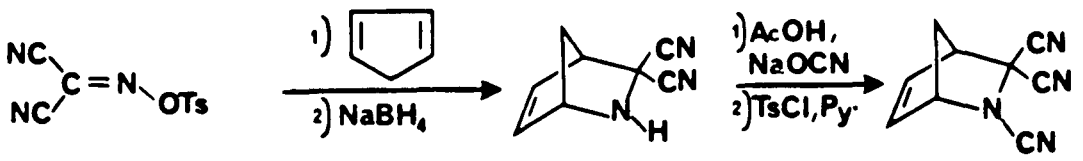
R = R' = CN or R = CN , R' = $COOCH_3$

Adduct 54 is a mixture of two stereoisomers which we were unable to separate:





Cycloadduct 53 was characterized by comparison with the material prepared previously by the following route.[38]



To explore the possibility of producing these novel imines in a pure state which would permit the study of their polymerizations we set out to extrude the imines from the corresponding adducts by retro Diels-Alder reactions of the adducts 51 and 52. Pyrolyses were carried out in a quartz tube packed with quartz fragments at 750°C and at 0.1 mm Hg. No imine formation was observed. Instead, polymeric compounds and/or unreacted adducts were recovered.

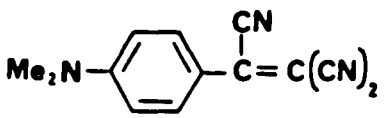
Attempted cycloaddition reaction of the dilute solution of diethyl N-cyanomethaniminedicarboxyalte, 49, with 2,3-dimethylbutadiene always resulted in polymerization of the diene. The catalytic amount of titanium tetrachloride was still present in the toluene solution and initiated the cationic polymerization of butadiene. Therefore, the cycloaddition of 49 could not be studied.

Electrophilic Aromatic Substitution

Deeply colored charge transfer complexes were obtained from the reaction of 26 with moderately electron-rich compounds such as anisole or hexamethylbenzene. The more electron-rich N,N-dimethylaniline underwent electrophilic aromatic substitution to give 55.

26 55

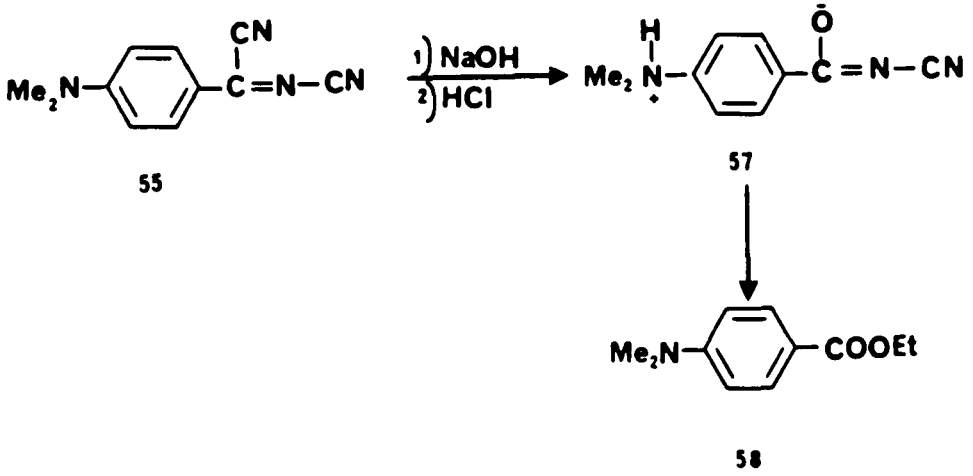
This is similar to the reaction of TCNE with N,N-dimethylaniline which was reported by McKusick.[39] TCNE readily reacts with both tertiary and secondary aromatic amines, attacking the ring to give 4-tricyanovinyl-N,N-dimethylaniline 56.



56

Compound 55 is a red crystalline solid which decomposes at 234-235°C. The IR spectrum shows the characteristic CN stretching band at 2173 cm^{-1} and the C=N band at 1612 cm^{-1}. The ^1H NMR shows two sets of chemically nonequivalent protons for the benzene ring at 6.8 and 8.0

ppm in addition to a singlet at 3.2 ppm for the methyl group. Further proof for the structure of 55 came from its stepwise hydrolysis in the presence of ethanol which afforded the known ethyl 4-dimethylaminobenzoate, 58, presumably through intermediate 57.



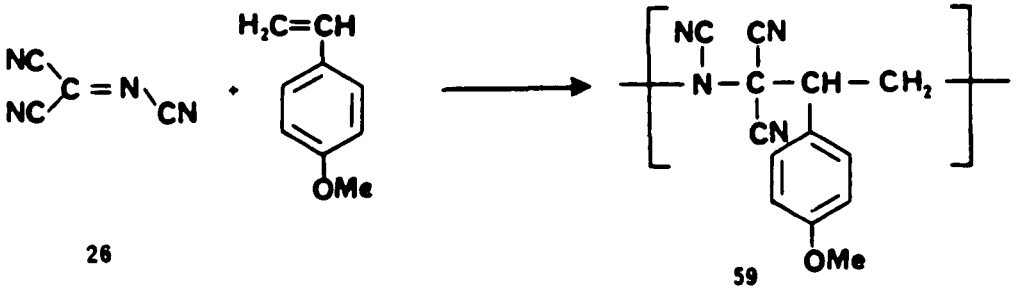
55 57 58

Intermediate 57 is a strong acid. It is formulated as a zwitterion on the basis of its infrared spectrum (3500 cm^{-1} for NH) like TCNE. However, reaction of 39 with N,N-dimethylaniline resulted in the formation of a colored solution. This is an indication of the greater reactivity of 26 over 39 in electrophilic aromatic substitutions.

Polymerization

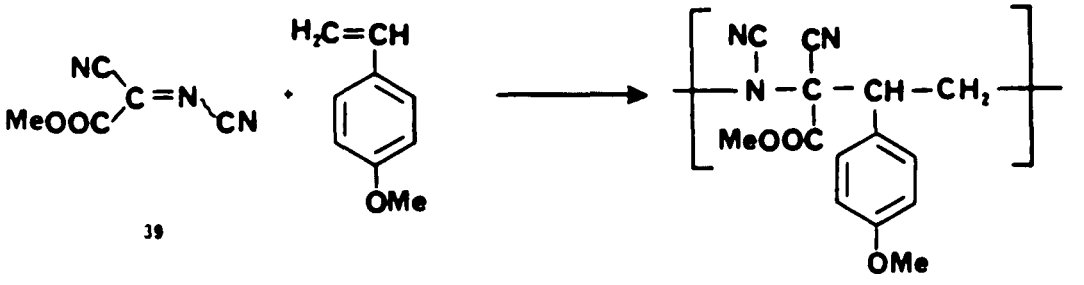
The electrophilic imines 26 and 39 polymerized spontaneously upon attempted isolation. These polymers (or oligomers) are completely insoluble in organic solvents and can only be characterized by infrared spectroscopy and chemical analysis. They are yellow powders which do not melt but decompose at temperatures above 120°C.

Spontaneous copolymerization of 26 and 39 with p-methoxystyrene produced copolymers 59 and 60, respectively, which based on NMR and chemical analysis were almost perfectly alternating.



26

59

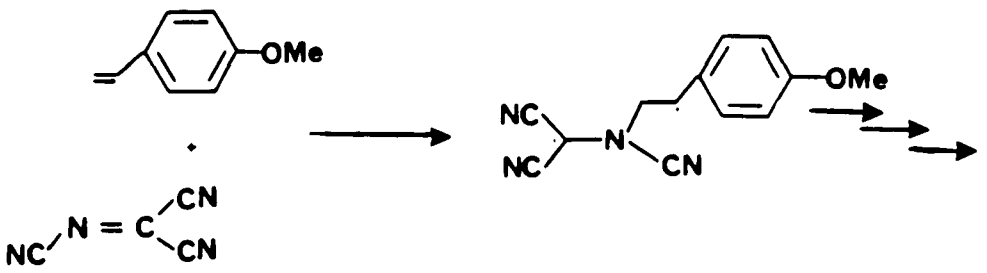


39

60

Copolymer 59 was soluble in chloroform. The backbone methylene protons are observed at 3.7 ppm in the NMR spectrum, confirming the structure of the polymer as shown. Size exclusion chromatography revealed a maximum of 2000 versus polystyrene standards. Copolymer 60 was insoluble in chloroform, but soluble in DMSO. The NMR spectrum confirms structure 60.

In the spontaneous copolymerization the initiation step can be explained in terms of our Bond-Forming Initiation Theory, in which a tetramethylene intermediate is the initiator. In this case, the initiation would be presented in the following way:



An equivalent mixture of 26 and styrene did not result in the formation of a copolymer. The reaction was run both with and without radical initiator. In both cases the homopolymer of 26 was the only product in both instances.

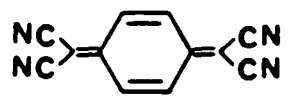
CHAPTER 3

SYNTHESIS AND SPONTANEOUS POLYMERIZATION OF 7,8-DICYANO-7-ETHOXYCARBONYL-8-PHENYLQUINODIMETHANE

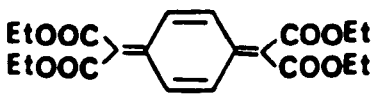
BACKGROUND

Polymerization Behavior of 7,8 Acceptor Group Substituted Quinodimethanes.

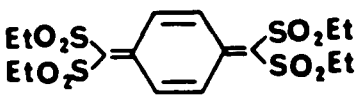
The identity of the acceptor group in homosubstituted quinodimethanes greatly affects the polymerizability of the compound.



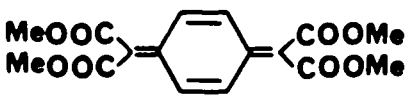
61



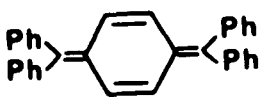
63



62



64

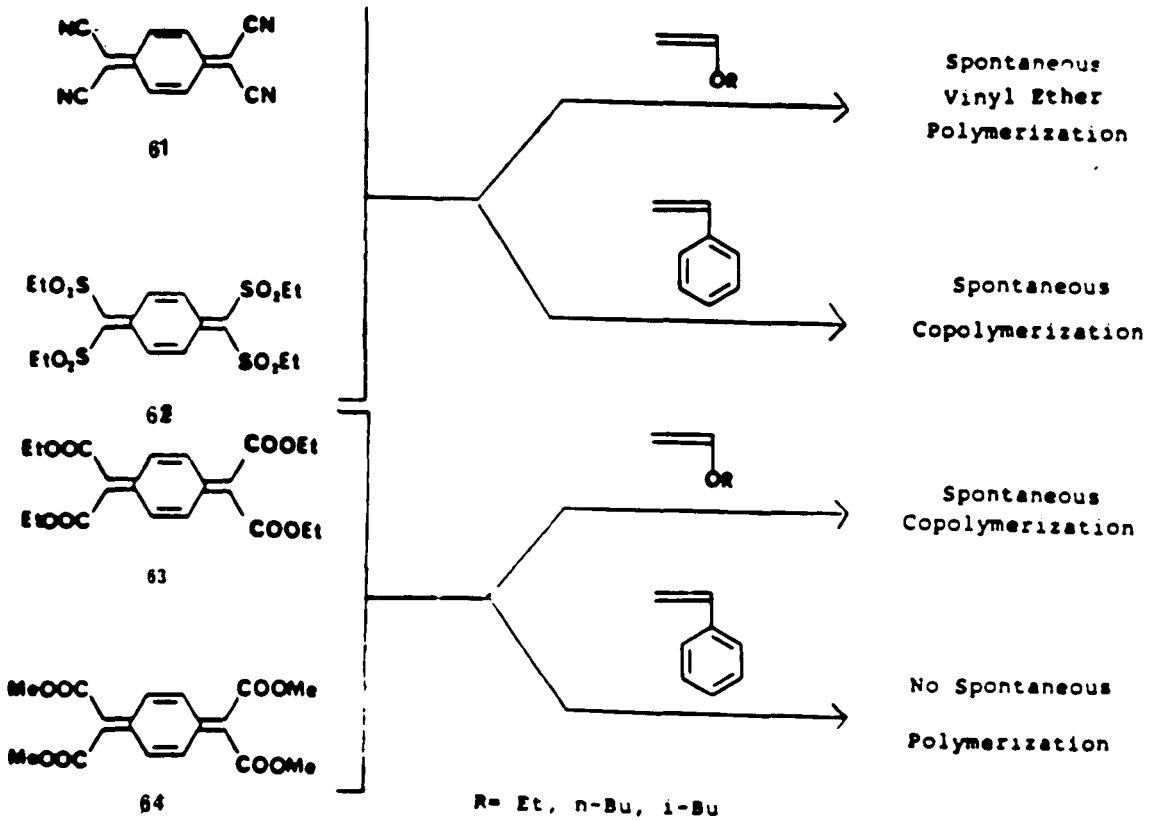


65

Tetracyanoquinodimethane (TCNQ, 61) and tetraethoxysulfonyl-quinodimethane (TESQ, 62) do not homo-polymerize.[40,41]

Tetraethoxycarbonylquinodimethane (TECQ, 63) is difficult to homopolymerize while its methyl ester analog (TMCQ, 64) homopolymerizes [41] spontaneously at room temperature.[43] Spontaneous copolymerizations between these acceptor substituted quinodimethanes and olefins have been extensively investigated.[42-45] The spontaneous copolymerization behavior of the homosubstituted quinodimethanes with donor monomers is summarized below in Scheme 11.

Scheme 11:



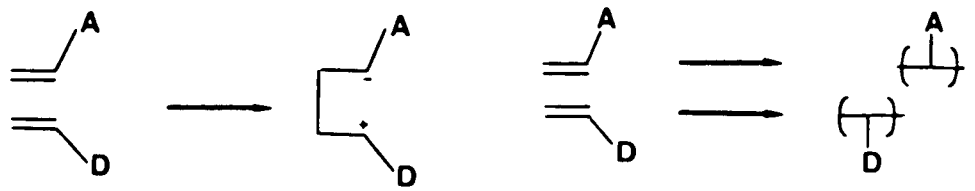
When the difference in electron density is large, spontaneous homopolymerization of donor monomer results. Intermediate differences in electron density lead to copolymerizations and small differences do not give spontaneous polymerizations.

Tetraphenylquinodimethane 65 was described by Thiele and Balhorn in 1904[46] and it was completely stable to polymerization.

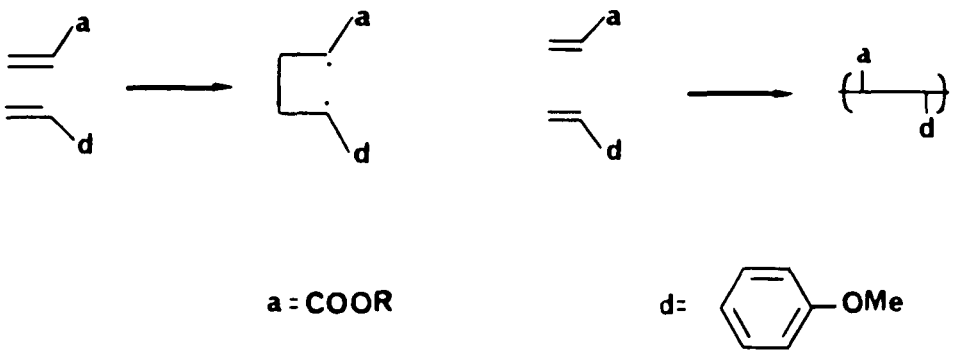
Bond-forming Initiation

Hall has proposed that spontaneous polymerizations between electron-rich and electron-poor olefins are initiated by a tetramethylene species which is the result of bond formation[47] (Scheme 12).

Scheme 12:

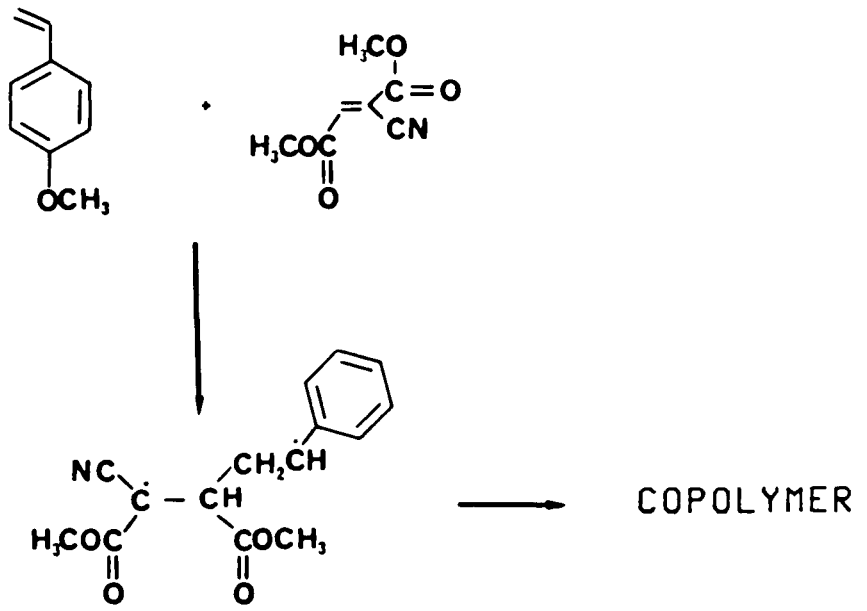


A = CN D = NR_2



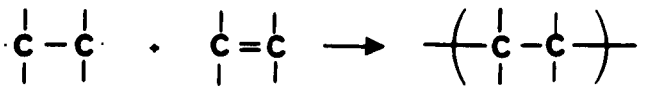
The tetramethylene may be written as a zwitterion or diradical. The form in which it actually exists is considered to be a resonance hybrid of the two. When the difference in monomer electron density is large (when there are strongly electron- accepting group(s) at one tetramethylene terminus and strongly electron-donating group(s) at the other) the tetramethylene is highly zwitterionic in character. The spontaneous homopolymerizations which occur in such systems may be attributed to cationic homopolymerization initiated by the donor terminus or anionic polymerization beginning at the acceptor terminus. In case where the donor and acceptor groups are not as strong, the tetramethylene is expected to be highly diradical in character. The spontaneous copolymerizations observed between olefin monomers are attributed to initiation by one of both of these termini. The spontaneous copolymerization of dimethyl cyanofumarate

and p-MeOSt was recently studied in exhaustive detail.[48] Kinetic studies and trapping experiments strongly supported bond formation resulting in a diradical tetramethylene as the initiation step:

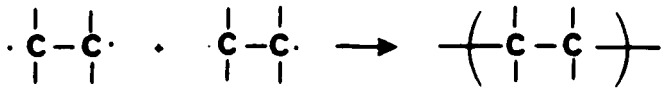


It should be noted that there are two possible modes of propagation following diradical formation: chain growth in which monomer adds to the radical center and radical coupling in which diradical species consisting of two or more monomers combine:

Chain growth:



Radical coupling:

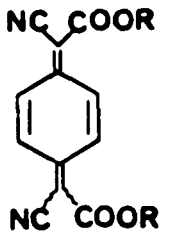


In either case radical coupling or monomer addition does not result in termination. Bond formation initiation theory has been supported by a large amount of experimental evidence and more recently by theoretical calculations.[49]

7,8,7,8 Acceptor Group Substituted Quinodimethanes

In 1982 groups at the University of Arizona and Mie University in Japan reported the synthesis of two new quinodimethanes: Di(methoxycarbonyl)dicyanoquinodimethane **68a** and its ethyl ester analogs **66b**. These were the first examples of exocyclic heterosubstituted 7,8,7,8-substituted quinodimethanes. In terms of structure and electron accepting ability the di(alkoxycarbonyl)dicyanoquinodimethanes (DADCQs) are intermediate between TCNQ and the

tetraesterquinodimethanes. As shown by initial studies, the polymerizability of the DADCQs was very different from any of the homosubstituted quinodimethanes. DADCQs homopolymerize with great facility. Homopolymerization can be achieved simply by dissolution of monomer in common solvents. All attempts to copolymerize DADCQs with donor monomers led to only DADCQ homopolymers.



66

a R = Me
b R = Et
c R = Bu

Through the work of Iwatsuke et al. it has become clear that these facile polymerizations occur via an anionic mechanism. Iwatsuki correlated the ability of a solvent to polymerize DADCQs with the basicity of the solvent. Weakly basic solvents such as dimethyl-sulfoxide and methanol initiate rapid polymerization of DADCQ, while neutral solvents such as toluene and chloroform do not act as initiators. Although slow polymerization of DADCQs occurs in these solvents, it may be attributed to nucleophilic impurities. Further evidence for an anionic mechanism was the finding that when the butyl ester DADCQ 66c was combined with St or (p-MeOSt) and radical initiator in acidified solution, copolymerizations resulted. This result showed that DADCQ

homopolymerizations could be effectively inhibited by the addition of acid. Iwatsuki reported that under acidic conditions, with radical initiator, DADCQs copolymerized alternatingly with p-MeOSt and randomly with St.

Spontaneous Polymerizations of Di(ethoxycarbonyl)-dicyanoquinodimethane

Relatively slow spontaneous polymerizations of di(ethoxycarbonyl)dicyanoquinodimethane (DEDCQ) were observed under some of the conditions investigated. The conditions and polymerizations are described in Table 3.[13]

The spontaneous polymerizability of DEDCQ was found to be dependent on rather small changes in polymerization temperature. While polymerizations proceeded at room temperature (23-25°C) they did not occur at 4°C. Furthermore exposure to ambient light accelerated homopolymerization at room temperature. As seen in Table 4, lines 4 and 5, the molecular weights of the homopolymers at 15% and 50% are identical by gel permeation chromatography. From this fact it might be concluded that propagation was occurring by chain addition which predicted that high molecular weight polymer was produced at low conversion.[14]

7,8-Diphenylquinodimethane was much more stable than p-quinodimethane but still underwent spontaneous polymerization at room temperature.[46]

TABLE 3

SPONTANEOUS POLYMERIZATION OF DEDCQ IN DARK AND AMBIENT LIGHT[a]
REACTIONS UNDER DARK CONDITIONS[b]

Run no.	DEDCQ mg	Temp. °C	Time hr.	Yield %	$M_n \times 10^6$
1	125	4	43	-	
2	112	25	25	-	
3	117	25	45	13	1.4
	REACTION IN (FLUORESCENT) AMBIENT LIGHT				
4	115	25	24	15	1.5
5	120	25	45	55	1.5
6	69.0b	25	72	-	
7	117	30	24	20	3.4

a) In 4 mL $CHCl_3$ containing 80 μL CH_3COOH
b) In 3 mL $CHCl_3$ containing 60 μL CH_3COOH and 20 mg tetramethylpiperidinyl oxide

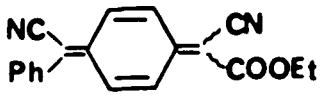
The phenyl-substituted quinodimethane was synthesized by Green in 1985.[13]

7,8-Di(methoxycarbonyl)-7,8-diphenylquinodimethane (DMDPQ) was isolated as a mixture of cis and trans isomers:

The non-polymerizability of DMDPQ resembled that of tetraphenyl-quinodimethane. It was totally inert to both anionic and free radical homopolymerization and copolymerization. Furthermore when a radically polymerizable monomer such as p-MeOSt was stirred in the presence of radical initiator and DMDPQ, it also failed to polymerize. The only reaction which was observed to occur at the 7 and 8 positions was the addition of methanol across the system when the quinodimethane was treated with an excess of sodium methoxide. As with the case of tetraphenylquinodimethane the inert nature of DMDPQ was attributed to steric crowding around the reactive 7,8 positions.

The next phenyl-substituted quinodimethane, 7,8-dicyano-7,8-diphenylquinodimethane (DCDPQ), was synthesized by Brandt in 1988.[50] The resistance to homopolymerization of DCDPQ is similar to that of tetraethoxycarbonyl-quinodimethane 63. With radical initiation DCDPQ did not copolymerize with isobutyl vinyl ether but formed a good yield of copolymer with p-methoxystyrene and p-aminostyrene.

Our interest in quinodimethanes and the spontaneous reaction of electron rich and electron poor monomers led us to synthesize the new unsymmetrical quinodimethane 7,8-dicyano-7-ethoxycarbonyl-8-phenylquinodimethane (DCEPQ 72) and to extend Bond Formation Theory to a new type of monomer.



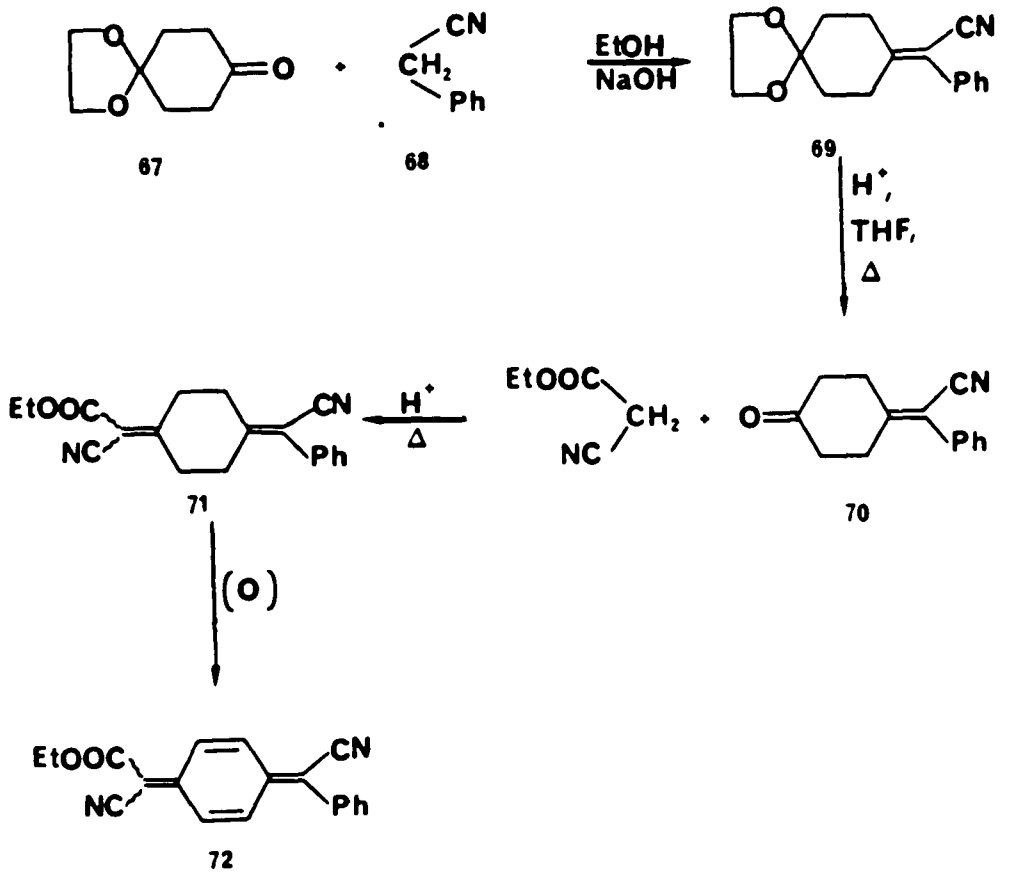
72

RESULTS AND DISCUSSION

1- Synthesis

We planned on synthesizing DCEPQ 72 from 1,4-cyclohexanedione monoethylene ketal, 67, according to Scheme 13.

Scheme 13:



The Knoevenagel reaction[51] of 67 with benzyl cyanide was carried out smoothly at room temperature and in the presence of sodium hydroxide in ethanol. The product 69 was recrystallized from hexanes as a crystalline solid in 70% yield with mp 66.5-67°C. The IR spectrum showed the characteristic -CN at 2206 cm^{-1} and the absence of the exocyclic keto group. The ^1H NMR spectrum (Fig. 2) shows four well separated triplets for the cyclohexyl ring protons at 2.89, 2.50, 1.89, and 1.69 ppm. These four sets of chemically nonequivalent protons are an indication of the loss of symmetry of this molecule as compared to starting ketal 67 which shows only two sets of protons for methylene units and one peak for the ethylene ketal hydrogens.

The mechanism for this first step (Scheme 14) is the formation of carbanion and its subsequent nucleophilic attack on the carbonyl group. Dehydration of the intermediate alcohol 73 produces the product 69.

Figure 2 ^{1}H NMR Spectrum of 69

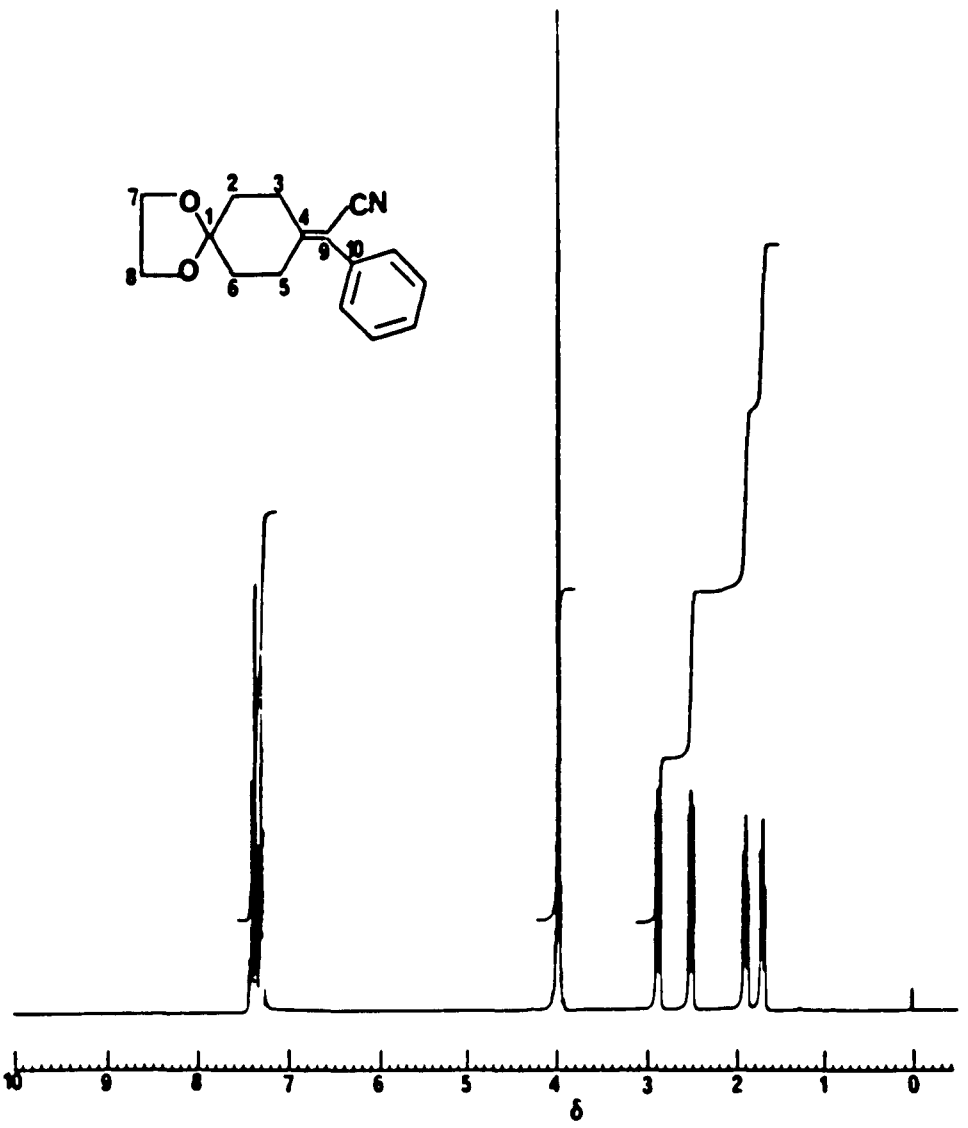
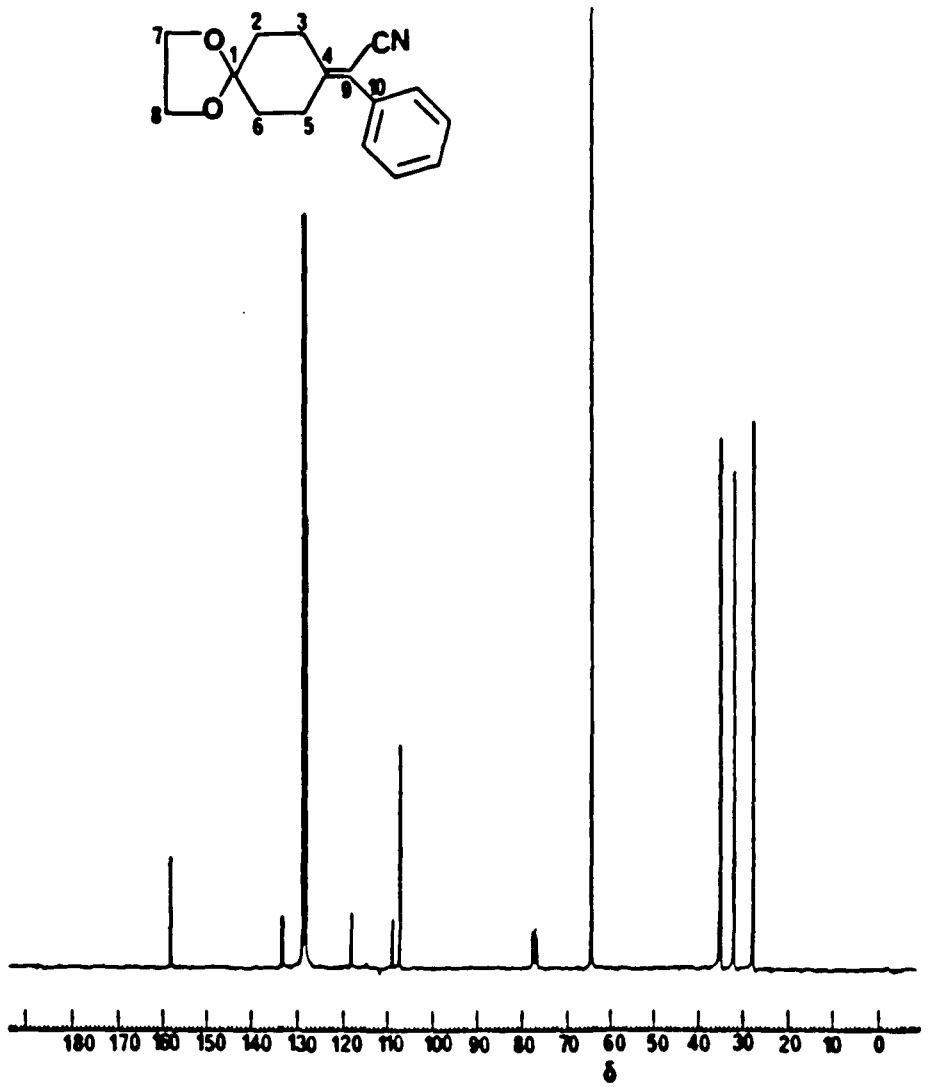
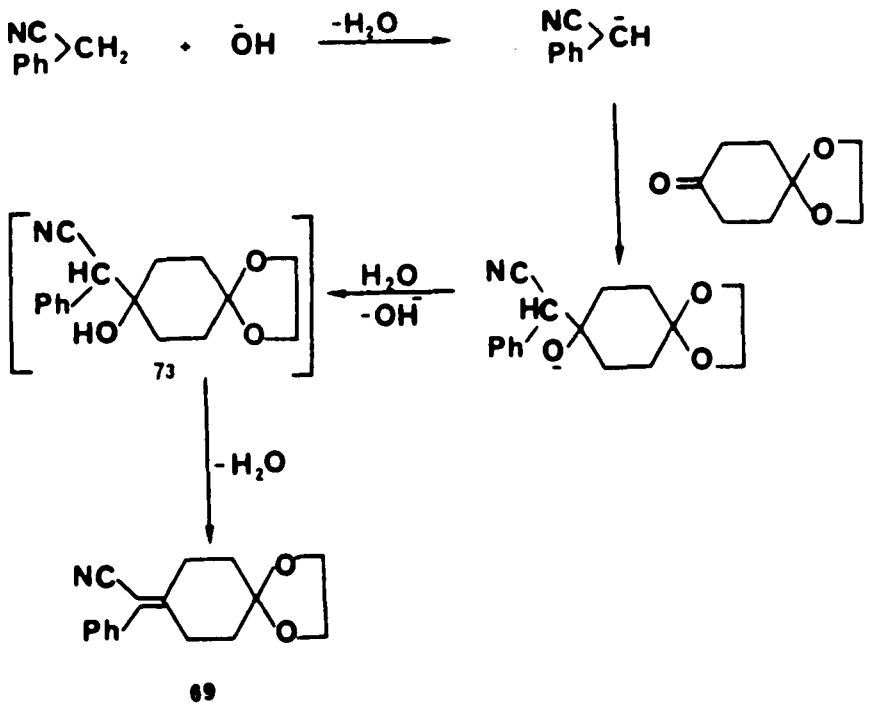


Figure 3 ^{13}C NMR Spectrum of 69



Scheme 14:



Treatment of a solution of 69 in THF with hydrochloric acid removed the protecting group generating the free ketone 70 in 78% yield as a crystalline compound, mp 56-56.5°C. The IR spectrum shows the characteristic carbonyl group at 1712 cm^{-1}. The ^{1}H NMR spectrum (Fig. 4) contains four well defined triplets for the cyclohexyl ring protons at 3.10, 2.77, 2.63, and 2.43 ppm, which show an overall downfield shift with respect to 69. The ^{13}C NMR (Fig. 5) showed the carbonyl resonance at 208.90 ppm.

The synthesis of 1-cyano-1-phenylmethylene-4-cyano-4-ethoxycarbonylmethylenecyclohexane 71 was accomplished by the addition of ethyl cyanoacetate to a benzene solution of

FIGURE 4 ^{1}H NMR Spectrum of 70

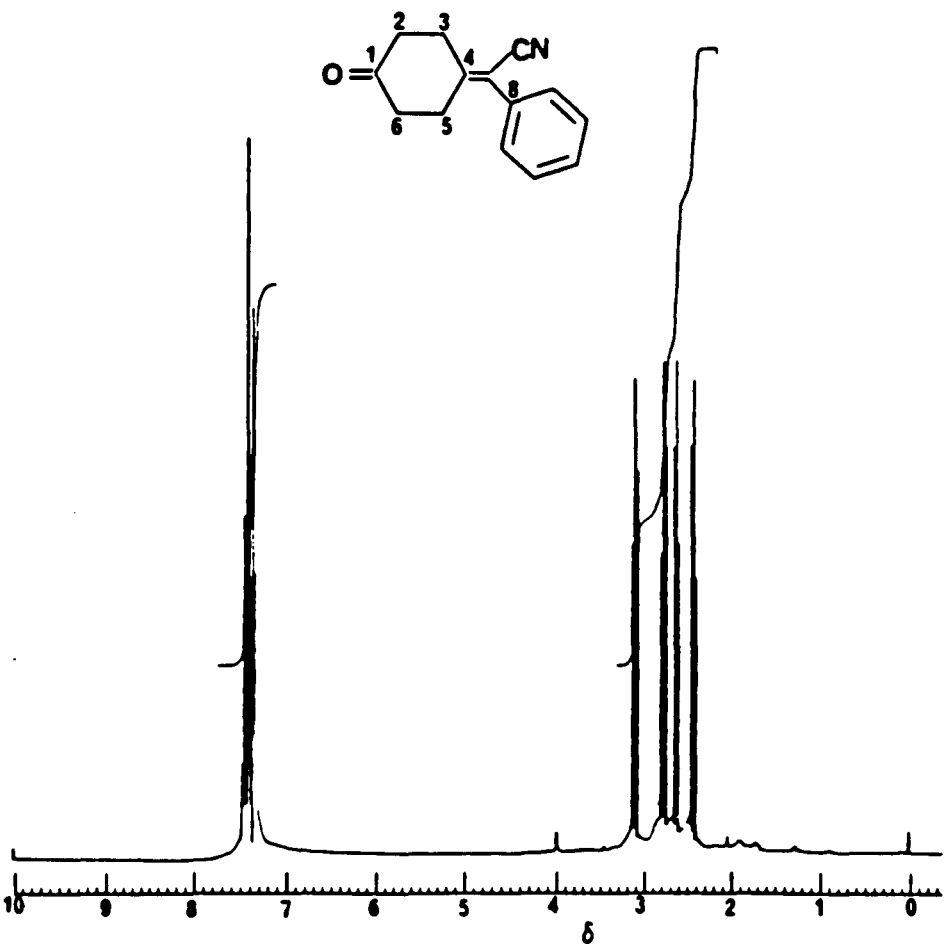
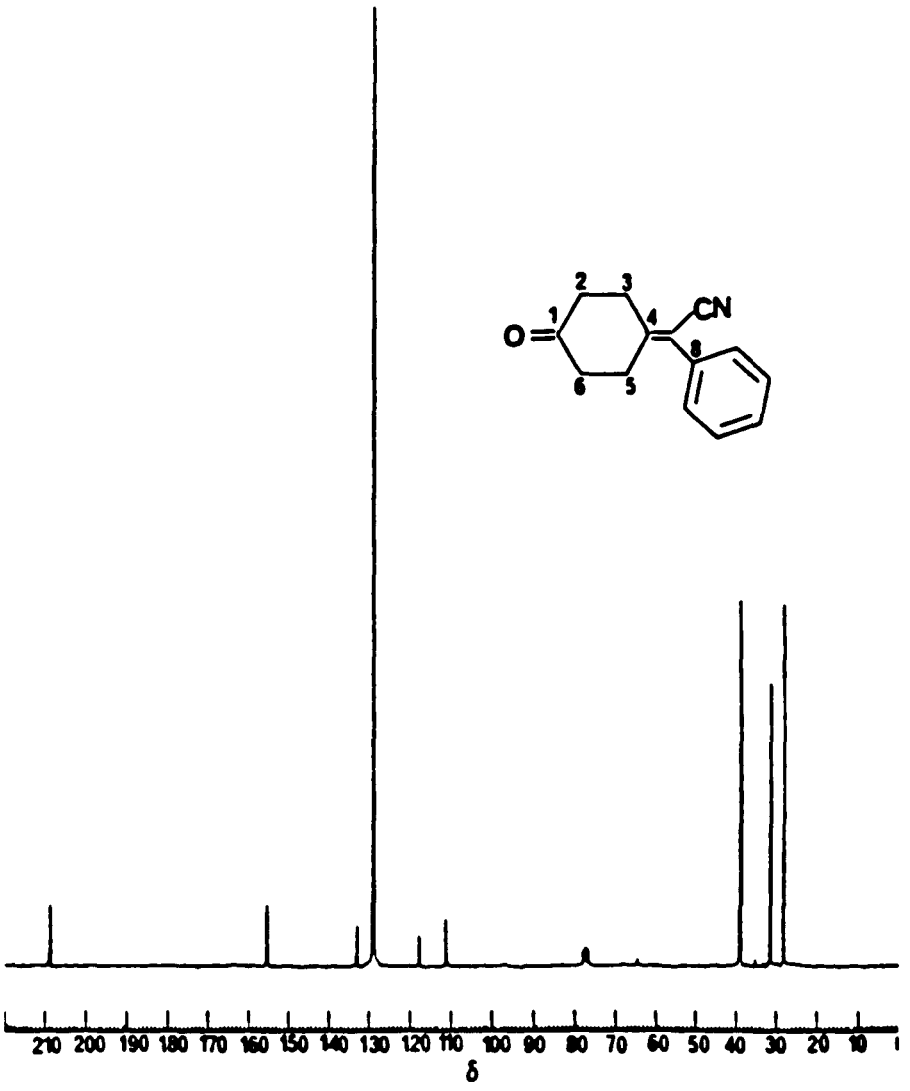


FIGURE 5 ^{13}C NMR Spectrum of 70



70 in the presence of catalytic amount of ß-alanine and acetic acid. Azeotropic distillation of water is needed for completion of the reaction. After separation and purification a 62% yield of 71 was obtained as a white powder, mp 134-135.5°C. The IR spectrum indicated the removal of the exocyclic ketone. The NMR spectra of 71 indicate the presence of two geometric isomers:

^{1}H NMR ($CDCl_3$, Fig. 6) showed that the eight cyclohexyl hydrogens moved to lower field than in the starting material 70 because of the formation of the olefinic bond and the presence of two extra electron-withdrawing groups. The ^{13}C NMR spectrum (Fig. 7) showed a peak at 174.0 ppm for the C=O of the ester group and distinct peaks at 114.0 and 117.0 for the CN groups. The peak corresponding to the carbonyl group of the cyclohexanone moeity was not detected.

The mechanism of formation of 71 is outlined in Scheme 15.

FIGURE 6 ^{1}HNMR Spectum of 71

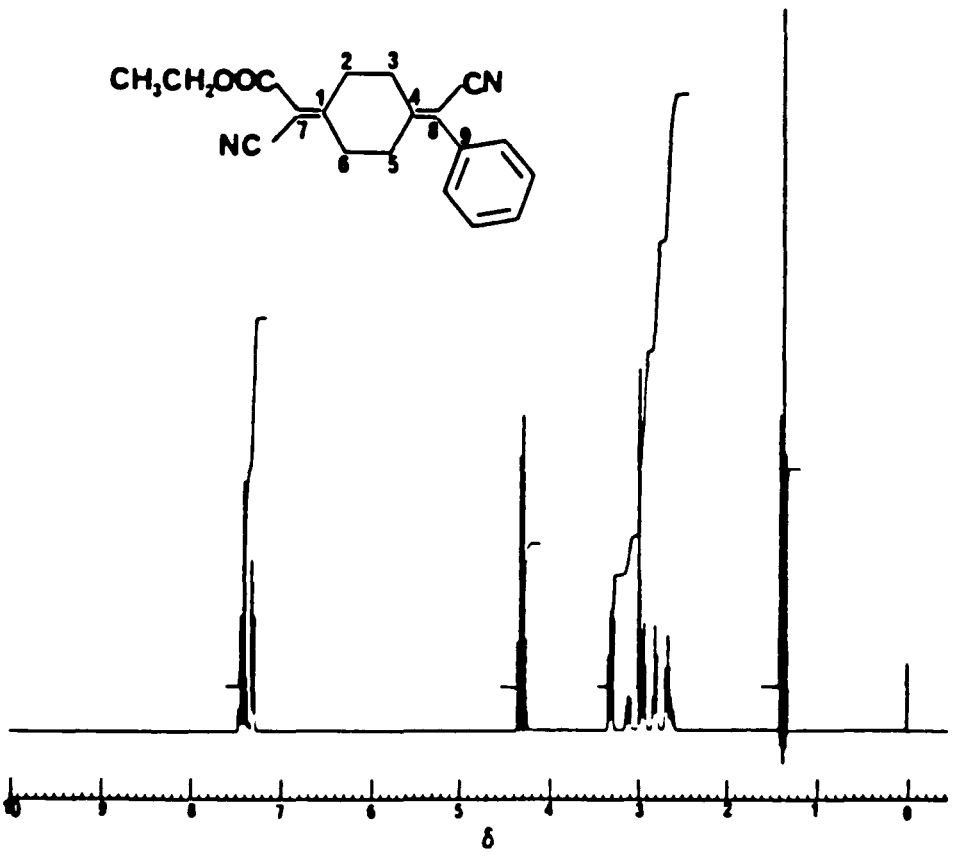
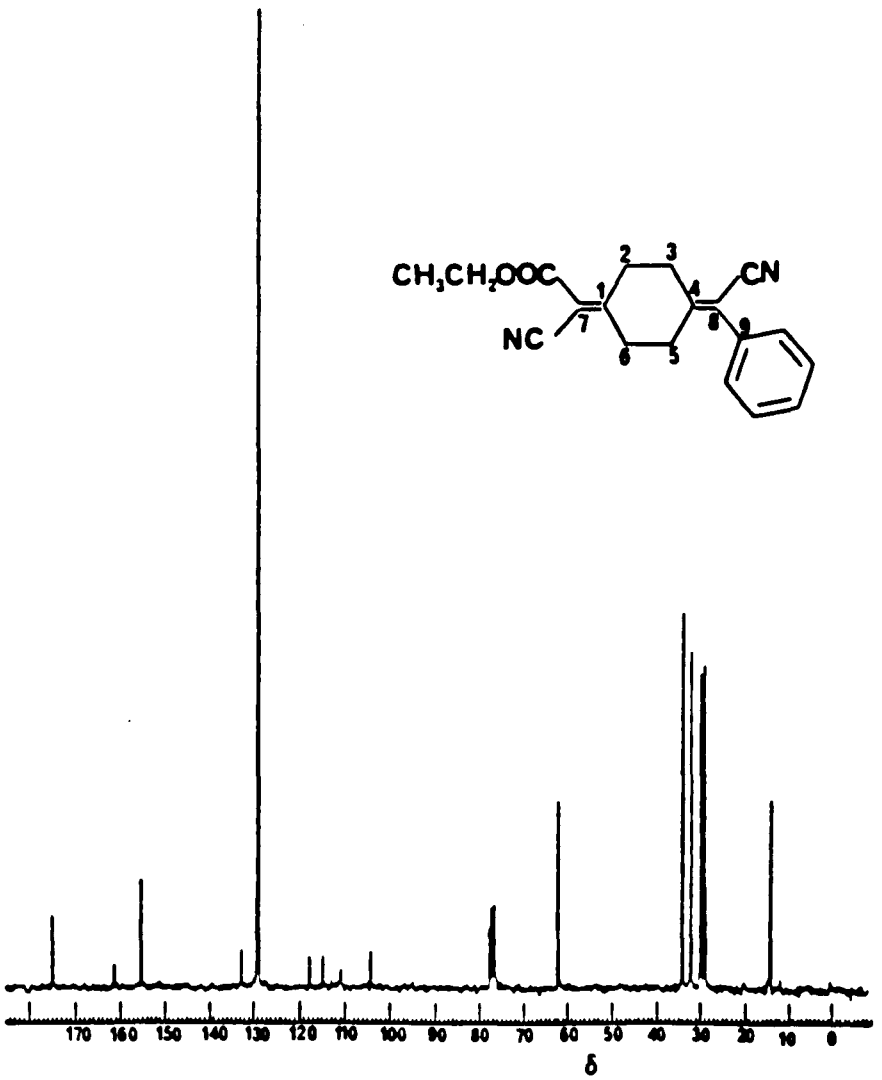
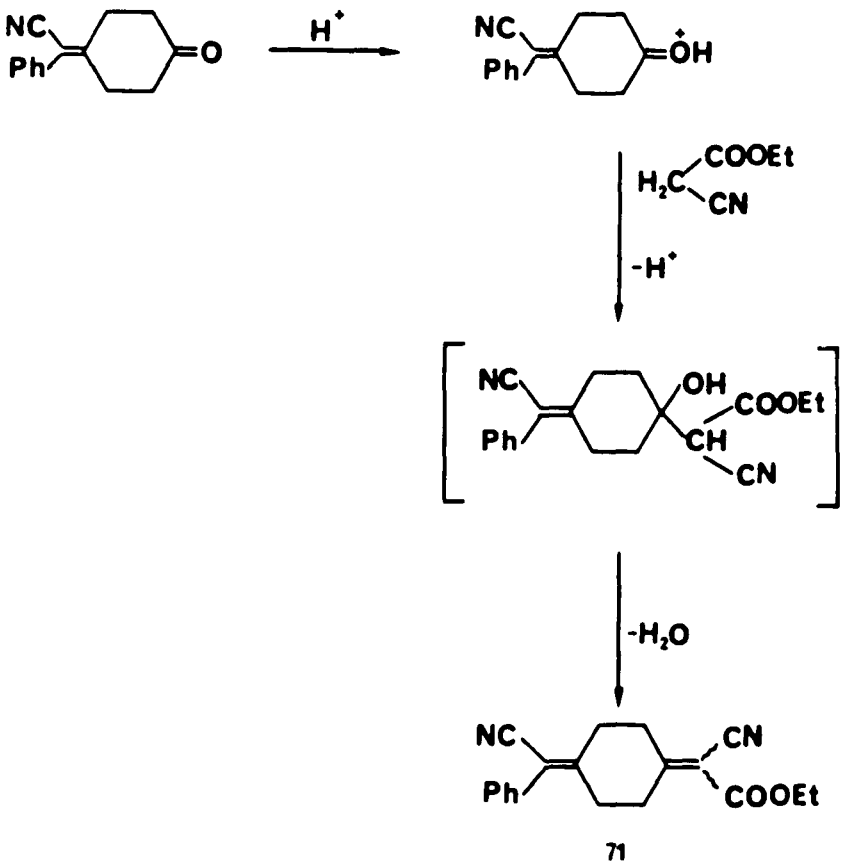


FIGURE 7 ^{13}C NMR Spectrum of 71



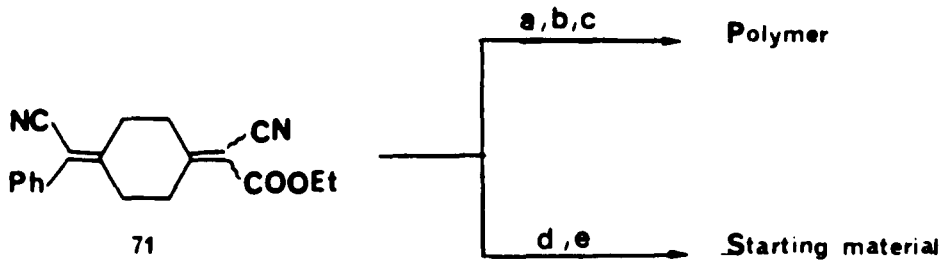
Scheme 15:



71

7,8-Dicyano-7-ethoxycarbonyl-8-phenylquinodimethane (DCEPQ, 72) was expected to form upon the oxidation of 71 with mild oxidants like NBS and NCS.[51] However, our efforts towards oxidation of 71 with these oxidizing agents under different reaction conditions, shown in Scheme 16, failed.

Scheme 16:

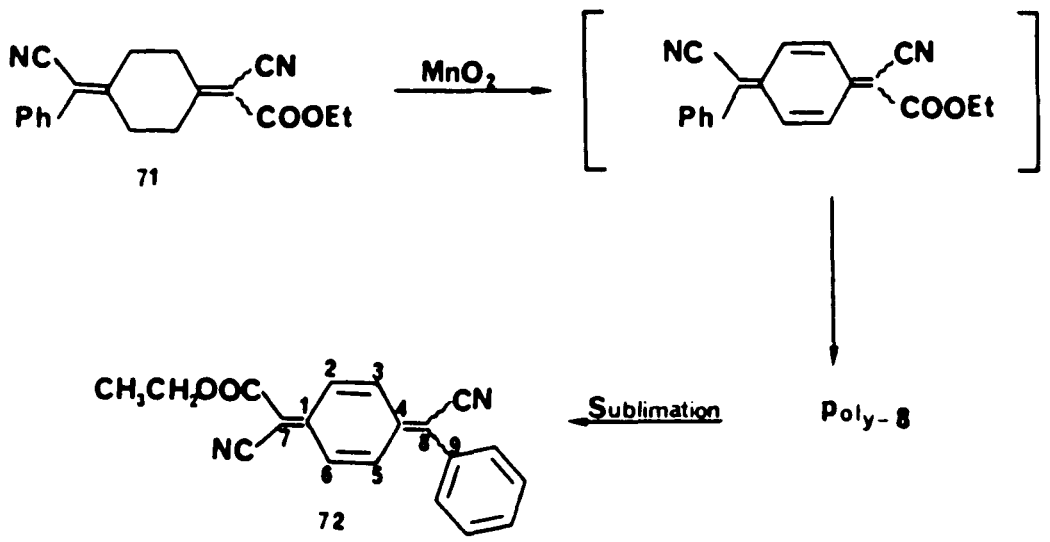


a) NBS, MeCN, Et_3N, RT and O°C, 2 hr.
b) NBS, MeCN, Et_3N, RT, 7 min.
c) NCS, MeCN, Et_3N, RT, 2 hr.
d) NCS, MeCN, Et3N, O°C, 2 hr.
e) NBS, MeCN, Py, RT, 2 hr.

On the other hand when 71 was refluxed with active manganese dioxide[53,54] in benzene or chloroform it reacted completely after 30 minutes. Analysis of the crude reaction mixture with ^1H NMR indicated the presence of the desired product DCEPQ, 72, along with a polymeric material. Complete removal of the solvent under reduced pressure led to total polymerization. However, refluxing the reaction mixture for only 5-10 minutes and then analyzing the reaction mixture indicated the presence of only the monomer 72. The monomer undergoes rapid polymerization upon evaporation of the solvent. All efforts towards isolation of pure monomer from the reaction mixture were frustrated by its rapid polymerization. Thermal depolymerization of quinodimethane homopolymers under vacuum has been previously reported.[43]

By heating poly-tetramethoxycarbonylquinodimethane, TMCQ, at reduced pressure, TMCQ was recovered in appreciable yield. Furthermore, Iwatsuki noted that poly-dibutoxycarbonyldicyanoquinodimethane, DBCQ, regenerated small amounts of monomer upon standing in light.[55]

Sublimation of the polymeric product from the reaction at 120 -140°C and reduced pressure resulted in the isolation of an orange solid which did not have a sharp melting point:



The 500 MHz ^{1}H NMR spectrum of this material (Figs. 8, and 9) suggested the presence of monomer DCEPQ, 72, as cis and trans isomers as evidenced by the pair of peaks at 1.38 and 1.37 ppm for the methyl group:

Further evidence for the presence of monomer 72 came from mass spectrum and elemental analysis. However, when the polymeric product was sublimed at a relatively higher temperature, 160-180°C, one single isomer was obtained as the major product. In the 500 MHz ^{1}H NMR spectrum of this compound, shown in Figs. 10 and 11, there are four distinct peaks at 8.36, 7.65, 7.48, and 7.30 ppm, all clean doublets of doublets. Selective double irradiation NMR experiments showed that the proton at 8.36 ppm is coupled to the proton at 7.30 ppm with a coupling constant of 10.2 Hz and to the proton at 7.48 ppm with a small coupling of 1.9 Hz. Similarly, when the proton at 7.65 ppm was selectively irradiated the proton at 7.48 ppm collapsed to a doublet losing the large coupling of 9.8 Hz. The small coupling of 2.1 Hz is to the proton at 7.30 ppm.

The chemical shifts and the coupling pattern are indicative of four chemically non-equivalent protons. When this spectrum is compared with the ^{1}H NMR spectrum of DCDPQ, a large downfield shift of about 0.8 ppm is observed for one of the protons of DCEPQ. The most logical explanation for

FIGURE 8 ^{1}H NMR Spectrum of 72

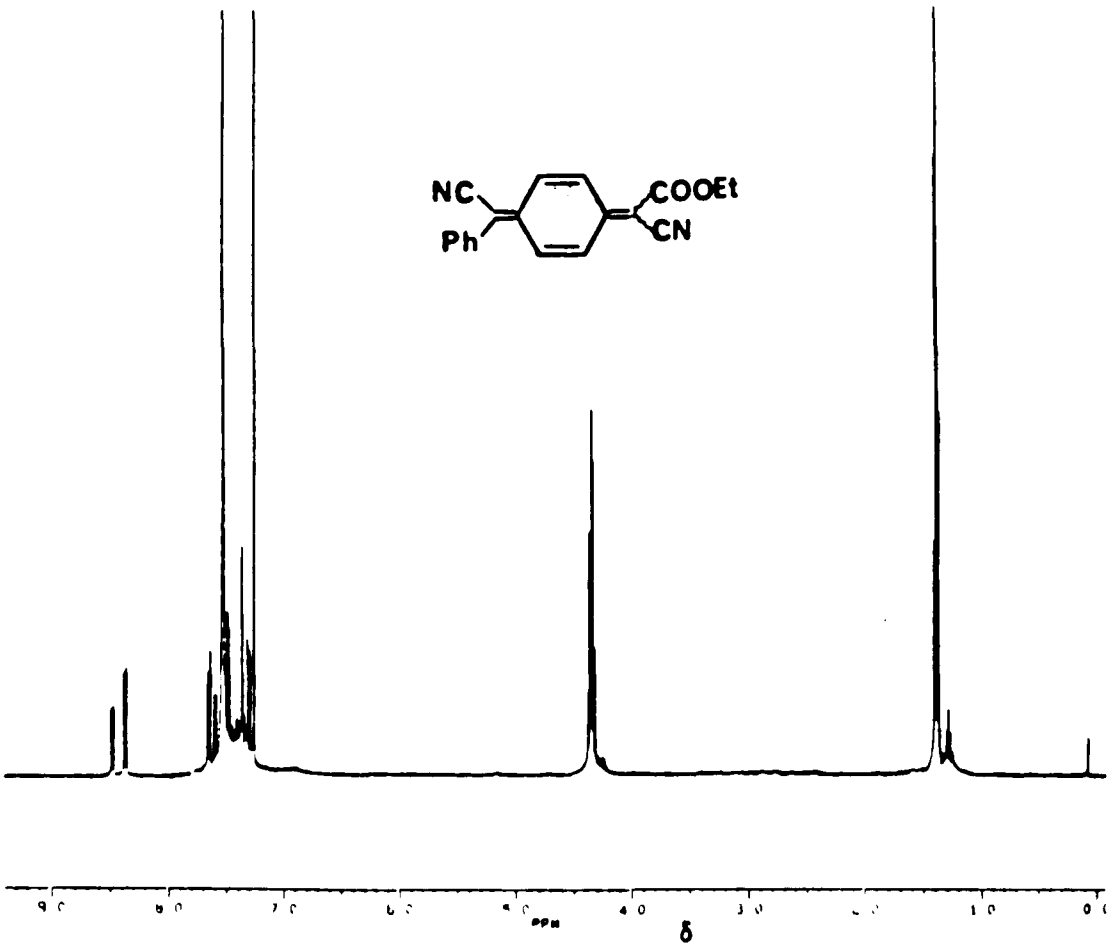


FIGURE 9 ^{1}H NMR Spectrum of 72

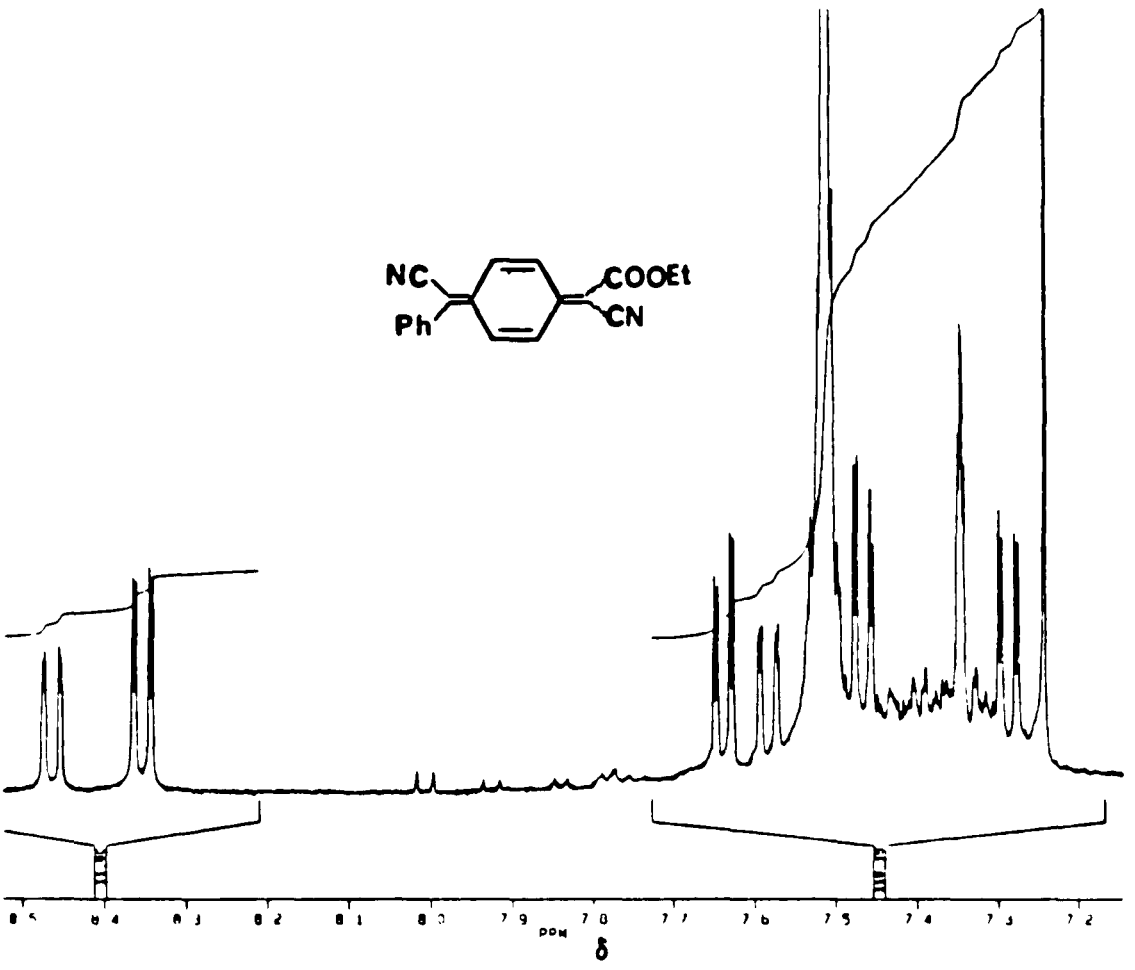


FIGURE 10 ^{1}H NMR Spectrum of 72

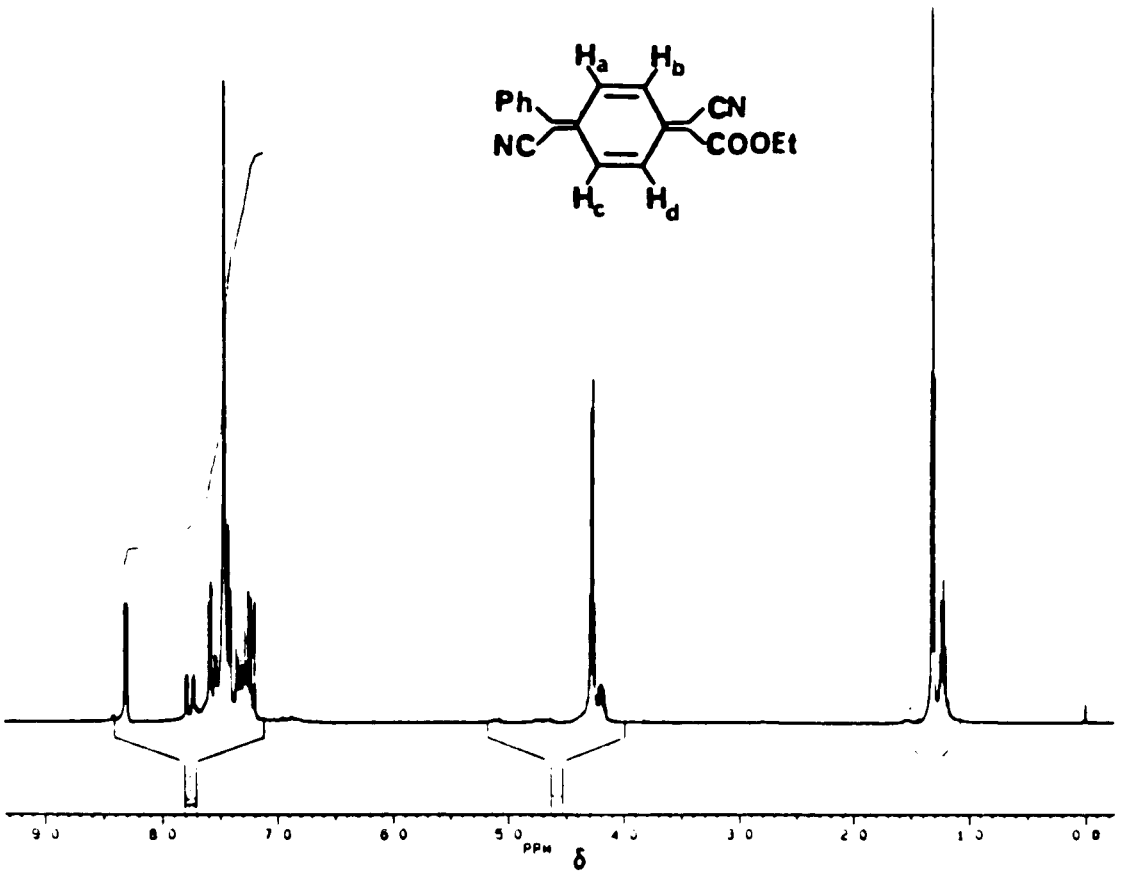
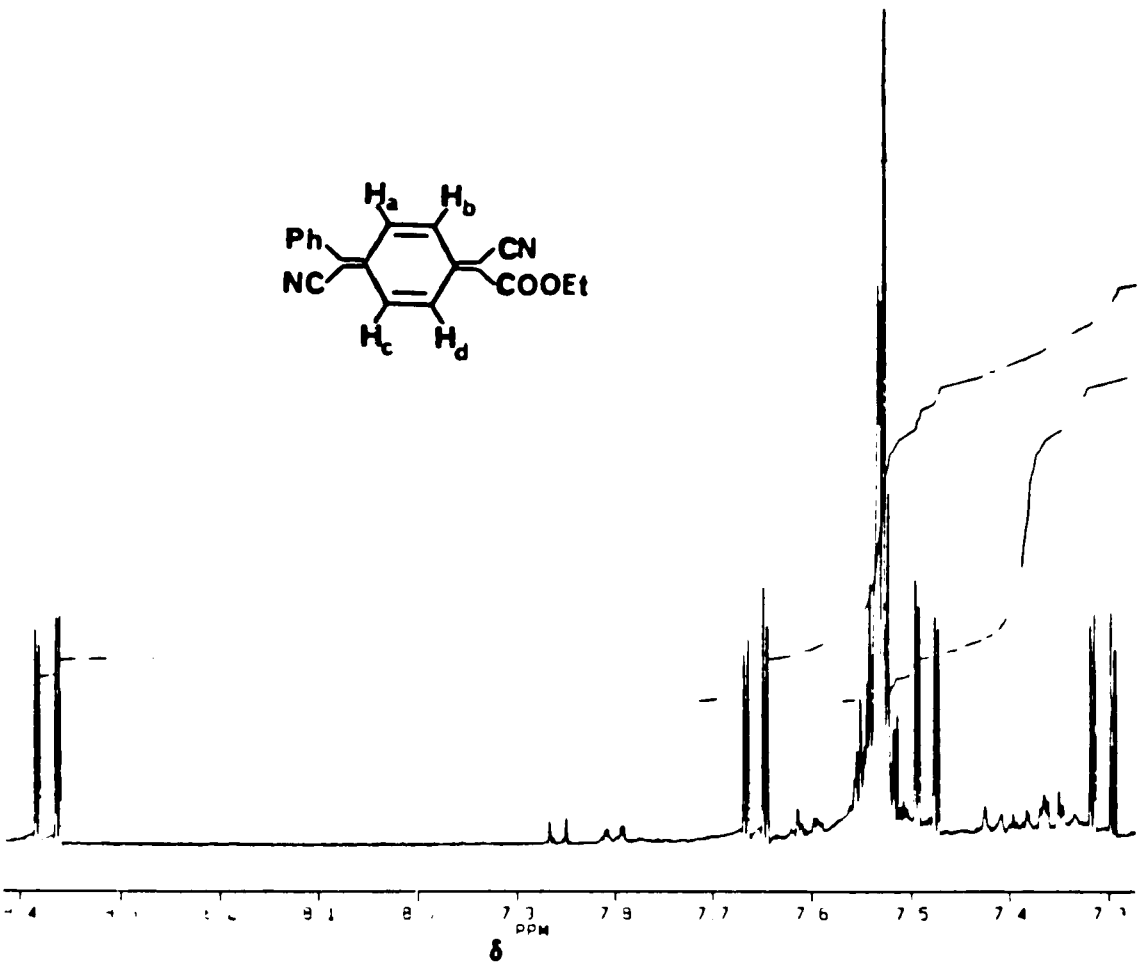


FIGURE 11 ^{1}H NMR Spectrum of 72



this shift would be the shielding effect of the phenyl ring. This would require the near coplanarity of this ring with the quinonoid ring. The existence of four distinct quinonoid protons as doublets of doublets is indicative of the different chemical environments of these protons. This is best rationalized by a trans structure for DCEPQ. For the cis isomer one would expect less drastic changes in the chemical environments of the quinonoid protons which lie on the same side as the nitrile groups (H_a, and H_b,). This is clearly manifested by the spectrum of the mixture of the two isomers (Fig. 8). The quinonoid proton peaks belonging to the other isomer (cis) are at 8.49, 7.58, 7.52, and 7.35 ppm. The coupling pattern of the peak at 7.35 ppm is similar to that reported for cis DCDPQ while the splitting for the peaks at 8.49 ppm and 7.58 ppm, which are coupled to each other with a large coupling constant of 10.1 Hz, is similar to that reported for trans DCDPQ. With these in mind we assign the product of sublimation at 160-180°C as the trans isomer and the product formed alongside trans at 120-140°C as the cis isomer. It appears that the cis-trans isomerization is a consequence of high temperatures. We did not observe any change in the ratio of the two isomers when left at room temperature in solution for a long period of time.

7,8-Dicyano-7-ethoxy-8-phenylquinodimethane (DCEPQ, 72) is an orange solid which forms a yellow or orange

solution depending on concentration. DCEPQ is very soluble in chloroform, benzene, and dichloromethane (50 mg/3mL), but less soluble in THF and 1,2-dichloroethane (50 mg/6mL). Neutral solvents such as toluene and benzene do not act as initiators for 72 while weakly basic solvents such as methanol and diethyl ether initiate rapid polymerization. Slow polymerization of DCEPQ occurs in some neutral solvents especially chloroform. It may be attributed to the presence of nucleophilic impurities. Considering the NMR results which demonstrate the presence of both the cis and trans forms the melting point range of 144-149°C seems logical.

POLYMERIZATION

Homopolymerization of DCEPQ:

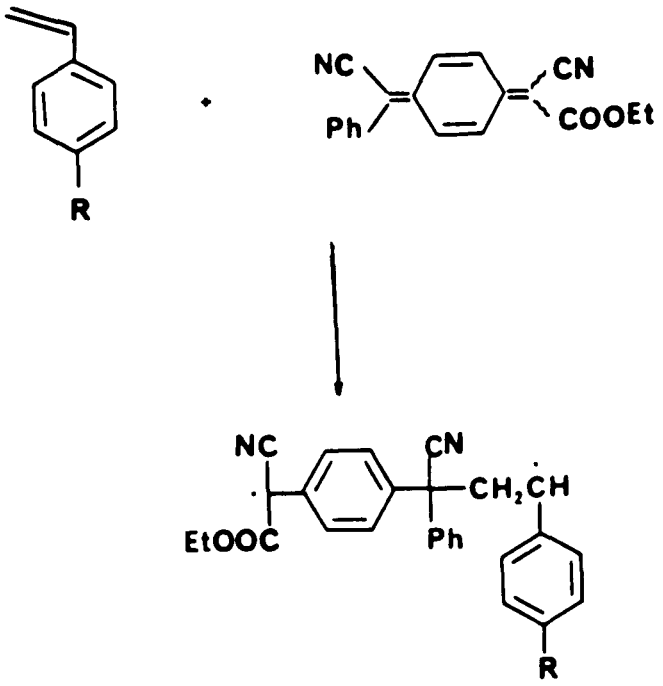
The formation of polymer during the oxidation of 7-cyano-1-phenylmethylene-4-cyano-4-ethoxycarbonylmethylenecyclohexane, 71,to DCEPQ, 72, was taken as an early indication that DCEPQ would homopolymerize.

Anionic homopolymerization of DCEPQ in THF using n-BuLi or KCN as initiators at -78°C showed that DCEPQ was polymerized. Polymerization with BuLi was faster than with KCN initiator. After four hours stirring at -78°C the polymerization was complete.

The low symmetry the monomer DCEPQ leads to a polymer which is soluble in most common solvents.

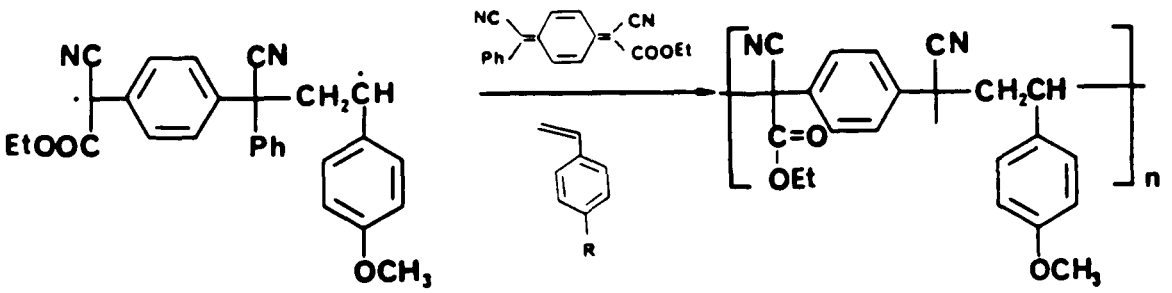
Spontaneous copolymerization of DCEPQ, 72, with selected monomers:

DCEPQ 72 spontaneously copolymerized with styrene at temperatures under 65°C. The conversion was complete after three days. Similarly DCEPQ copolymerized with p-methylstyrene spontaneously at similar conditions and conversion was complete after two days. With p-methoxystyrene at the same conditions, after less than 24 hours the conversion was complete. The higher reactivity of p-methoxystyrene is consistent with initiation by bond formation as the increase in the strength of the donor substituent increases the push-pull stabilization of the tetramethylene intermediate:



R = H , CH_3 , OCH_3

Spontaneous copolymerization produced high molecular weight polymer at low conversion and molecular weight did not increase during the course of polymerization (Table 4). Therefore, copolymerization propagates by chain addition:



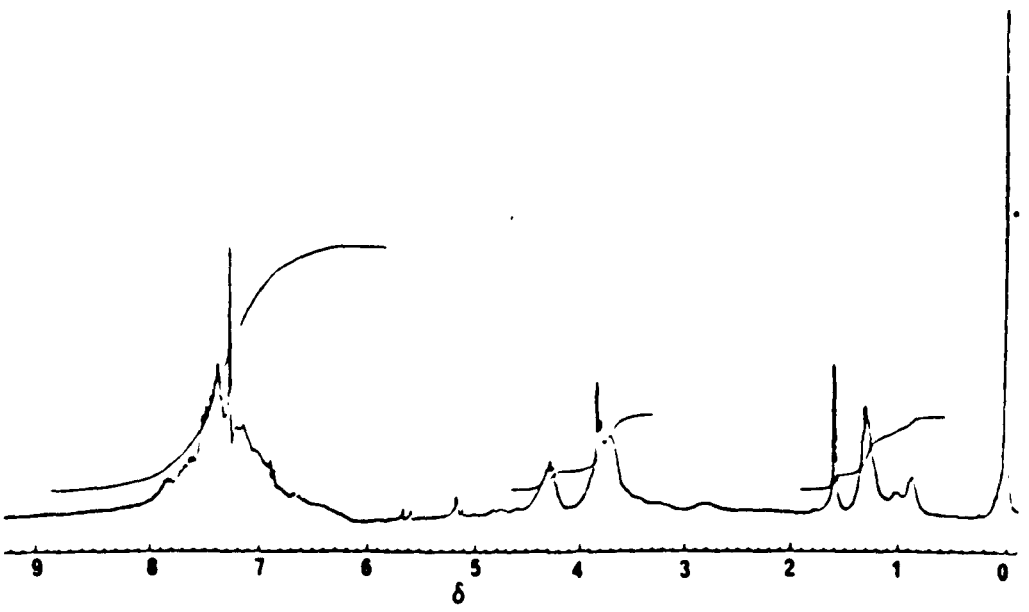
It is not surprising that coupling between two tertiary centers would be a slower process than chain addition of monomer which results in ring aromatization. But from the reaction of stronger donor monomer N-vinylcarbazol (NVC) with monomer 72 under the same conditions (dichloroethylene or toluene, 65°C and no initiator) after ten days mostly homopolymer of NVC and unreacted DCEPQ were obtained. DCEPQ, 82, may be acting as cationic initiator for homopolymerization of NVC:

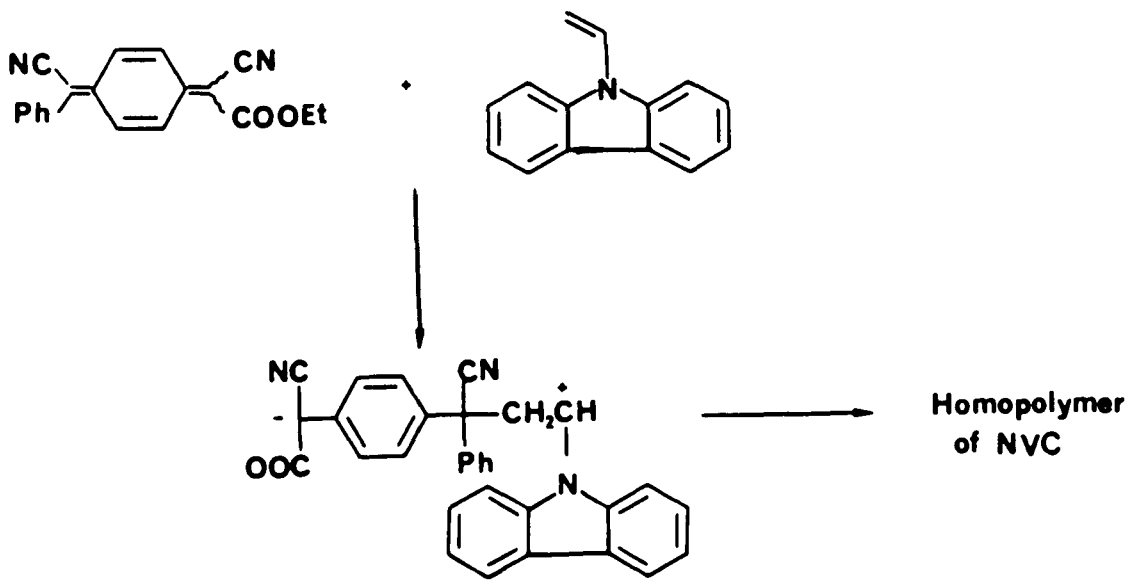
TABLE 4

Spontaneous Copolymerization of DCEPQ with p-MeOSt

Run no.	DCEPQ	p-MeOSt mg	Solvent mL	Time hr	polymer mg	yield %	M_n
1	50	22.3	5	2	10	13.8	9392
2	50	22.3	5	5	20	27	10078
3	50	22.3	5	8	35	48.8	8852
4	50	22.3	5	12	54	75	9066
5	50	22.3	5	24	72	100	10801

FIGURE 12 ^{1}H NMR Spectrum of DCEPQ - p-MeOSt copolymer





These findings further support Hall's Bond Forming Initiation Theory.

Copolymer Characterization:

The copolymers were isolated as soluble white powders. The ^{1}H NMR spectra of the p-MeOSt copolymer is shown in Fig. 12. By comparing the area of the aromatic region with the area of the backbone proton region one may estimate the copolymer compositions. Elemental analysis and the ^{1}H NMR area comparison indicate that the copolymers have close to 1:1 composition. The small upfield resonances may be attributed to the backbone protons of neighboring donor atom.

CHAPTER 4

Conclusion

To explore the reactivity and polymerizability of highly electrophilic imines, with two acceptor groups on carbon and a cyano group on nitrogen, two novel imines tricyanomethanimine, 26, and methyl 3-aza-α,ß-dicyanoacrylate, 39, were successfully synthesized. Isolation of these imines was complicated by their extreme reactivity, however, they were characterized in solution.

By comparing the behavior of the electrophilic imines 26 and 39 with TCNE, a standard electrophilic olefine, we reach the following conclusions:

1) Imines 26 and 39 are somewhat less electrophilic than TCNE, as shown by the AM1 calculations, the cyclic voltammetry, and a rough comparison of their rates of cycloaddition reaction with electron-rich dienes.

2) TCNE is stable at room temperature while these electrophilic imines are only stable in dilute solutions.

3) TCNE readily forms a cycloadduct with p-methoxystyrene via a zwitterionic tetramethylene intermediate. Both electrophilic imines 26 and 39 copolymerize spontaneously with p-methoxystyrene which the nature of the polymerization, in this case free radical copolymerization,

indicates that the initiating tetramethylene had diradical character.

4) TCNE does not polymerize. Both imines 26 and 39 spontaneously homopolymerize and copolymerize with p-methoxystyrene. The nature of the homopolymerization is not clear, as neither free radical nor anionic inhibitors had any effect of the reaction.

Synthesis and polymerization of unsymmetrical quinodimethanes has been successfully carried out in order to explore and explain the polymerization behavior of quinodimethane monomers and their comparison with more common olefin monomers.

7,8-Dicyano-7-ethoxycarbonyl-8-phenylquinodimethane, DCEPQ, is a reactive monomer toward polymerization. High molecular weight copolymers were obtained from spontaneous polymerization of DCEPQ with styrene, p-methoxystyrene, and p-methylstyrene. Molecular weight did not increase during the course of polymerization. Therefore, copolymerization propagates by chain addition. But from the reaction of stronger donor monomers N-vinylcarbazol (NVC) with DCEPQ homopolymer of NVC and unreacted DCEPQ were obtained. It seems that DCEPQ is acting as cationic initiator for homopolymerization of NVC. These findings support Hall's Bond Forming Initiation Theory.

CHAPTER 5

Experimental

Instrumentation: Melting points were measured with a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model PE983 infrared spectrophotometer. ^{1}H NMR spectra at 250 MHz and ^{13}C NMR spectra at 62.9 MHz were recorded on a Bruker WM-250 FT NMR spectrometer using a 5 mm tube and tetramethylsilane as the internal standard. ^{1}H NMR spectra at 500 MHz were recorded on a Bruker AM-500 FT NMR spectrometer. The deuterated solvent showm for each compound was used to lock the instrument. All spectra were recorded at ambient temperature. Mass spectra were determined on a Hewlett-Packard Model 5988A, RTE-6/vM Data System Direct Insertion Probe. Size exclusion chromatography was run in chloroform using a Spectra Physic UV detector. Elemental analyses were performed by Desert Analytics, Tucson, AZ. All reagents were obtained from Aldrich Chemical Company and were used as delivered unless specified otherwise.

1,1-Dicyano-2,2-diazidoethylene 25: A solution of 1,1-dichloro-2,2-dicyanoethylene, 21, (0.5 g, 3.35 mmole) in small amount of acetone (1 mL) was added at -20 to -15°C to a solution of sodium azide (1 g, 16 mmol) in 6 mL of acetone/water (1:1). After a few seconds a yellow liquid phase separated, 450 mg, 85%. Caution! This compound may decompose with explosion. It is better to prepare it exactly before the next step, not making more than 0.5 g each time: IR (neat): ν_{max}; 2160 cm^{-1}($-N_3$).

Methyl 3,3-diazido-2-cyanoacrylate 33: The solution of 3,3-dichloro-2-cyanoacrylate (0.54 g, 3.0 mmole) in 1.0 mL acctone was added to a solution of sodium azide (1 g, 16.0 mmole) in 6 mL acetone/H_2O (1:1) at -15°C. After a few seconds spectroscopically pure diazide 33 precipitated from the solution. Washed with cold diethyl ether and dried in vaccum at room temperature in pvc container (it is better not to have more than 0.5 g of 33 each time). 0.5 g (36%) pale yellow-green crystalline material was obtained. It was recrystallized from dichloromethane/ehter at room temperture: mp 70°C; IR (KBr): ν_{max}; 2180, 2160 cm^{-1} (CN, and N_3), 1710 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 3.87 ppm (s, 3H, -OCH_3).

Tricyanomethanimine 26: Freshly synthesized 1,1-dicyano-2,2-diazidoethylene 25 was separated, dried over molecular sieves, and diluted with 10 mL of dried benzene, 1,2-dichloroethane, or toluene. Addition of this solution to 300 mL of warm (60-65°C) dried benzene, 1,2-dichlorethane or toluene under argone, evoluted N_2 gas. The reaction was completed after 1 hr at the same temperature. Based on the yields of subsequent reactions, the solution is about 0.01 M in C_4N_4. The IR spectrum of this solution shows the characteristic C=N (1714 cm^{-1}) and -CN (2246, and 2240 cm^{-1}) bands. No azide absorption at 2160 cm^{-1} was present. ^{13}C NMR (d_6-benzene):δ 107.5, 109.3, and 110.1 ppm for three -CN carbon atoms.

Methyl 3-aza-α,β-dicyanoacrylate (39): A solution of compound 33 (500 mg, 2.3 mmole) in 50 mL dried benzene or toluene was heated to 55-60°C under argon atmosphere with stirring for 1 hour. The IR spectrum of this solution shows the characteristic C=N stretching (1749 cm^{-1}); ^1H NMR (d_6-benzene): δ 2.9 and 3.1 (CH_3); ^{13}C NMR (d_6-benzene): δ 53.55, 54.01 (CH_3); 109.0, 109.4, 110.5, 112.0 (CN); 149.9, 150.55 (C=O) and 152.5 (C=N); MS (DCI): m/e 137 $(M+1)^+$.

Attempted synthesis of diethyl N-cyanomethanimine-dicarboxylate 49: Titanium tetrachloride (0.1 mL) was added to a solution of bis(trimethylsilyl)cabodiimide (0.9 g, 0.005 mole) diethyl ketomalonate (0.8 g, 0.005 mole) in toluene (50 mL). A yellow clear solution was obtained. After three hours stirring the IR spectrum showed bands at 2207 (CN), 1755 (C=O), and 1690 (C=N) cm^{-1}. Removal of the solvent afforded a precipitate the IR spectrum of which showed the formation of the polymer (no C=N band at 1690 cm^{-1}).

Dimethyl N-cyanimidocarbonate (50): Freshly synthesized 1,1-dicyano-2,2-diazidoethylene 25 (450 mg, 2.8 mmole) was separated (danger!) and was added to 15 ml of warm methanol (60-65°C) dropwise by stirring. Warming the solution was continued until no more evolution of N_2 was detected. The methanol was removed by rotary evaporation. The resulting residue was subjected to Kugelrohr distillation to give 248 mg (2.1 mmole, 72%) of 50 as light yellow crystals. Crystallization from a mixture of ether and petroleum ether gave white crystals: mp 60°C; ^1H NMR($CDCl_3$): δ 3.9 (s,6H); IR (KBr): ν_{max}; 2213 (-CN), 1620 (C=N) cm^{-1}; MS $C_4H_6N_2O_2$, m/e 114 (M^+). Anal. Calcd. for $C_4H_6N_2O_2$: C,42.10; H, 5.30; N, 24.55. Found: C,42.12; H, 5.27; N, 24.49.

Methyl 2-(N-cyanimino)-2-methoxyacetate (41): Methyl alcohol (5 mL) was added dropwise to a toluene solution of 39 at 60°C with stirring. The greenish yellow solution changed to colorless immediately. After stirring for another half hour the solvent was removed under reduced pressure. Recrystallization of the resulting residue from diethyl ether afforded colorless crystalline 41, 55% yield based on consumed 31; mp 54°C; ^{1}H-NMR($CDCl_3$): δ 3.95, 3.89 (s, 6H, Me); ^{13}C-NMR($CDCl_3$): δ 54.07, 57.78 (Me), 110.06 (CN), 155.05, 164.28 (C=N, C=O).

Cycloaddition of 26 and 39 with 2,3-dimethyl-1,3-butadiene (51 and 52): An excess amount of 2,3-dimethyl 1,3-butadiene (4 equivalents) was added dropwise to benzene or toluene solution of 26 or 39 at room temperature with stirring. The greenish yellow solution changed to colorless after 15 mins. Stirring was continued for one more hour. Removal of solvent and excess 2,3-dimethyl 1,3-butadiene by rotary evaporation gave the cycloadduct 51 or 52. The crude product was recrystallized in ether to give a white needle crystal (~60% yield based on 21 or 31).

Cycloadduct 51: mp 80-80.5°C; IR(KBr): ν_{max} 2227 (CN) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.7 and 1.8 (s,6H), 2.95 (s,2H,CH_2), 3.95 (s,2H, N-CH_2); ^{13}C NMR ($CDCl_3$); δ 15.76, 18.38 (C_8, C_7), 39.58 (C_5), 50.66 (C_2), 49.81 (C_6), 110.77, 111.47 (C_9, C_{10}, C_{11}), 120.12, 122.56 (C_3, C_4); MS: m/e 186 (M^+); Anal. Calcd. for $C_{10}H_{10}N_4$: C, 64.5; H, 5.41; N, 30.09. Found: C, 64.52; H, 5.36; N, 30.13.

Cycloadduct 52: mp 81-82°C; IR(KBr): ν_{max} 2226 (C=N), 1756 (C=N) cm^{-1}; ^1H-NMR ($CDCl_3$): δ 3.96 (CH_3O-), 3.86 (CH_2-NCN), 2.85 (d, J=17.7 Hz), 2.75 (d, J=17.7 Hz, 2H, $H_2CC(CN)COOMe$) and 1.72 (s, 6H, CH_3); Anal. Calcd. for $C_{11}H_{13}N_3O_2$: C, 60.26; H, 5.98; N, 19.15. Found: C, 59.92; H, 5.91; N, 19.07.

Cycloaddition of 26 and 39 with Cyclopentadiene (53, 54): Four fold of cyclopentadiene was added to benzene or toluene solution of 26 or 39 at room temperature with stirring. A colorless solution was obtained after 1 hr. Removal of solvent and recrystallization from ether formed white crystalline solid (~50% based on compounds 21 and 31).

Compound 53: IR (KBr): ν_{max} 2221 cm^{-1} (CN); ^1H NMR ($CDCl_3$): δ 2.1 (2H, CH_2), 4.2 (1H $(NC)_2C$-CH), 4.9 (1H, N-CH), 6.7 and 6.9 (2H HC=CH); Anal. Calcd. for $C_9H_6N_4$: C, 63.5; H, 3.5; N, 32.9. Found; C, 63.7; H, 3.4; N, 33.0.

Compound 54: IR (KBr): ν_{max} 2216, 2161 (C≡N), 1761 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.9 (2H, CH_2), 4.3 (1H, MeOOC(CN)CCH), 4.9 (1H, N-CH), 6.8, 6.9 (2H, CH=CH) and 4.1 (CH_3O-); Anal. Calcd. for $C_{10}H_9N_3O_2$: C, 58.53; H, 5.36; N, 20.48. Found: C, 58.31; H, 5.29; N, 20.38.

Synthesis of 55: A 5-fold of N,N-dimethylaniline was added to benzene solution of **26** at room temperature with stirring. A red solution was formed. The solution was stirred overnight, and filtered to separate compound 55. Recrystallization with glacial acetic acid gave red crystals (30% based on compound **25**). IR (KBr): ν_{max} 2173 (CN), 1612 (C=N) cm^{-1}; ^1H-NMR ($CDCl_3$): δ 3.2 (6H, $2CH_3$), 6.8 and 8.0 (ring). Anal. Calcd. for $C_{11}H_{10}N_4$: C, 66.65; H, 5.09; N, 28.27. Found: C, 66.43; H, 5.07; N, 28.43.

Hydrolysis of 55: 1M NaOH (25 mL) was added to 55 (200 mg, 10 mmole) and the slurry was stirred for 2 days at room temperature. A clear light yellow solution was obtained which was acidified with 4N HCl. Filtration gave light yellow crystal of 57 (100 mg). IR (KBr): ν_{max} 3500 (NH), 2245, 2226 (CN) cm-1; ^1H NMR ($CDCl_3$): δ 7.5 (2H, ring), 6.5 (2H ring), 2.8 (6H, $2CH_3$). Compound 57 (50 mg) was dissolved in 2 mL of absolute ethanol and 1 mL of conc. HCl was added. The alcoholic solution was refluxed for 2 hrs. After neutralization with sodium hydroxide, ethyl 4-

dimethylaminobenzoate 58 was formed: mp 63.5-64.5°C; ^{1}H NMR ($CDCl_3$): δ 7.2 (2H, ring), 6.2 (2H, ring), 3.6 (2H, CH_2), 2.4 (6H, $2CH_3$), 1.7 (3H, CH_3); IR (KBr): ν_{max} 1693 (C=O) cm^{-1}, no C=N and CN.

Copolymerization. A 4-fold (based on 21, 31) of p-methoxystyrene was added to benzene solution of 26 or 39 at room temperature under argon atmosphere. The yellow color of the solution changed to dark red, and then after 1 hr stirring, a pale yellow color was formed. Removal of benzene gave a viscous material, which was dissolved in an minimal amount of chloroform. The chloroform solution added dropwise to 100 mL ether with vigorous stirring. The alternating copolymer was obtained as a yellow solid.

Copolymer 59: IR (KBr): ν_{max} 2210, 2100 (CN) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.4-7.4 (broad), 3.6-3.9 (broad); Anal. Calcd. for $C_{13}H_{10}N_4O$: C, 65.53; H, 4.23; N, 23.52. Found: C, 64.22; H, 4.28; N, 22.82.

Copolymer 60: IR (KBr): ν_{max} 2216, 2228 (CN), 1777 (C=O) cm^{-1}; ^{1}H NMR (DMSO): δ 6.9-7.5 (broad, ring), 3.7-4.05 (broad, CH_3O-) and 3.3-3.6 (broad): Anal. Calcd for $C_{14}H_{13}N_3O_3$: C, 61.98; H, 4.33; N, 15.49. Found: C, 60.94; H, 4.79; N, 15.42.

1- Cyano-1-phenyl-4-cyclohexanone ethylene ketal 69: Aqueous sodium hydroxide (4.0 mL, 40%) was added dropwise to a solution of 1,4-cyclohexanedionemonoethylene ketal 67 (7.8 g, 0.05 mole) and benzylcyanide 68 (5.85, 0.05 mole) in 50 mL 95% ethanol with stirring within 20 minutes at room temperature. Stirring was continued for two days. A dark brown solution was obtained. Extraction was done by 100 mL ether. The ethereal solution was washed with water (5 times, 30 mL). Dried the yellow ether solution with magnesium sulfate. Removed the ether. A yellow liquid was obtained (11.29 g, 88.5% yield). Distillation under low pressure gave a light yellow liquid (9 g, 70% yield). This liquid changed to solid in 5°C. Recrystallization with hexane gave a white crystalline solid, mp 66.5-67°C; IR (KBr): ν_{max} 2206 (CN) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.42-7.26 (m, 5H), 4.00 (m, 4H), 2.89 (t, 2H), 2.50 (t, 2H), 1.89 (t, 2H), 1.69 (t, 2H); ^{13}C NMR ($CDCl_3$): δ 158.58 (C_9), 133.39 (C_{10}), 128.52 (benzene ring), 118.19 (CN), 108.90 (C_4), 107.23 (C_1), 64.35 (C_7, C_8), 34.98, 34.86, 31.82, 27.68 (C_2, C_6, C_3, C_5); Anal. Calcd. for $C_{16}H_{17}O_2N$: C, 75.27; H, 6.71; N, 5.49; Found: C, 75.41; H, 6.51; N, 5.49.

1-Cyano-1-phenylmethylene-4-cyclohexanon 70: A mixture of ketal 69 (12.7 g, 0.05 mole), 100 mL THF, and 15 mL of 10% aqueous HCl was refluxed for two days. The mixture was cooled, stripped to ca. 25 mL, and partitioned between water

and ethylacetate. The organic layer was washed with water (3 times, 30 mL) and dried (Mg SO_4). Removal of ethylacetate gave 10.25 g yellow liquid. Column chromatography (70 g silica gel, 70-230 mesh, 60 Å with 20% ethylacetate/hexane gave 1.8 g of 69 and 7.6 g of pure crystalline 70 (73% yield, 90% total yield): mp 56-56.5°C; IR (KBr): ν_{max} 2210 (CN), 1712 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.34-7.43 (m, 5H), 3.10 (t, 2H), 2.77 (t, 2H), 2.63 (t, 2H) and 2.43 (t, 2H); ^{13}C NMR ($CDCl_3$): δ 208.98 (C=O), 155.4 (C_7), 132.82 (C_8), 128.69 (benzene), 117.6 (CN), 111.04 (C_4), 38.68, 38.60, 31.15, 27.88 (C_2, C_6, C_3, C_5); Anal. Calc. for $C_{14}H_{13}ON$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.13; H, 6.16; N, 6.44.

Synthesis of 1-cyano-1-phenylmethylene 4-cyano-4-ethoxycarbonyl-methylene cyclohexane 71. Ethyl cyanoacetate (1.13 g, 0.01 mole) was added to a solution of 70 (2.11 g, 0.01 mole) in 30 mL benzene, ß-alanine (0.1 g) and acetic acid (0.1 mL). The mixture was refluxed (azotropic) for 24 hours. Cooled the solution to room temperature and filtered. The benzene was removed from the filtrate. A light yellow liquid was obtained. By adding 5 mL diethylether and scratching the solution, a white pure precipitate was formed after a few minutes, (1.9 g, 62%); mp 134-135.5°C, IR (KBr): ν_{max} 2210, 2205 (CN), 1728 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.41 and 7.29 (m, 5H), 4.29 (q, 2H),

3.30 (t, 2H), 2.95 (t, 2H), 2.81 (t, 2H), 2.67 (m, 2H), 1.35 (m, 3H); ^{13}C NMR ($CDCl_3$): δ, 174.88 (C=O), 161.28 (C7), 155.28 (C8), 132.66 (C_9), 128.76 (benzene ring), 117.63 (CN), 114.78 (CN), 110.79 (C_1), 104.16 (C_4), 61.97 (CH_2), 33.80, 31.95, 31.85, 29.68, 28.97, 28.53 (belong to C_2, C_3, C_5 and C_6, different isomer), 13.96 (CH_3); Anal. Calc. for $C_{19}H_{18}O_2N_2$: C, 74.44; H, 5.80; N, 9.11. Found: C, 74.49; H, 5.92; N, 9.15.

7,8-Dicyano-7-ethoxycarbonyl-8-phenylquinodimethane 72: A mixture of 1-cyano-1-phenylmethylene-4-cyano-4-ethoxycarbonylmethylene cyclohexane 71 (306mg, 1mmol) in 10 mL dry benzene, 3A molecular sieves (1g) and active MnO_2 (1.2 g) was stirred at reflux for 5 minutes, cooled and filtered on celite. The orange filtrate was stripped to give crude 72. Sublimation of crude product under reduced pressure and 120-140°C gave 137.5 mg (45%) of orange solid as a mixture of cis and trans isomers of 72. Sublimation of crude product under reduced pressure and 160-180°C gave mostly trans isomer of 72 (45% yield). IR (KBr): ν_{max} 2201 (CN), 1746, 1707 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): for trans isomer, δ 8.36 (dd, 1.9 Hz, 10.2 Hz; H_c), 7.65 (dd, 2.1 Hz, 9.8 Hz, H_b), 7.48 (dd, 1.9 Hz, 9.8 Hz, H_a) 7.52 (m, phenyl ring, 5H), 7.30 (dd, 2.1 Hz, 10.2 Hz, H_d), 4.34 (q, CH_2), 1.38 (t, CH_3). For cis isomer, δ 8.49 (dd, 0.98 Hz, 10.1 Hz, $H_{a'}$), 7.58 (dd, 1.15 Hz, 10.1 Hz, $H_{b'}$), 7.52 (m, $H_{c'}$, and

phenyl ring, 6H), 7.35 (m, $H_{d'}$), 4.28 (q, CH_2), 1.29 (t, CH_3); ^{13}C NMR ($CDCl_3$): For trans isomer, δ 162.13 (C=O), 149.66, 140.10 (C_8), 133.89, 131.12, 131.12, 131.09, 130.44, 130.01, 129.24, 128.52, 128.08, 127.84, 127.69 (C_{1-6}, phenyl ring), 120.80, 117.75 (CN), 62.35 (CH_2), 14.09 (CH_3); MS: m/e 302 (M^+); Anal. calcd. for $C_{19}H_{14}O_2N_2$: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.27; H, 4.48; N, 9.05.

Copolymerization procedure: Donor monomer was added to a solution of DCEPQ (50 mg, 1/6 mmole) in dry and freshly distilled 1,2-dichloroethane (or toluene in the case of NVC) with stirring. The polymerization mixture was immediately frozen then degassed by the freeze thaw method, sealed, and stirred under 60-65°C. Isolation of polymeric products was achieved by precipitating the reaction mixture into 100 mL of vigorously stirred hexane. The precipitated polymer was concentrated by centrifuge and decanted the solvent and then filtered. Further purification was achieved by redissolving the polymeric product in chloroform, reprecipitation in ten times volume of hexane, centrifuge, decantation and then filtration.

REFERENCES

1- For example: Chow, Y.L. Tetrahedron Lett., 1965, 2473.

2- Kitayama, T.; Hall, H.K. Jr. Macromolecules, 1987, 20, 1451.

3- Hall, H.K. Jr.; Miniuti, D.L. Tetrahedron Lett. 1984, 25, 943.

4- Hall, H.K. Jr.; Kim, J.B. Macromolecules , in press.

5- Swarc, M. Nature, 1947, 160, 403.

6- Errede, L.A.; Swarc, M. Quart. Rev. Chem. Soc., 1958, 12, 301.

7- Mulvaney, J.E. Poly. Sci. Tech., 1984, 25, 311.

8- Iwatsuki, S. Adv. Polym. Sci., 1984, 58, 94.

9- Iwatsuki, S. "The Chemistry of Quinonoid Compounds", Vol. II, Eds. Patai, S. ; Rappoport, Ed., Wiley and Sons, 1988, P 1067.

10- Mulvaney, J.E. in "New Monomers and Polymers", Eds. Culbertson, B.M.; Pittman, C.V., Jr.; Plenum, 1984.

11- Hall, H.K. Jr.; Cramer, R.J.; Mulvaney, J.E. Poly. Bull., 1982, 7, 165.

12- Iwatsuki, S.; Itoh, T ; Nishihara, K. Chem. Lett., 1982, 517.

13- Mulvaney, J.E.; Greeen, G.D. J. Poly. Sci., In Press.

14- Brandt, M.W.; Mulvaney, J.E.; Hall, H.K. Jr. Macromolecules, 1988, 21, 155.

15- Kitayama, T.; Padias, A.B.; Hall, H.K. Jr. Poly. Bull., 1987, 17, 417.

16- Hall, H.K. Jr.; Snow, L.G. "Ring Opening Polymerization", Saegusa, T.; Ivin, K.J.; Eds.; Elseviers: London, 1984, P83.

17- Sato, H.; Tsuruta, T.J. Macromol. Sci. Chem., 1970, A4, 295.

18- Smith, W.; Norton, D.G.; Ballard, S.A. J. Am. Chem. Soc.; 1953, 75, 33.

19- Ioffe, B.V.; Zelenin, K.N. Izv. Vyssh. Uchebn. Zaved., Khim. Tekhnol., 1963, 6, 78; Chem. Abs., 1963, 59, 6244a.

20- Ioffe, B.V.; Zelenin, K.N. Dokl. Akad. Naak. SSSr., 1961,141, 1369; Chem. Abs., 1962, 56, 140386.

21- Kim, J.B.; Hall, H.K. Jr. Macromolecules, 1988, 21, 1547.

22- White, W.A.; Weingarten, H. J. Org. Chem., 1967, 32, 213.

23- Josey, A.D.; Dickinson, C.L.; Dewhirst, K.C.; Mckusick, B.C. J. Org. Chem., 1967, 32, 1941.

24- Ardis, A.E. U.S. Patent 2,774,783 (1956).

25- (a) Dickinson, C.L.; Wiley, D.W.; McKusick, B.C. J. Am. Chem. Soc., 1960, 82, 6132. (b) Dickinson, C.L.; McKusick, B.C. J. Org. Chem., 1964, 29, 3087.

26- Carrie, R.; Danion, D.; Ackermann, E.; Saalfrank, W. Angew. Chem. Inter. Ed. Engl., 1982, 21, 287.

27- Hall, H.K. Jr.; Ramezanian, M.; Saeva, F.D. Tetrahedron Lett.; 1988, 29, 1235.

28- Saalfrank, R.W.; Ackermann, E.; Fischer, M.; Wirth, U. Chem. Ber., 1987, 120, 2003.

29- For recent reviews see: a) Hassner, A. in "Azides and Nitriles: Reactvity and Utility", Scriven, E.F.V., Ed.; Academic Press, Orlando, 1984; Chapter 2. b) Nair, V. in "Small Ring Heterocycles", Hessner, A., Ed.; Willey: New York, 1983; Vol. 42, Part 1, pp 215-332. c) Moore, H. W.; Goldish, D.M. in "The Chemistry of Functional Groups, Suppl. D.", Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Chapter 8, P 321.

30- Hassner, A.; Wiegand, N.H.; Gottieb, H.E. J. Org. Chem., 1986, 51, 3176.

31- Dewar, M.J.S.; Starch, D.M. J. Am. Chem. Soc., 1985, 107, 3898.

32- Gompper, R.; Topfl, W. Chem. Ber., 1962, 95, 2861.

33- Gompper, R.; Kunz, R Chem. Ber., 1962, 99, 2900.

34- a) Lahti, P.M.; Berson, J.A. J. Am. Chem. Soc., 1981, 103, 7011.
b) Kirmse, W.; Schnurr, O.; Jendralla, H. Chem. Ber., 1979, 112, 2120.

35- Birkofer, L.; Ritter, A. Tetrahedron Lett., 1962, 5, 195.

36- Aumuller, A.; Hunig, S. Angew. Chem. Inter. Ed. Engl., 1984, 23, 447.

37- Jenko, B.; Lipovsek, F.; Lindie, Z.; Jeraj, F. Ger. Offen. DE3225249, 1983, 99, 157854y.

38- Flury, D. Unpublished results, these laboratories.

39- Mckusick, B.C.; Heckert, R.E.; Cairns, T.L.; Coffman, D.D.; Mower, H.F. J. Am. Chem. Soc., 1957, 80, 2806.

40- Acker, D.S.; Hertler, W.R. J. Am. Chem. Soc., 1962, 84, 3370.

41- Herter, W.R.; Benson, R.E. J. Am. Chem. Soc., 1962, 84, 3475.

42- Iwatsuki, S.; Itoh, T.; Yokotoni, I. Macromolecules, 1983, 16, 1817.

43- Hall, H.K. Jr.; Bentley, J.H. Poly. Bull., 1980, 3, 203.

44- Iwatsuki, S.; Takahito, I. Macromolecules, 1979, 12, 208.

45- Iwatsuki, S.; Takahito, I. Macromolecules, 1980, 13, 983.

46- Thiele, J.; Balhorn, H. Ber., 1904, 37, 1463.

47- Hall, H.K. Jr. Angew. Chem. Int. Ed. Engl., 1983, 22, 440.

48- Hall, H.K., Jr.; Padias, A.B.; Tanka, H. Macromolecules, 1987, 20, 247.

49- Jug, K. J. Am. Chem. Soc., 1987, 109, 3534.

50- Brandt, M.W.; Mulvaney, J.E.; Hall, H.K. Jr.; Green, G.P. J. Am. Chem. Soc. Polymer Preprints, 1989, 30(1), 346.

51- Kulp, S.S. J. Chem. Educ., 1988, 65, 742.

52- a) Hyatt, J.; Krutak, J. J. Org. Chem., 1977, 42, 169. b) Chem, C.; Reynolds, G.; Cossar, B. J. Org. Chem., 1981, 46, 2752. c) Fadiat, A. Synthesis, 1976, 133.

53- Hyatt, J.A. J. Org. Chem., 1983, 48, 129.

54- Iwatsuki, S.; Itoh, T.; Iwa, T.; Sawada, H. Macromolecules, 1985, 18, 2726.