To the Graduate Council:

I am submitting herewith a dissertation written by Kenneth Joseph Muschelewicz entitled "The Synthesis and Characterization of a Methacrylic Polymer containing a Pendant Electroactive TCNQ Moiety." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

James Q. Chambers, Major Professor

We have read this dissertation
and recommend its acceptance:

Accepted for the Council:

Vice Provost
and Dean of The Graduate School

THE SYNTHESIS AND CHARACTERIZATION OF A METHACRYLIC POLYMER CONTAINING A PENDANT ELECTROACTIVE TCNQ MOIETY

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Kenneth Joseph Muschelewicz

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ABSTRACT

The synthesis of poly[2-(7,7,8,8-tetracyano-p-quinodimethane)-ethylmethacrylate], a polymer containing an electroactive TCNQ group pendant to the polymer backbone, was attempted using two methods. The first approach involved the polymerization of 2-(2,5-dioxocyclohexyl)ethylmethacrylate, which had been prepared via a series of reactions from a monoalkylated cyclohexanedione, which in turn, had been formed by an enamine alkylation reaction, resulting in a highly crosslinked, insoluble polymer which could not be further modified to the target polymer. The second method, involved the treatment of poly(methacryloyl chloride) with an alkoxide resulting in a precursor polymer. The precursor polymer was further modified to form a TCNQ-methacrylate polymer having a degree of polymerization near 29. Infrared spectroscopy and elemental analysis indicated that a copolymer comprised of the TCNQ-methacrylic polymer and poly(methacrylic acid) was actually formed instead of the homopolymer. The copolymer and copolymer intermediates were also analyzed by visible spectroscopy as films. The electrochemical behavior, of the copolymers in solution and as films, was examined using cyclic voltammetry. The copolymer intermediates showed little or no evidence of electroactivity, while the TCNQ-copolymer, on the other hand, exhibited an electrochemical response. The TCNQ-copolymer was further studied in aqueous solution at various pH's. The electrochemical results for the TCNQ-copolymer suggested that the carboxylic acid derivative was influencing the voltammetry resulting in quasi-reversible behavior.

TABLE OF CONTENTS

CHAPTER		PAGE
I	INTRODUCTION	1
II	LITERATURE REVIEW	8
	A. Electrode Modification	8
	B. Electroactive Polymers	9
	C. Synthesis of TCNQ's, 1,4-Cyclohexanedione, and Their Substituted Derivatives	18
III	RESULTS AND DISCUSSION	28
	A. Monomer Preparation	28
	B. Polymer Preparation	55
	C. Degree of Polymerization for PMMA and the Target Polymer, obtained from the Molecular Weight of PMMA	80
	D. Electrochemical Analysis	82
IV	EXPERIMENTAL	98
	A. Materials and Equipment	98
	B. β-Ketoester Alkylation	100
	C. Practice Monomer Synthesis	102
	D. Target Monomer Synthesis	106
	E. Polymerization	109
	F. Polymer Modification	111
	G. Spectrometric Analysis	112

CHAPTER PAGE

H. Molecular Weight Determination of PMMA, used to estimate the Degree of Polymerization of the Target Polymer 113

I. Electrochemical Analysis 115

V CONCLUSION 117

LIST OF REFERENCES 123

VITA 129

LIST OF TABLES

TABLE		PAGE
I	Enamine of Cyclohexanone Data	34
II	Ethyl(2-oxocyclohexyl)acetate Data	35
III	Ethylene Ketal of Ethyl(2-oxocyclohexyl) acetate Data	36
IV	Ethylene Ketal of 2-(2-Oxocyclohexyl)-ethanol Data	37
V	Ethylene Ketal of 2-(2-Oxocyclohexyl)-ethylmethacrylate Data	41
VI	2-(2-Oxocyclohexyl)ethylmethacrylate Data	42
VII	2-(Cyclohexane)ethylmethacrylate Data	44
VIII	7, 12-Dioxaspiro[5.6]dodecan-3-one Data	47
IX	Enamine of 7, 12-Dioxaspiro[5.6]dodecan-3-one Data	48
X	Ethyl(2,5-dioxocyclohexyl)acetate Data	49
XI	Bisethylene Ketal of Ethyl(2,5-dioxocyclohexyl)-acetate Data	52
XII	Bisethylene Ketal of 2-(2,5-dioxocyclohexyl)-ethanol Data	53
XIII	Bisethylene Ketal of 2-(2,5-dioxocyclohexyl)-ethylmethacrylate Data	57
XIV	2-(2,5-Dioxocyclohexyl)ethylmethacrylate Data . .	58

LIST OF FIGURES

FIGURE		PAGE
1	The overall strategy for the preparation of a polymer containing a pendant TCNQ moiety	4
2	The direct esterification of a 1,4-cyclohexanedione alcohol with methacryloyl chloride	30
3	The attempted alkylation of 2,5-dicarbomethoxy-1,4-cyclohexanedione	31
4	The overall synthesis of 2-(2-oxocyclohexyl)ethylmethacrylate	32
5	The mass spectrum of compound 9.	39
6	The formation of the cyclized enol ether of 2-(2-oxocyclohexyl)ethanol	40
7	The synthesis of 2-(cyclohexyl)ethylmethacrylate .	43
8	The overall synthesis of 2-(2,5-dioxocyclohexyl)-ethylmethacrylate	45
9	The mass spectrum of compound 15	51
10	The mass spectrum of compound 17	56
11	The proposed synthesis of poly[2-(7,7,8,8-tetracyano-p-quinodimethane)ethylmethacrylate using the chemical modification of a polymeric diketone intermediate	59
12	The preparation of the two model polymers and the chemical modification of the practice polymer intermediate	61
13	IR spectrum of practice polymer P1 cast as a film on a NaCl cell	62
14	IR spectrum of the practice polymer intermediate polymer P2 cast as a film on a NaCl cell	63
15	IR spectrum of the chemically modified polymer P3 cast as a film on a NaCl cell	65

FIGURE PAGE

16 Attempted polymerization of 2-(2,5-dioxocyclohexyl)ethylmethacrylate 66

17 The overall synthesis of the TCNQ methacrylic copolymer P7-PCOOH 69

18 Carbon NMR spectrum of the reaction product of compound 17A and poly(methacryloyl chloride) . . . 71

19 IR spectrum of polymer P4-PCOOH dried at 68°C under vacuum (KBr pellet) 72

20 IR spectrum of polymer P5-PCOOH (KBr pellet) . . . 73

21 IR spectrum of polymer P6-PCOOH (KBr pellet) . . . 75

22 IR spectrum of polymer P7-PCOOH (KBr pellet) . . . 76

23 Visible spectrum of polymer P7-PCOOH in DMF . . . 78

24 The composite visible spectra of the four chemically modified polymers cast as films onto microscope slides 79

25 IR spectrum of PMMA prepared from PMC cast as a film on a NaCl cell 81

26 Plot of the reduced viscosity [n_{red}] vs concentration 83

27 The composite cyclic voltammograms of polymer films P4-PCOOH, P5-PCOOH, and P6-PCOOH in 0.1M $TBABF_4$/MeCN, potential vs. Ag:AgCl, 20 mV/s . 85

28 The cyclic voltammogram of polymer film P7-PCOOH, 0.1M $TBABF_4$/MeCN, potential vs. Ag:AgCl, 20 mV/s . 86

29 The proposed mechanism for the internal protonation of the TCNQ radical anion 87

30 The composite polymer film cyclic voltammograms of P7-PCOOH at pH = 5.4, 7.8, 9.0, 10.0, in 0.5M NaCl, potential vs. SCE, 20 mV/s 89

31 The solution cyclic voltammograms of P5-PCOOH and P6-PCOOH in 0.1M TBAP/DMF, potential vs. Ag:AgCl, 30 mV/s 91

FIGURE PAGE

32 The solution cyclic voltammogram of P7-PCOOH in 0.1M TBAP/DMF, potential vs. Ag:AgCl, 30 mV/s . . 93

33 The effect of the addition of $TBA^{+}OH^{-}$ to the polymer solution of P7-PCOOH, in 0.1M TBAP/DMF, potential vs. Ag:AgCl, 20 mV/s 94

34 The cyclic voltammogram of pyridine in 0.1M TBAP/DMF after the addition of an equal portion of acid, potential vs. Ag:AgCl, 20 mV/s . 95

35 The attempted synthesis of a TCNQ methacrylate polymer 118

36 The successful preparation of a methacrylic TCNQ - methacrylic acid copolymer (P7-PCOOH), by the chemical modification reactions on methacrylic polymer intermediates (P4-PCOOH, P5-PCOOH, and P6-PCOOH) 119

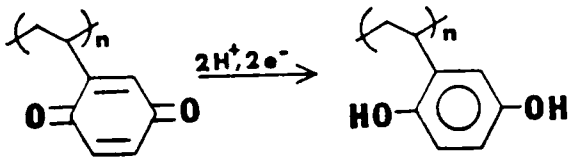
CHAPTER I

INTRODUCTION

The study of polymers displaying electrical activity has been of interest to scientists for many years. In discussing the electrical activity of polymers, one can describe their conductive or electron exchange behavior.[1] In fact, a charge transfer polymer usually exhibits some form of conductivity. In this study, the electron exchange behavior of polymers is of great concern due to the role it plays in modifying electrodes. Polymer film modified electrodes have been used, for example in potentiometric sensors, reference electrodes, and in electrochromic, electrocatalytic and bilayer film devices.[2]

The distinctive characteristic of polymer film modified electrodes is that the polymer films contain electrochemically and/or chemically reactive sites. It is these electrochemically active centers that undergo the electron transfer with the electrode surface.[3] When the polymer contains a moiety that accepts electrons, it is referred to as an acceptor polymer, and when the moiety gives up electrons, it is termed an electron donor. Charging of the films involves a combination of processes, such as counter ion migration, electron hopping, and/or expulsion of co-ions initially absorbed in the film as an ion pair. During film charging, the neutral polymer coating is converted to an ion exchange polymer, and therefore, the electrode process can be viewed as an

electrodeposition of ions into the polymer film. An example of this charging can be seen in the electrochemical reduction of poly(vinyl benzoquinone).[1]



(1)

The resulting charge transport throughout a polymer film is influenced by a few overlapping factors in the film charging process. Coupled chemical reactions, for instance, can occur, leading to dimerization or ion-pair formation, or irreversible coupling reactions may take place resulting in electrochemical crosslinking.[4] These factors in the charging process distinguish electroactive polymer films from their corresponding electrically active monomeric materials in solution, since they mostly occur in the polymer phase.

One of the most widely studied electron acceptor molecules is tetracyanoquinodimethane (TCNQ) which forms a variety of stable radical anion salts.[5] The TCNQ radical anion is relatively insensitive to oxygen and water. Since the electrochemical behavior of the TCNQ monomer was well understood, interest arose in comparing the electroactivity of the TCNQ monomer with a polymer containing the TCNQ moiety. Polymers containing the TCNQ moiety were therefore prepared in our laboratory by Day[6] and Francis.[7] The polymers formed, based on the same TCNQ diol, were a polyester from adipyl chloride, and three polyurethanes derived from hexamethylene

diisocyanate (HMDI), 2,4-toluene diisocyanate (TDI), and methylene bis(4-phenyl diisocyanate) (MDI). All of the polymers (prepared via polycondensation reactions) contained the electroactive center as part of the polymer backbone. The TCNQ polymers had the ability to undergo two, one-step reversible electron exchange reactions, forming the polymeric anion radical and polymeric dianion. Studies on the TCNQ polymers, by Chambers and co-workers,[8,9] showed that charge transport through the polymer films was influenced by pH and solvents, which was directly related to the material's backbone structure. Because of this, we were interested in preparing a polymer containing an electroactive moiety pendant to the polymer chain instead of part of it.

The goal of this research project, therefore, is to prepare a polymer where the TCNQ group is pendant to the polymer chain, since its moiety should behave more like the TCNQ molecule. By preparing the TCNQ polymer using an addition polymerization process, the molecular weight of the polymer obtained in this manner should be higher than those formed by polycondensation reactions.

In order to prepare a polymer with the TCNQ pendant to the backbone, several strategies, as outlined in Figure 1, were proposed. The initial idea was to first prepare a TCNQ-monomer and then polymerize it to the TCNQ-polymer (Figure 1, equation a). But this scheme probably would not work since the reaction conditions that would be used to prepare the TCNQ monomer could possibly destroy the double bond which is needed for polymerization. If the

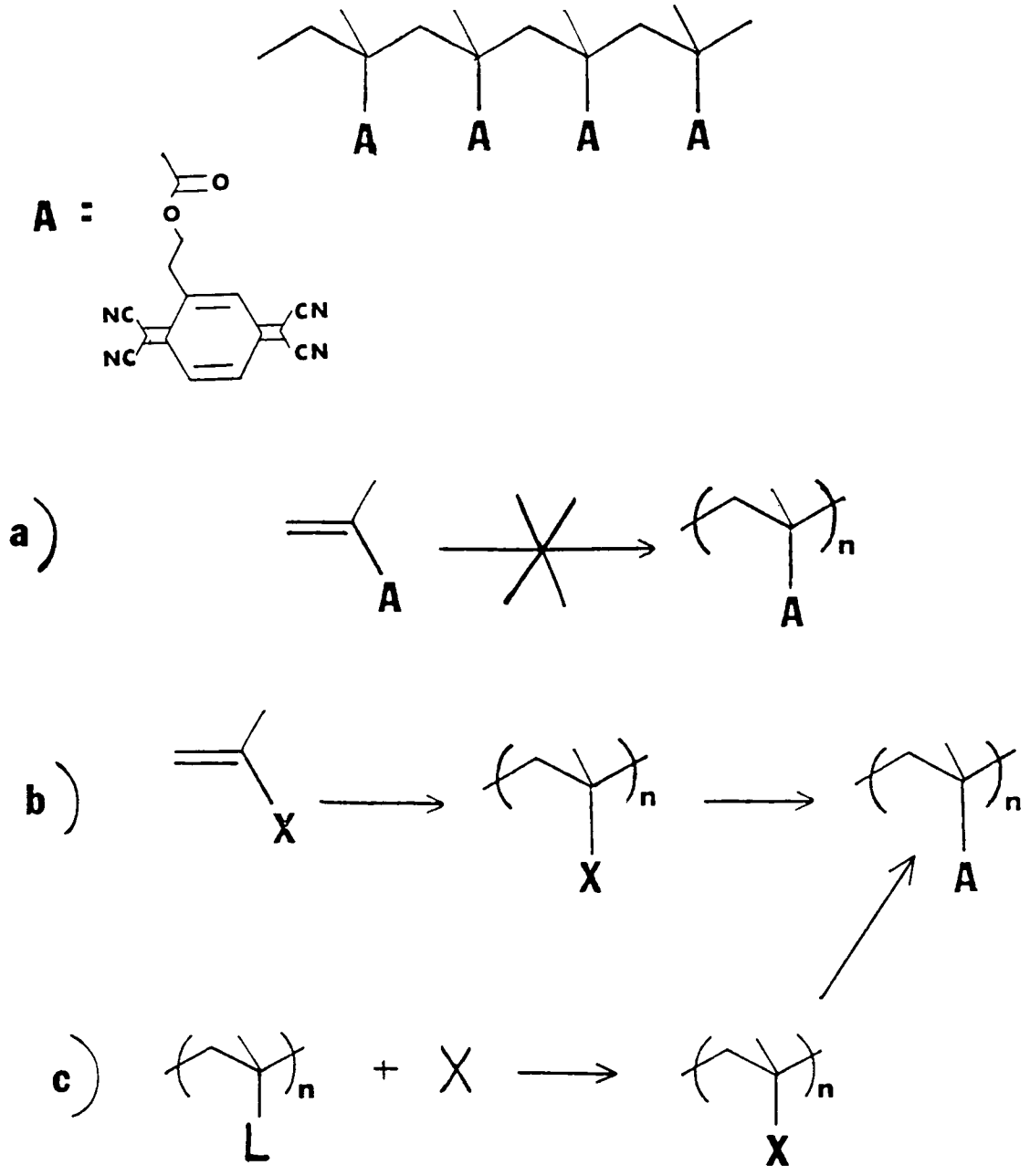
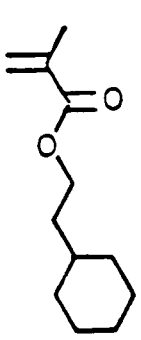


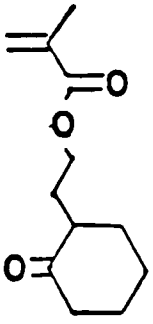
Figure 1. The overall strategy for the preparation of a polymer containing a pendant TCNQ moiety.

monomer could eventually be prepared, then the quinone-like nature of the TCNQ group would probably be the cause of uncontrollable polymerization conditions, since the moiety may inhibit free radical or ionic initiation. As a consequence, two alternate routes were proposed. In Figure 1, equation b shows a way of preparing the target polymer by first forming a monomer, polymerizing it, and then chemically modifying the precursor polymer to the TCNQ polymer. If this route should fail for any reason, then the last route (Figure 1, equation c) can be attempted. Equation c is similar to equation b, except that an existing polymer is modified by reacting it with a small intermediate molecule forming a precursor polymer which is then chemically modified to produce the TCNQ polymer. In this study, a methacrylic polymer was chosen to be the backbone for the polymeric TCNQ for the following reasons: (1) acrylic systems have been well studied, and for the most part are easily polymerized;[10] (2) a functionalized methacrylate can be prepared using the acid chloride of methacrylic acid and an alcohol;[11 - 13] and most importantly for this work since the polymer must not degrade during the chemical modification reactions, (3) possible crosslinking or degradation would be prevented by the protected tertiary carbon on the backbone.[14] The preparation and characterization of the electroactive methacrylic polymer will be attempted during the course of this study. Specifically, the goals of this research project are as follows:

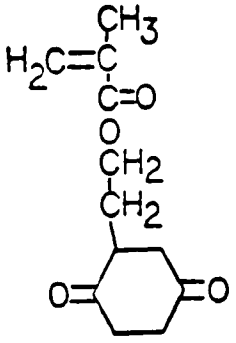
1. Two model monomers, 2-(cyclohexyl)ethylmethacrylate (I) and 2-(2-oxocyclohexyl)ethylmethacrylate (II) will be prepared and characterized, along with their intermediates, by infrared and nuclear magnetic resonance spectroscopy. Once the reaction conditions have been worked out, a similar synthetic scheme used to form compound II will then be used to prepare the target monomer, 2-(2,5-dioxocyclohexyl)ethylmethacrylate (III).



I



II



III (2)

2. Both of the model monomers will be polymerized by a chain growth polymerization process using AIBN as the initiator. The same procedure and reaction conditions used to polymerize 2-(2-oxocyclohexyl)ethylmethacrylate will then be used to form the model precursor polymer poly[2-(2-oxocyclohexyl)ethyl-methacrylate], which will then be chemically modified in order to determine whether chemical modifications of the target precursor polymer can be achieved.

3. The preparation of the target precursor polymer, poly[2-(2,5-dioxocyclohexyl)ethylmethacrylate] will be attempted and if it is successfully made, then a series of reactions will be

performed on the polymer in order to prepare the presumeably electroactive target polymer.

4. If for any reason the target polymer can not be made in the manner previously described, the alternative route as seen in Figure 1, equation c, will be attempted. Poly(methacryloyl chloride), an existing polymer, will be treated with the bisethylene ketal of 2-(2,5-dioxocyclohexyl)ethanol to form the substituted polymethacrylate, which will then be chemically modified via a series of reactions, to produce the TCNQ methacrylate polymer. The chemical structural change of the polymer will be monitored using infrared spectroscopy and elemental analysis. Ultraviolet-visible spectroscopy will also be performed on the TCNQ polymer since the spectra of the TCNQ films contain characteristic bands in the visible region.
5. The electrochemical behavior of the chemically modified polymer intermediates and the final polymer will be studied using cyclic voltammetry. The voltammetry experiments shall be used to show that the final modified polymeric material displays some form of charge transfer capacity. The new polymeric TCNQ will be used in the future for further electrochemical studies.

CHAPTER II

LITERATURE REVIEW

A. Electrode Modification

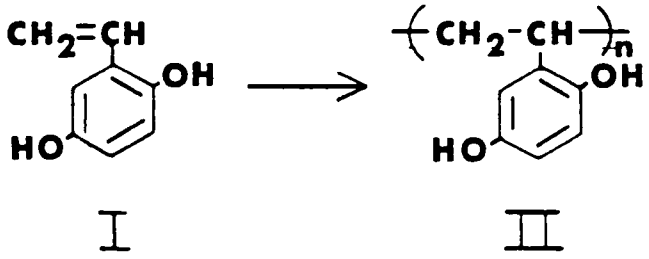
Chemical modifications of electrodes have been accomplished using various techniques such as chemisorption, chemical bonding of small molecules onto electrodes, and film deposition of electroactive substances on electrode surfaces. Chemisorption is the strong irreversible adsorption of an electroactive species on an electrode. Hubbard and Lane[15, 16] were the first to demonstrate the idea of immobilizing a redox functionality having known chemisorption tendencies. Even though chemisorption involves interactions with fairly strong bonding, in most cases the interactions are not stable. Covalent bond-forming immobilizations therefore surfaced. The covalent bonding of an optically active compound[17] and a catalytically active group[18] on carbon electrodes, and of electroactive molecules on metal oxide electrodes have been reported.[19] Since these reports, much work involving the attachment of electrically active polymeric materials to electrode surfaces has also been done.

The idea of coating electroactive polymers on electrode surfaces originated from the work of Kaufman,[20] Bard[21] and Miller.[22] In Bard's study, for example, the electrochemical behavior of poly(vinylferrocene) coated onto a platinum electrode was compared to the electrochemical behavior of the same polymer in solution.

Soon after this work, interest arose in the use of electoactive polymeric materials cast as films onto electrode surfaces, in order to modify the electrochemical behavior of electrodes. The history of electroactive polymers will be examined in the following section.

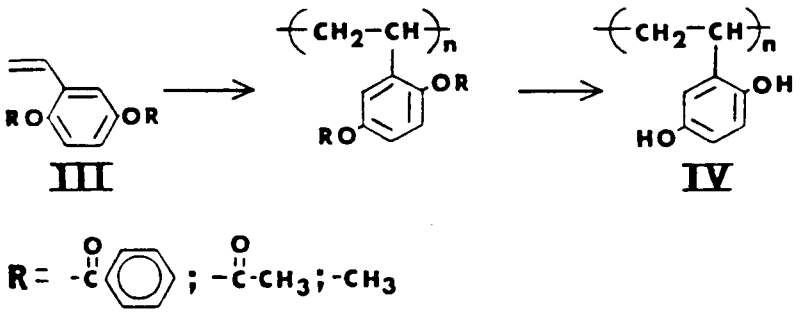
B. Electroactive Polymers

Electroactive polymers have existed for over 50 years but their importance in electrode modification has only recently been recognized. Initially, polymers that displayed charge transfer were thought of solely as ion exchange polymers. From a study directed by Cassidy, however, the electoactive behavior of a different class of polymers undergoing charge transfer, which were referred to as electron exchange polymers, was observed.[23] The first electron transfer polymer studied by Cassidy was a poly(vinylhydroquinone - benzoquinone) system. This specific polymer was suitable for study since a) it underwent a rapid reversible oxidation - reduction couple, and b) much fundamental work had previously been done on hydroquinone and its derivatives.[24] Poly(vinylhydroquinone) was synthesized by the free radical polymerization of 2-vinyl-1,4-hydroquinone (I) resulting in low molecular weight material (II).



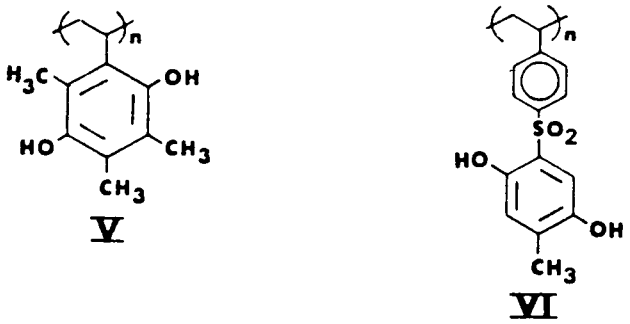
I II (3)

Low molecular weights occurred since the hydroquinone acted as an inhibitor to chain propagation. Because of this, the hydroxyl groups were first protected by forming the dibenzoate,[25] diacetate,[26] or dimethoxy derivatives,[27] and the protected monomers (III) were then polymerized. Following polymerization, the protecting groups were removed resulting in high molecular weight poly(vinylhydroquinone) (IV).



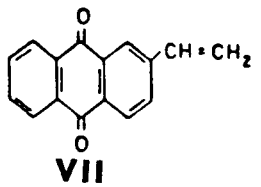
(4)

Kun[28] discovered that the poly(vinylhydroquinone) was sensitive to pH. With increase in pH, the polymer became very susceptible to irreversible oxidation. To prevent this oxidative degradation from occurring, functionalized poly(vinylhydroquinones) were prepared. The methylated (V) and sulfone (VI) derivatives were reported.[28, 29]

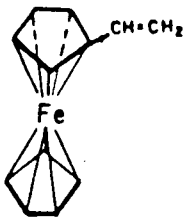


(5)

Other charge transfer polymers prepared from vinylanthraquinones (VII),[30] vinylferrocene (VIII),[31] vinylphenothiazine (IX),[32] and a polymer derived from a vinylpyridinium salt (X)[33] were also studied.

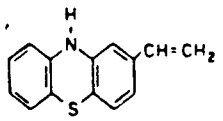


VII

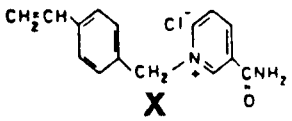


VIII

(6)



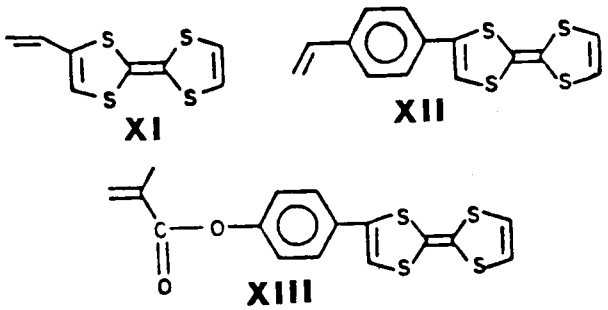
IX



X

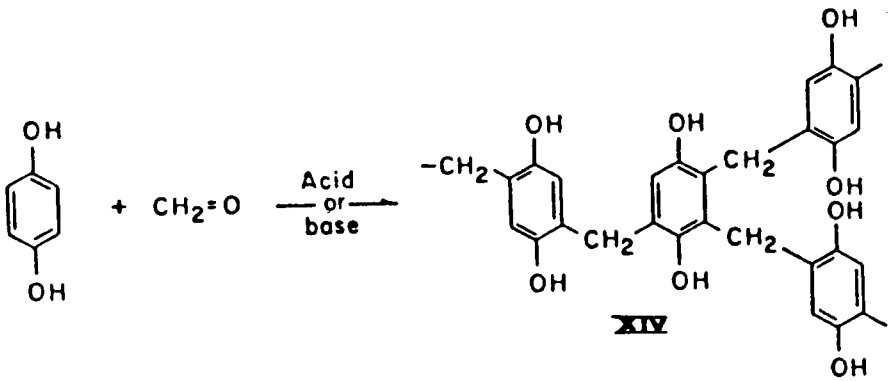
A series of polymers based on the electron exchange moiety, tetrathiafulvalene (TTF), has also been reported. Green and Allen[34] showed that vinyltetrathiafulvalene (XI) polymerizes on standing or during exposure to UV radiation or azo initiation to give low molecular weight poly(vinyltetrathiafulvalene). Another TTF monomer, (p-vinylphenyl)tetrathiafulvalene (XII), was thermally polymerized in bulk by Kaplan,[35] but attempts to use either anionic or free radical polymerization techniques were unsuccessful. Poly(p-vinylphenyl)tetrathiafulvalene was found to be insoluble in all attempted solvents, and it was difficult to characterize. Pittman and workers[36] reported the synthesis of a homopolymer derived from p-(tetrathiafulvalene)phenylmethacrylate (XIII), and a copolymer formed from the same monomer XIII and methyl methacrylate.

Again, as in the case with the polystyrene TTF polymer, the methacrylic homopolymer was polymerized in bulk and the resulting polymer was virtually insoluble in all common solvents.



(7)

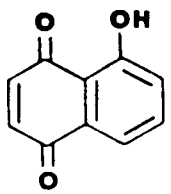
Electron transfer polymers have also been prepared by polycondensation reactions. Hydroquinone - formaldehyde polymers (XIV) were formed in this manner but they were highly crosslinked and insoluble.



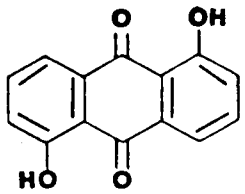
(8)

Also, the hydroquinone - formaldehyde polymers would undergo irreversible oxidation. Because of this, the polymers were derivatized in order to increase their stability and reduce

oxidative degradation.[37] Maneche and Bauer synthesized a variety of charge transfer condensation polymers using napthoquinone and anthraquinone derivatives such as juglone (XV) and anthrarufin (XVI), respectively.[38]



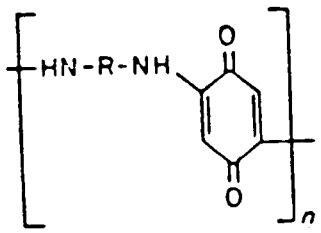
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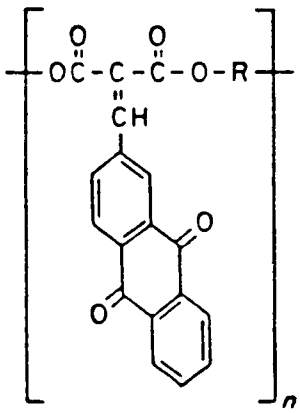
XVI

(9)

Polyaminoquinones (XVII) and substituted anthraquinone polyesters (XVIII) displaying charge transfer behavior have also been synthesized.[39, 40]



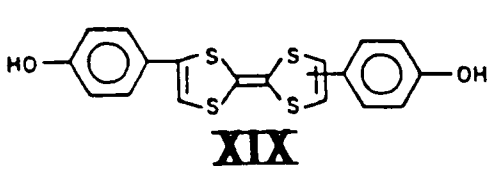
XVII



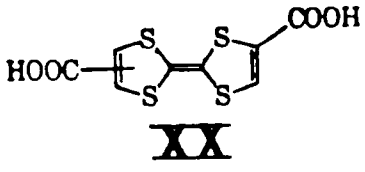
XVIII

(10)

Condensation polymers, based on a TTF diol (XIX) with diacid chlorides, diisocyanates, and disulfonyl chlorides have been prepared.[41, 42] Polyamides formed by the reaction of the TTF diacid (XX) and a variety of diamines were also reported.[43, 44]



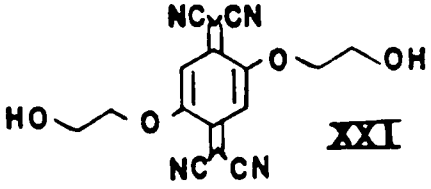
XIX



XX

(11)

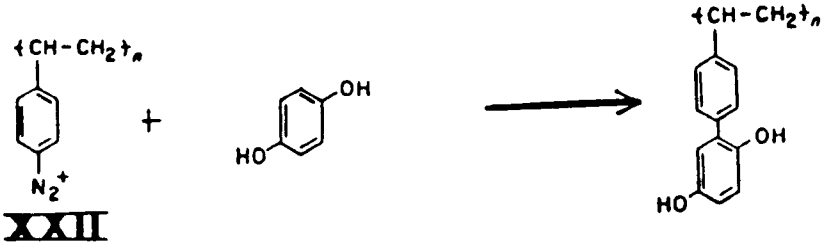
Most recently, a polyester[45] and polyurethanes[7] based on tetracyanoquinodimethane (TCNQ) have been formed, and their electrochemical behavior was studied. The polymers were prepared by the solution condensation the same TCNQ diol (XXI) with a diacid chloride and three different diisocyanates.



XXI

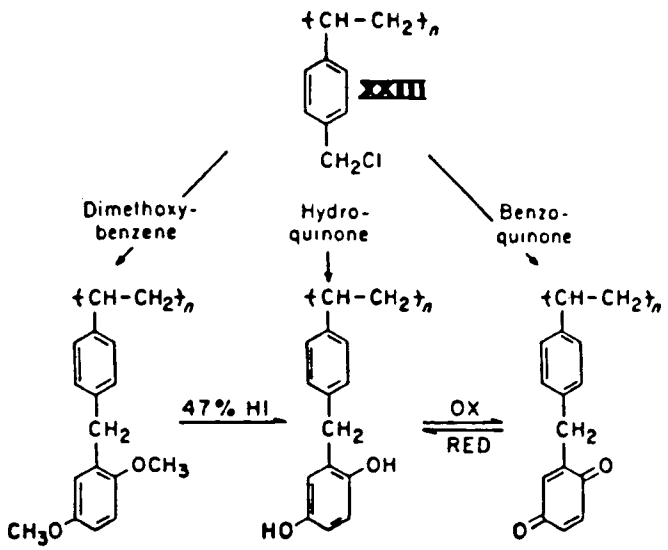
(12)

Recall that the previously reported charge transfer polymers prepared by either the addition or condensation polymerization reactions were often highly crosslinked, difficult to dissolve, and/or hard to work with. As an alternative, to overcome some of these difficulties, electroactive polymers have been prepared by attaching the electroactive species directly onto existing polymers. This approach allows for better control over the physical properties, but the resulting polymers may not be completely reacted or uniform. Many accounts of oxidation - reduction moieties bound onto derivatized polystyrene matrices have been reported. Rao[46] used poly(styrene diazonium salts) (XXII) to prepare hydroquinone bound styrene polymers.



XXII (13)

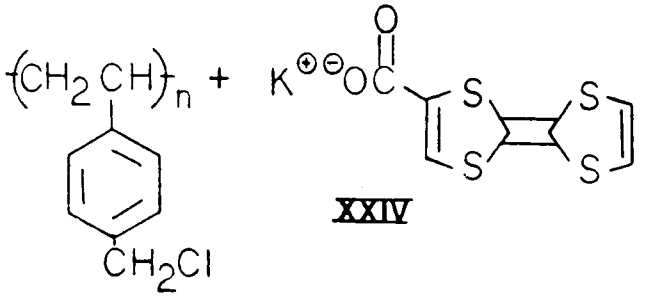
In addition to hydroquinone, other electron transfer moieties such as ferrocene,[47] p-phenylenediamine,[48] and 1,4-N-dimethylamino-benzene[49] were also attached to a polystyrene framework in this manner. The resulting polymers were crosslinked since the diazonium salt coupled with other parts of the polymer matrix. Kun[49, 50] prepared similar styrene quinone polymers by chemically modifying poly(vinyl benzylchloride) (PVBC, XXIII).



(14)

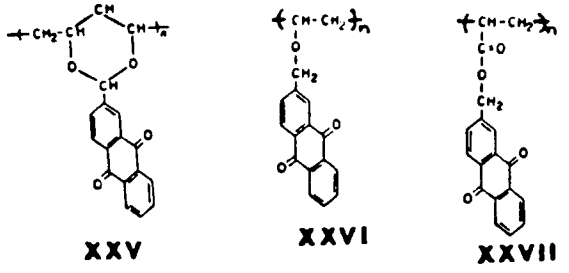
Benzoquinone, and either protected or unprotected hydroquinones reacted with PVBC, but many of the chloromethyl groups did not react with the quinone derivative, and therefore a copolymer was formed. Based on the fact that the addition of amines to chloromethylated

poly(styrene-divinylbenzene) results in anion exchange polymers, the unreacted chloromethyl groups in the hydroquinone polymer were also converted to the amine salts producing a redox polymer containing anion exchange groups. Kaufman[51] treated PVBC with the potassium salt of a monocarboxylic acid TTF derivative (XXIV) under various conditions, resulting in polymers having 30 - 90% incorporation of the TTF moiety. All of the polymers were soluble in N,N-dimethyl formamide.



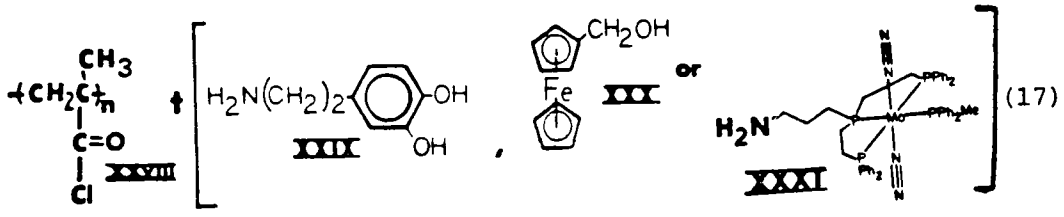
XXIV (15)

In addition to poly(vinyl benzylchloride), poly(vinyl alcohol) has been treated with electroactive compounds to produce charge transfer polymers. Poly(vinyl alcohol) was used to prepare a substituted pyridinium polymer[52] and an acetal linked 2-formal-anthraquinone polymer (XXV).[53] The acetal linked quinone was very susceptible to acid hydrolysis. When 2-chloromethylanthraquinone or 2-hydroxymethylanthraquinone were treated with poly(vinyl alcohol), ether linked quinone polymers (XXVI) were produced. 2-Hydroxy-methylanthraquinone has also been attached to poly(acrylic acid) to yield an acrylic quinone polymer (XXVII).[54]



XXV XXVI XXVII (16)

Poly(methacryloyl chloride) (PMC, XXVIII) has also been used to produce electroactive acrylic polymers. PMC has been functionalized with the electroactive moieties, dopamine (XXIX),[55] hydroxylmethylferrocene (XXX),[56] and a molybdenumdinitrogen complex (XXXI).[57]

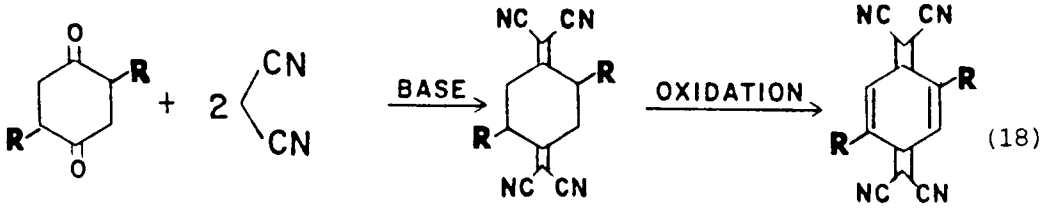


(17)

The previous reports demonstrate that not only can electroactive compounds be polymerized, but that the charge transfer moiety can also be attached directly onto the polymer backbone. Recall, that the aim of this research project is to prepare a polymer where an electroactive group, specifically a TCNQ moiety, would be pendant to the polymer chain. Prior to this report, no one had linked or attempted to bind TCNQ to the backbone of a polymer. The overall strategy for preparing a polymer containing the TCNQ moiety has previously been discussed in the Introduction chapter of this dissertation. The following section will deal with the synthesis of TCNQ, 1,4-cyclohexanedione, and their substituted derivatives.

C. Synthesis of TCNQ's, 1,4-Cyclohexanedione and Their Substituted Derivatives

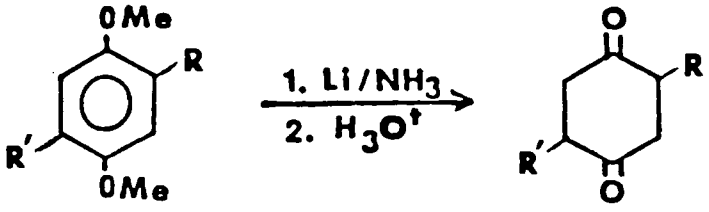
In 1965, Hertler[58] prepared TCNQ by the reaction of malononitrile with 1,4-cyclohexanedione to produce a tetracyano intermediate which was then oxidized. Soon after, several substituted TCNQ compounds were formed using the same synthetic pathway.[59, 60, 61]



(18)

R= CH_3; $CH(CH_3)_2$; C_2H_5

Two schemes have been employed in order to prepare substituted 1,4-cyclohexanediones (XXXIV). The first route, reported by Anderson,[59] involved the Birch reduction of a mono- or disubstituted, methyl protected hydroquinone. The reaction conditions are dangerous and low yields are produced.

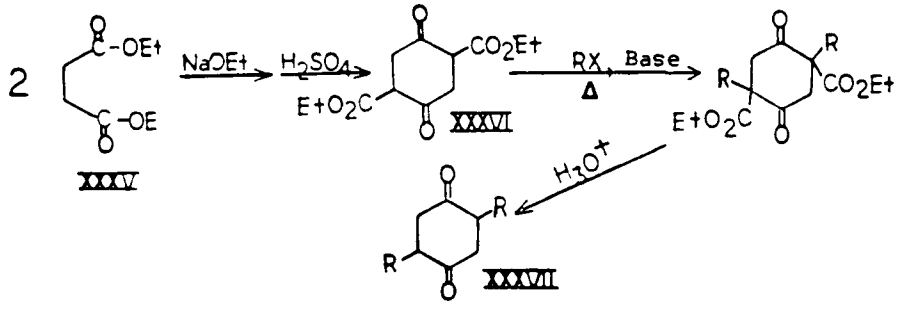


(19)

R ; R′= CH_3 ; CH_3 and $(CH_2)_nCOOCH_3$; H

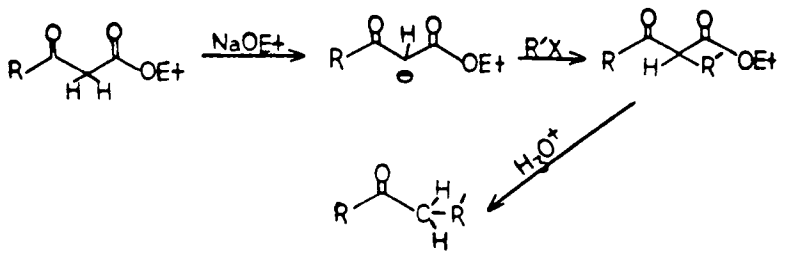
n=1,2

Another method for preparing substituted 1,4-cyclohexanediones begins with the alkylation of 2,5-dicarboethoxy-1,4-cyclohexanedione (XXXVI).[59] 2,5-Dicarboethoxy-1,4-cyclohexanedione, a β-keto ester, which had been prepared by the Dieckman self condensation reaction of diethylsuccinate (XXXV) in sodium ethoxide,[62] was alkylated using a base and an alkyl halide, and the resulting substituted ester was then allowed to undergo decarboxylation to form the substituted diketone derivative (XXXVII).



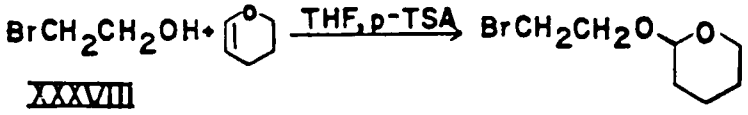
(20)

The alkylation of compound XXXVI follows the same mechanism as that for simple β-keto esters, where an enolate anion, formed by the abstraction of a proton from the center carbon with a strong base, reacts with an alkyl halide. Decarboxylation under acidic conditions then yields the substituted ketone.[63]



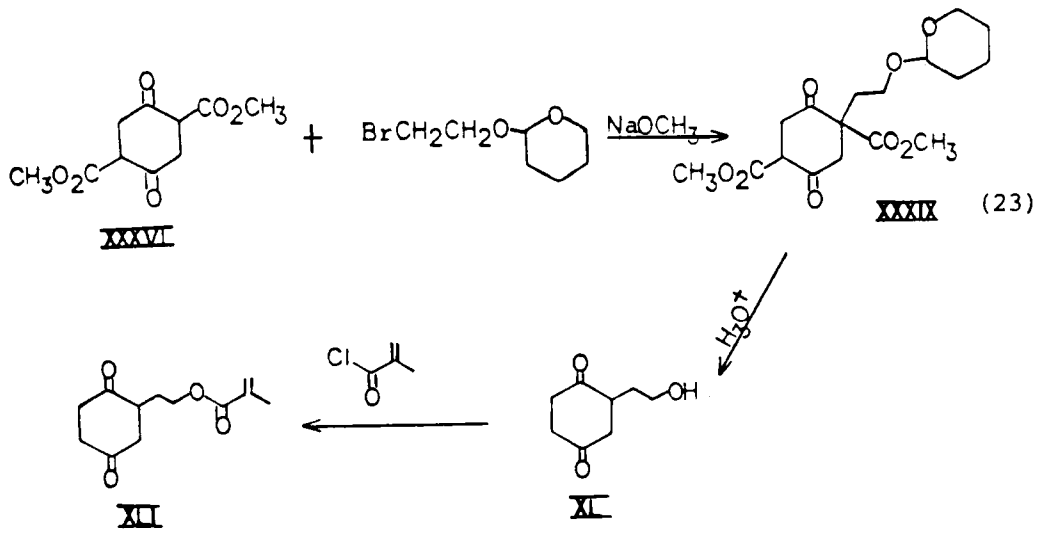
(21)

There are several drawbacks to the alkylation of β-keto esters in this manner since side reactions such as O-alkylation and dialkylation can occur. Also, elimination reactions are possible, particularly if a tertiary alkyl halide is used. Another limitation is that the alkyl group of the alkyl halide must be insensitive to base. Hydroxyl groups present in some alkyl halides are, for instance, base sensitive and must, therefore, be protected. One method of protecting an alcohol group is by forming an ether with dihydropyran.[64] This method was successfully used by Witiak[65] to protect the hydroxyl group in 2-bromoethanol (XXXVIII).



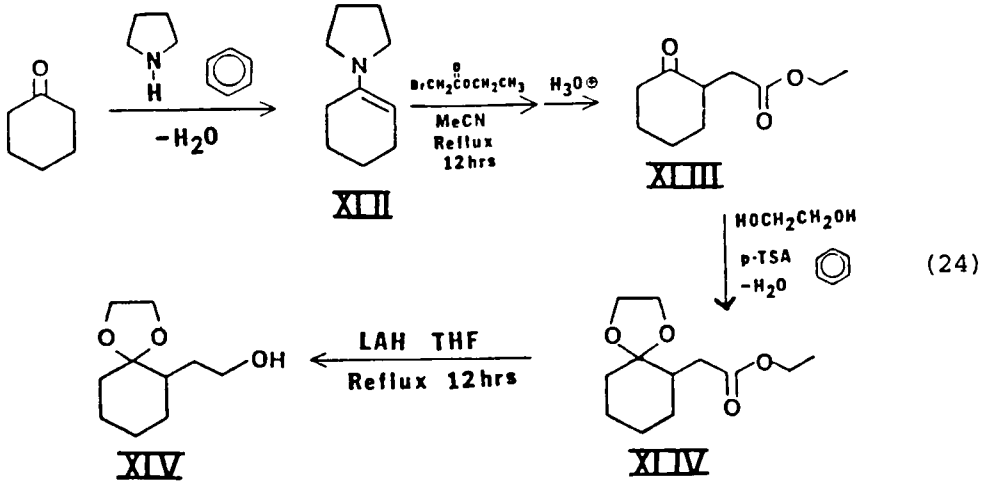
XXXVIII (22)

It was believed by this author that by treating one mole of the protected 2-bromoethanol with the β-keto ester (XXXVI), in the presence of a base, the monoalkylated mono-β-keto ester (XXXIX) could be formed. Treating compound XXXIX with acid should produce the alcohol (XL), which once isolated could later be condensed with the acid chloride of methacrylic acid to produce the 1,4-cyclohexanedione substituted methacrylate (XLI).

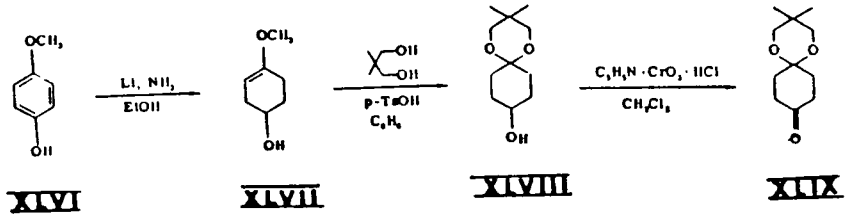


Recall, though, that in forming compound XXXIX many side products could form, making separation of the desired product difficult. If compound XLI could be made, it would then be polymerized resulting in a polymer which would be modified to generate the target TCNQ polymer. In case compound XXXIX can not be isolated, then another approach would be required to prepare the 1,4-cyclohexanedione alcohol derivative (XL).

Segre[66] successfully alkylated cyclohexanone using an enamine intermediate (XLII) and ethylbromacetate. The cyclohexanone ester (XLIII) was then converted to the alcohol derivative (XLV).



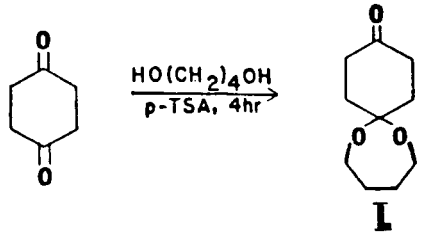
In order to prevent the ring carbonyl of the cyclohexanone ester from reacting with the reducing agent, lithium aluminum hydride,[67] it was protected by forming the ethylene ketal (XLIV).[68] For this study, in order to produce the monoenamine from 1,4-cyclohexanedione, the monoketal must first be prepared. The formation of 1,4-cyclohexanedione monoketals have been described by a variety of authors.[69 - 72] In most cases, however, the monoketals were formed in low yields since both carbonyls have identical reactivities. Marshall and Flynn[73] were able to greatly increase the yield of the 1,4-cyclohexanedione monoketal (XLIX) by first performing the Birch reduction on p-methoxyphenol (XLVI), ketalizing the reduced product (XLVII), and then oxidizing the hydroxyl group of compound XLVIII with pyridinium chlorochromate.



XLVI XLVII XLVIII XLIX (25)

Even though good yields are produced from Marshall and Flynn's procedure, the laboratory work-up is time consuming and involves some potential hazards. A convenient method to monoketalate 1,4-cyclohexanedione was devised by Hyatt.[74] In his study, when 1,4-cyclohexanedione was treated with ethylene glycol, propylene glycol, 1,3-propanediol, and neopentyl glycol, hard-to-separate product mixtures of unreacted 1,4-cyclohexanedione, the mono ketal,

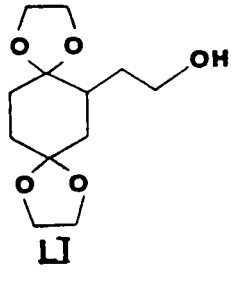
and the bisketal in ratios close to 1:2:1 were obtained. On the other hand, when the diketone was treated with 1,4-butanediol under normal ketalization conditions, mixtures of 6% unreacted diketone, 80% monoketal (L), and 14% bisketal formed. Even though distillation of the monoketal reduced the overall yield, the reaction could be completed in one day and the reaction conditions were not dangerous.



(26)

I

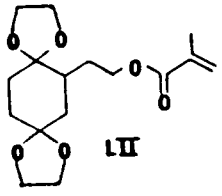
Once the 1,4-cyclohexanedione monoketal has been prepared using the Hyatt procedure, then Segre's reaction scheme involving the enamine alkylation of cyclohexanone can be used on 1,4-cyclohexanedione to produce the bisketal alcohol derivative, Compound LI.



(27)

LI

After formation of the bisketal alcohol (LI), the hydroxyl group will be esterified using the acid chloride, methacryloyl chloride, to produce the substituted methacrylate (LII).



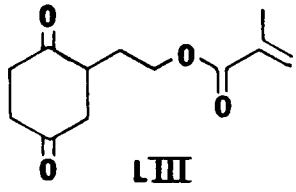
LII (28)

Often, the condensation of an acid chloride and hydroxyl compound is performed in the presence of an organic base such as pyridine or triethylamine to neutralize the hydrochloric acid (HCl) by-product.[75] Likewise, this procedure has been employed by a variety of authors to prepare methacrylate derivatives.[76 - 79]

$$CH_2=\overset{CH_3}{\overset{|}{C}}-CO_2Cl + ROH \xrightarrow{N(C_2H_5)_3} CH_2=\overset{CH_3}{\overset{|}{C}}-CO_2R + [HN(C_2H_5)_3]^+Cl^- \qquad (29)$$

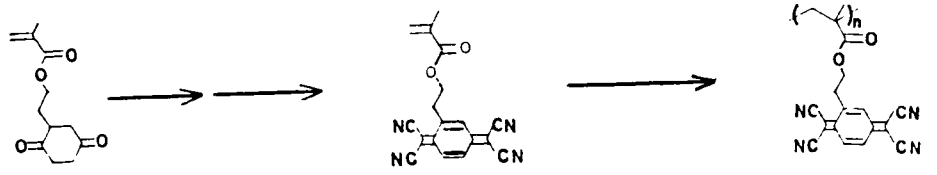
Even though this procedure has proved to be useful in preparing substituted methacrylates, a few problems exist: a) it is possible that low concentrations of acid may remain unreacted and, therefore, competing polymerization reactions can occur, b) the alcohol functionality may be sensitive to trace amounts of acid, and c) separation of the product mixture may be difficult. Banks[80] was able to eliminate the small amounts of HCl produced during esterification by employing 3Å molecular sieves to act as the acid trap, rather than an organic base. In his study, a series of methacrylate derivatives were prepared in this manner and allowed to

reflux for many hours without sign of polymer formation. Also, isolation of the product was simple, and high yields (around 90%) were achieved. For these reasons Bank's procedure will be used to form the substituted methacrylate (LII). Once the bisketal methacrylate is prepared, the ketal groups will be hydrolyzed resulting in the substituted 1,4-cyclohexanedione methacrylate (LIII).[81]



LIII (30)

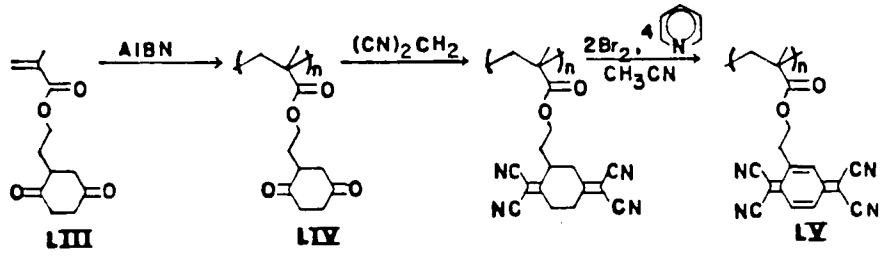
After the 1,4-cyclohexanedione methacrylate (LIII) is made then it could possibly be converted to a TCNQ methacrylate, which could be polymerized to produce a TCNQ polymer.



(31)

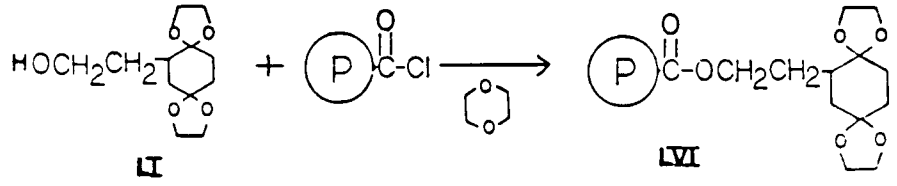
However, it is believed, by this author, that an alternative approach will be required due to difficulties associated with this type of reaction scheme. First there is the destruction of the acrylic double bond by the oxidation reaction using bromine. The other is, if the monomer could be prepared, then the quinone-like nature of the TCNQ would probably be the cause of uncontrollable

polymerization conditions, since the moiety would inhibit free radical or ionic initiation. Therefore it was decided that once the 1,4-cyclohexanedione methacrylate (LIII) is formed then it will be polymerized to form a precursor polymer (LIV). The precursor polymer LIV will be converted to the target TCNQ polymer (LV) using the procedure developed by Hertler for preparing TCNQ from 1,4-cyclohexanedione.



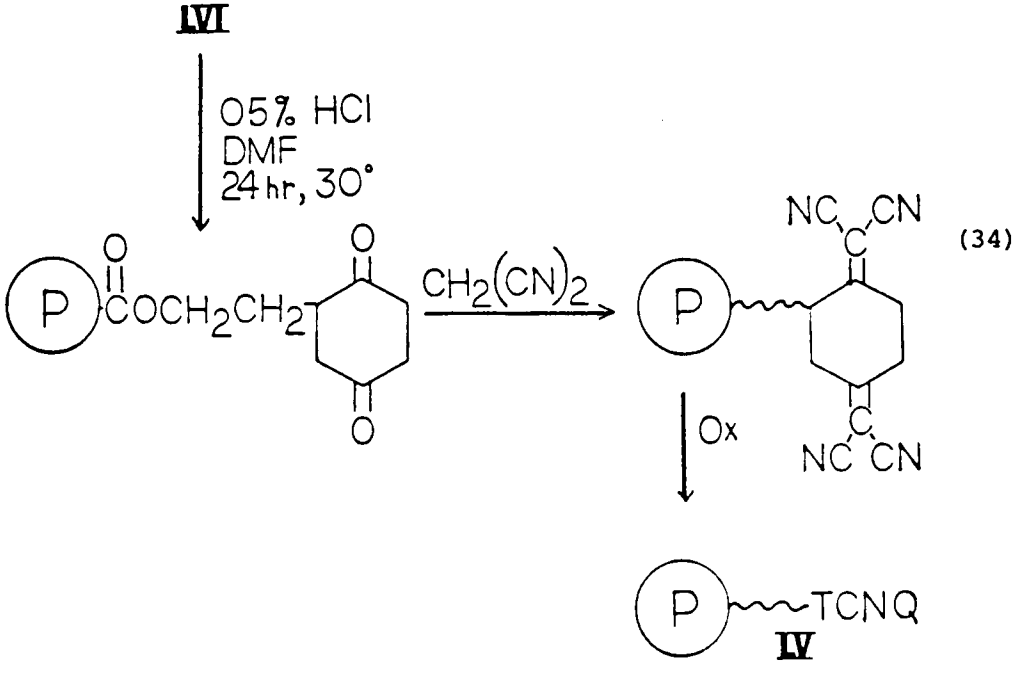
(32)

If for any reason, the target TCNQ polymer can not be synthesized by this technique, then an alternative scheme involving the chemical modification of poly(methacryloyl chloride) will be used.[55, 56, 57] If this is the case, then the bisketal alcohol (LI) will be reacted with the poly(methacryloyl chloride) to form the polymer LVI.



(33)

Then once the poly(bisketal)methacrylate (LVI) has been formed, both ketal groups will be hydrolized to form the precursor polymer which will be modified in two steps to make the target TCNQ polymer (LV).



(34)

CHAPTER III

RESULTS AND DISCUSSION

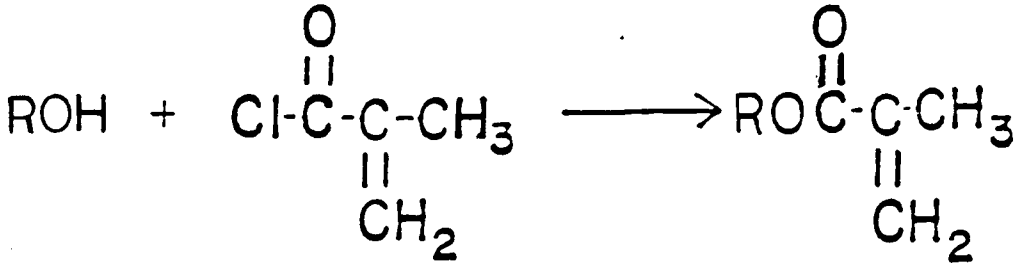
The main objective of this study was to prepare poly[2-(7,7,8,8-tetracyano-p-quinodimethane)ethylmethacrylate], a polymer containing electrically active tetracyanoquinodimethane (TCNQ) pendant groups, and then study its electrochemical behavior. To achieve this goal, two different methods were attempted in preparing the target polymer. The first approach involved the polymerization of the monomer 2-(2,5-dioxocyclohexyl)ethylmethacrylate, but the resulting precursor polymer could not be further modified to the TCNQ polymer because of problems associated with crosslinking. The second method, which involved the chemical modification of poly(methacryloyl chloride), was found to be a more successful way of preparing the target precursor polymer, which was then modified to the TCNQ polymer. The following sections will deal with the achievements and problems associated with the synthesis and characterization of poly[2-(7,7,8,8-tetracyano-p-quinodimethane)-ethylmethacrylate], beginning with the monomer preparation, followed by the polymer formation, and finally the electrochemical characterization of the polymer(s).

A. Monomer Preparation

The target monomer, 2-(2,5-dioxocyclohexyl)ethylmethacrylate, which was to be polymerized at some later time, was made by the

direct esterification of a 1,4-cyclohexanedione alcohol derivative and methacryloyl chloride (Figure 2). Two approaches were attempted in preparing the 1,4-cyclohexanedione alcohol derivative. The first approach, which involved the alkylation of the β-ketoester, 2,5-dicarbomethoxy-1,4-cyclohexanedione (1), as seen in Figure 3 (equation a through d), was unsuccessful since many side products were obtained during alkylation, and the desired ether (4), which was to be hydrolyzed (Figure 3, equation e), could not be isolated. Separation of the ether had been attempted using high performance liquid chromotography, but eight different fractions having similar retention volumes were observed making it almost impossible to separate the mixture. An alternative approach to the alkylation of 1,4-cyclohexanedione was needed.

In order to overcome the separation problem associated with alkylating β-ketoesters, another approach, which involved the mono carbon alkylation of 1,4-cyclohexanedione using an enamine, was proposed. The alkylation of carbonyls using an enamine had proven to be useful in the synthesis of many carbon alkylated compounds.[82] Segre and co-workers reported the use of an enamine intermediate (6) in their alkylation of cyclohexanone to form the ethylene ketal of 2-(2-oxocyclohexyl)ethanol (9) (Figure 4).[66] Since the blocking of one of the carbonyls in 1,4-cyclohexanedione results in a chemical structure similar to cyclohexanone, Segre's alkylation of cyclohexanone was repeated and used as a model for the preparation of the 1,4-cyclohexanedione alcohol derivative.



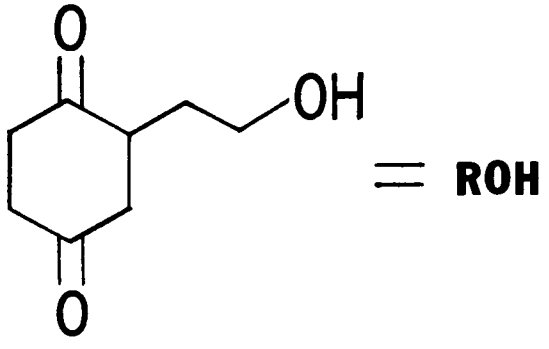


Figure 2. The direct esterification of a 1,4-cyclohexanedione alcohol with methacryloyl chloride.

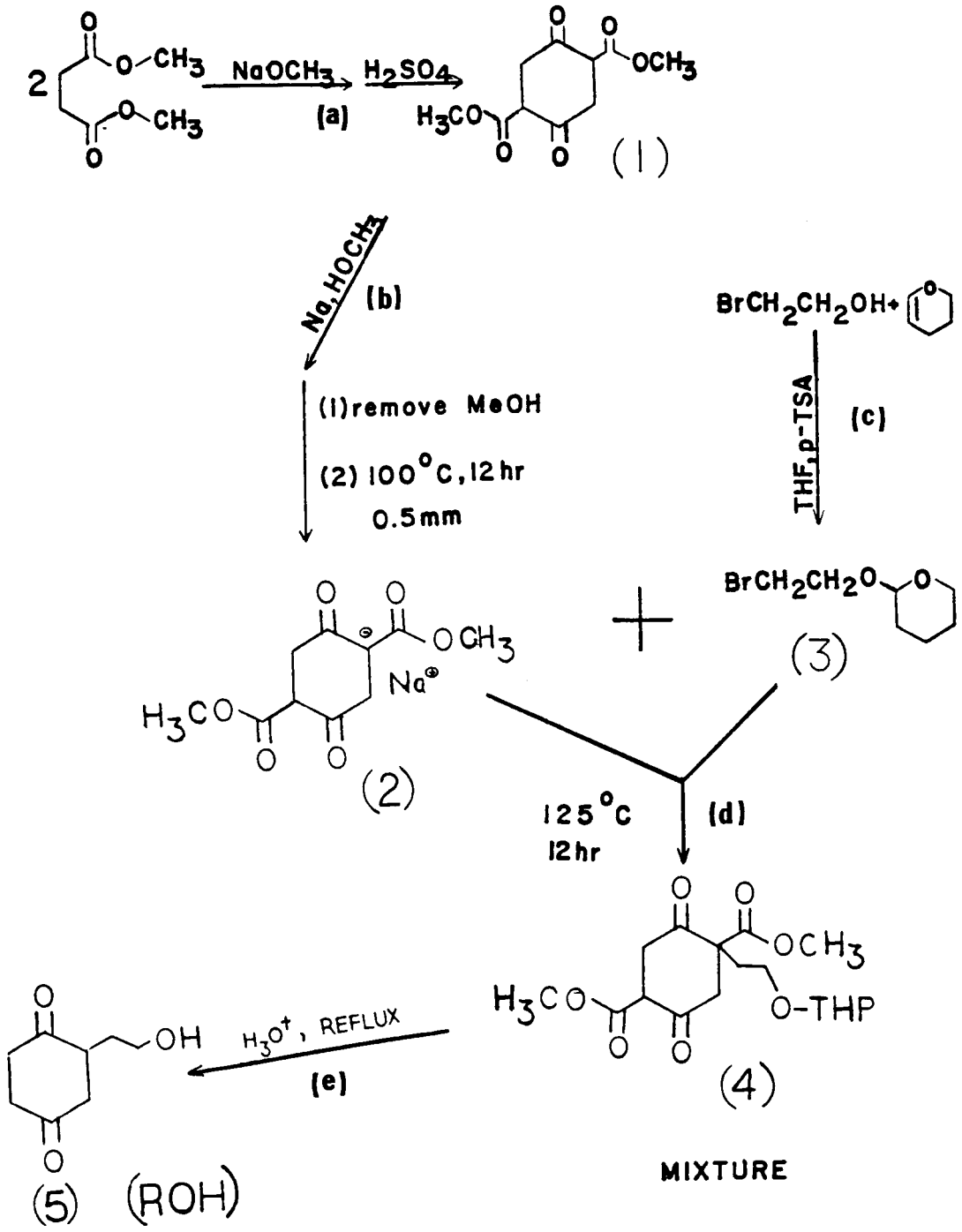


Figure 3. The attempted alkylation of 2,5-dicarbomethoxy-1,4-cyclohexanedione.

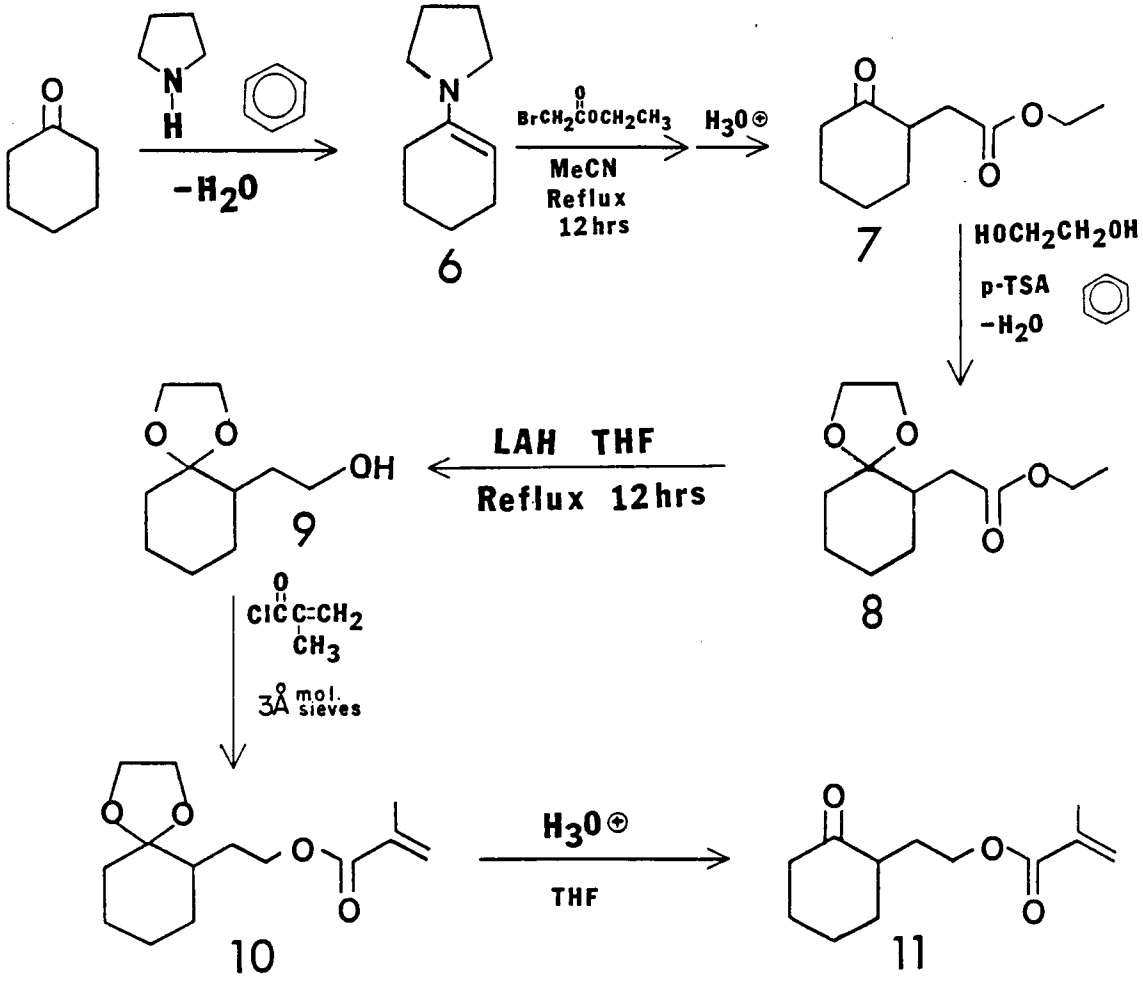


Figure 4. The overall synthesis of 2-(2-oxocyclohexyl)-ethylmethacrylate.

Using Segre's procedure, the cyclohexanone enamine of pyrrolidine (6) was prepared in a 97% yield and was characterized by infrared (IR) and proton nuclear magnetic resonance (PNMR) spectroscopy. The major IR bands and PNMR chemical shifts are listed in Table I, along with their assignments. In order to minimize discoloration and water contamination, the enamine was alkylated immediately with ethyl bromoacetate in dry acetonitrile resulting in a 70% yield of ethyl-(2-oxocyclohexyl)acetate (7). Both the ketone and ester functionality groups were observed in the IR spectrum, and the ethyl and ring protons were present in the PNMR (Table II). The carbonyl group on the ring of compound 7 was protected by reaction with ethylene glycol. The ethylene ketal ester (8) was produced in a 93% yield and was confirmed by IR and PNMR spectroscopy (Table III). The ester group of compound 8 was then reduced using LAH in anhydrous THF producing a 81% yield of the ethylene ketal of 2-(2-oxocyclohexyl)ethanol (9). The characteristic hydroxyl and ketal bands in the IR spectrum were observed, along with the disappearance of the carbonyl band. Using a D_2O exchange PNMR experiment, the hydroxyl proton was also identified (Table IV). The mass spectrum of the ethylene ketal alcohol is shown in Figure 5 and the major fragmentation assignments can be visualized in Table IV.

The acid hydrolysis of the ketal was not performed at this point due to formation of cyclized enol ethers as reported by Segre

TABLE I

Enamine of Cyclohexanone Data

Major IR bands

Wavenumber (cm^{-1})	Shape/Intensity		Assignment
3020	S	S	-C=C-H
2930	S	S	$-CH_2-$
2870	B	S	$-CH_2-$
1660	S	S	-C=C-
1300	S	S	-C-N-

PNMR

Multiplicity	δ	Integration	Assignment
Broad Singl.	4.2	1	a
Tripl.	3.0	4	b
Mult.	1.4-2.4	12	c & d

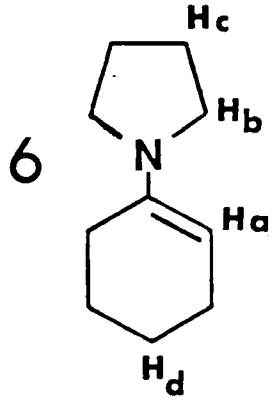


TABLE II

Ethyl(2-oxocyclohexyl)acetate Data

Major IR bands

Wavenumber (cm^{-1})	Shape/Intensity		Assignment
2950	S	S	$-CH_2-$
2875	S	S	$-CH_2-$
1730 - 1690	B	S	C=O
1200 - 1100	B	S	-C-O-

PNMR

Multiplicity	δ	Integration	Assignment
Tripl.	1.4	3	a
Quart.	4.1	2	b
Mult.	1.8 - 3.0	11	c & d

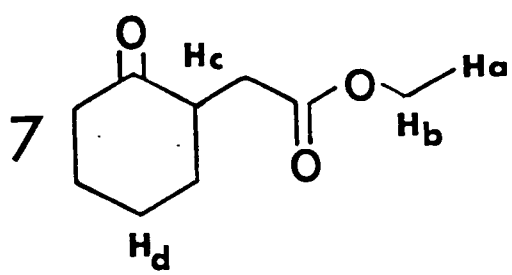


TABLE III

Ethylene Ketal of Ethyl(2-oxocyclohexyl)acetate Data

Major IR bands

Wavenumber (cm^{-1})	Shape/Intensity		Assignment
2950	S	S	$-CH_2-$
2875	S	S	$-CH_2-$
1725	B	S	C=O
1200 - 1100	B	S	-C-O-

PNMR

Multiplicity	δ	Integration	Assignment
Tripl.	1.3	14	a
Tripl.	1.5 - 3.0		b & c
Quart.	4.1	6	d
Singl.	4.0		e

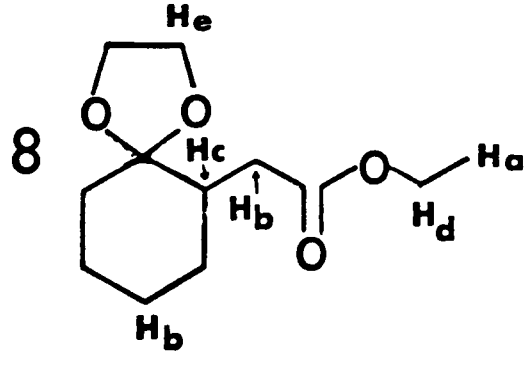


TABLE IV

Ethylene Ketal of 2-(2-Oxocyclohexyl)ethanol Data

Major IR bands

Wavenumber (cm^{-1})	Shape/Intensity		Assignment
3600 - 3200	B	S	-O-H
2950	S	S	$-CH_2-$
2870	S	S	$-CH_2-$
1200 - 1100	B	S	-C-O-

PNMR

Multiplicity	δ	Integration	Assignment
Singl.	3.9	4	a
Tripl.	3.6	4	b
Broad Singl.	3.7		c (D_2O exchange)
Multl.	1.2 - 2.0	11	d & e

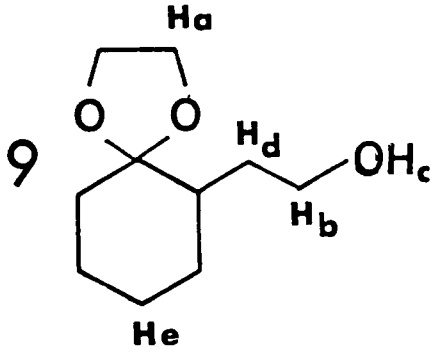
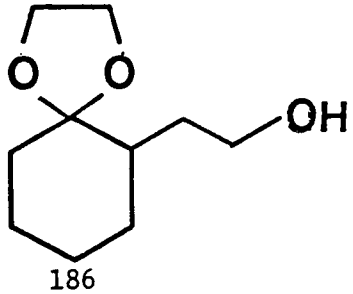
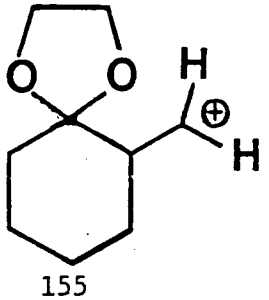


TABLE IV (continued)

Mass Spectral Assignments

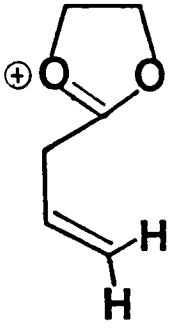


186

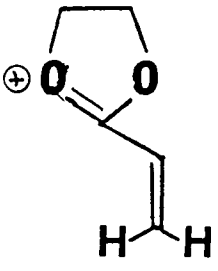


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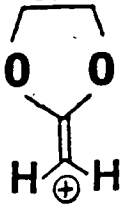
113



99



86



$C_4H_7^{\oplus}$ = 55

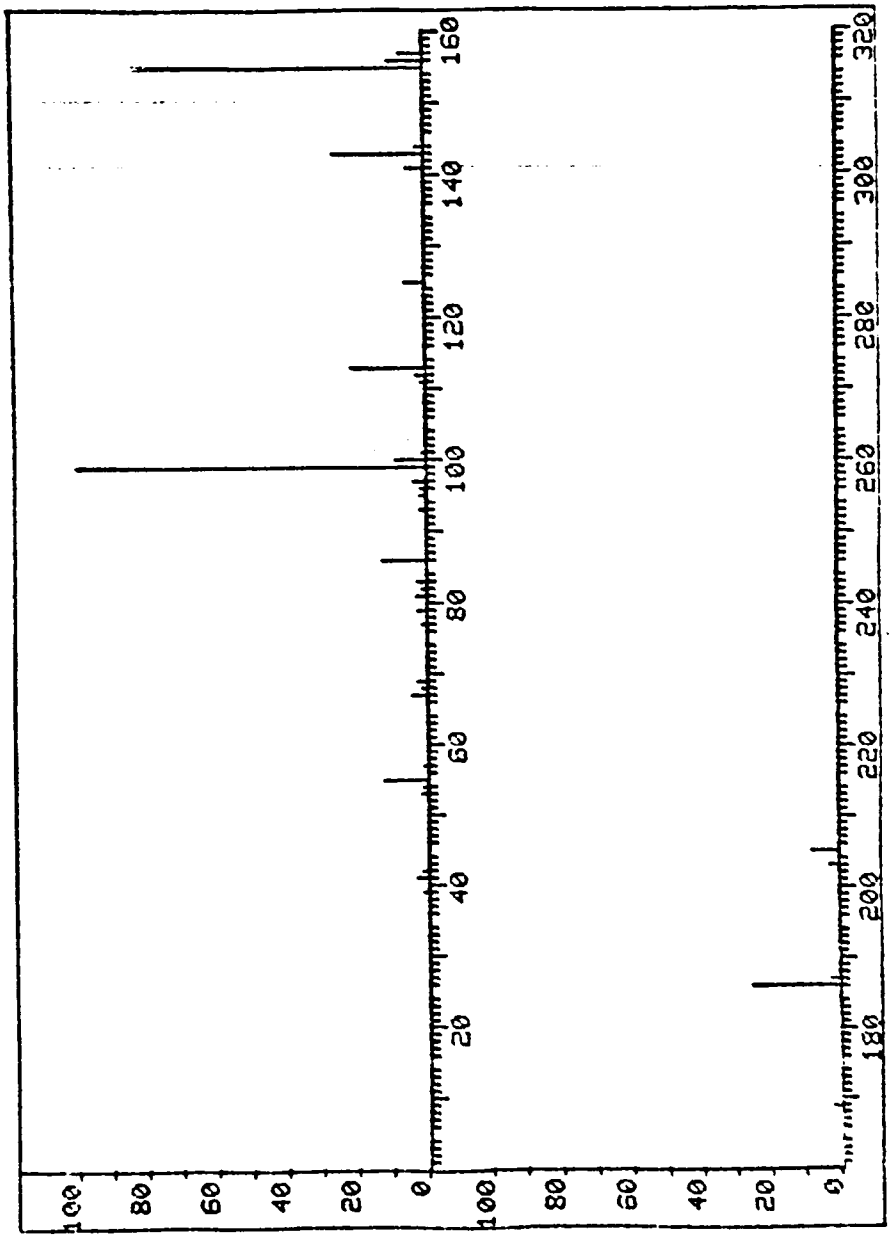


Figure 5. The mass spectrum of compound 9.

(Figure 6).[66] Instead the alcohol was esterified with methacryloyl chloride. Since both the ketal and acrylic groups are sensitive to acid, a procedure described by Banks was used in forming the methacrylate.[80] The alcohol and methacryloyl chloride were reacted in refluxing carbon tetrachloride along with 3Å powdered molecular sieves. The molecular sieves rapidly absorb the hydrogen chloride produced by the reaction of the alcohol with the acid chloride. The methacrylate was isolated in a 77% yield and characterized using IR and PNMR spectroscopy (Table V). The ketal was then hydrolized using acid to generate 2-(2-oxocyclohexyl)ethylmethacrylate (11) in a 75% yield. The IR spectrum indicates the presence of the ketone and ester, and the methylene double bond protons were identified in the PNMR spectrum (Table VI).

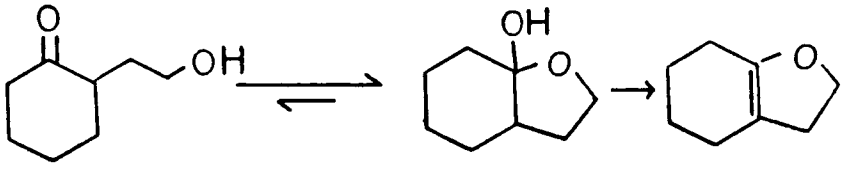


Figure 6. The formation of the cyclized enol ether of 2-(2-oxocyclohexyl)ethanol.

In addition to preparing the model monomer, another monomer, 2-(cyclohexyl)ethylmethacrylate (12) was also synthesized using Banks procedure, and was later polymerized. Compound 12 was formed by the esterification of 2-cyclohexylethanol and methacryloyl chloride in carbon tetrachloride along with 3Å molecular sieves in a

TABLE V

Ethylene Ketal of 2-(2-Oxocyclohexyl)ethylmethacrylate Data

Major IR bands

Wavenumber (cm^{-1})	Shape/Intensity		Assignment
3000 - 2850	B	S	$-CH_2-$
1725	B	S	C=O
1640	S	S	$-C=CH_2$
1200 - 1100	B	S	-C-O-

PNMR

Multiplicity	δ	Integration	Assignment
Singl.	6.2	1	a
Singl.	5.6	1	b
Singl.	4.0	6	c
Multl.	3.8 - 4.3		d
Multl.	1.4 - 2.4	11	e, f & g

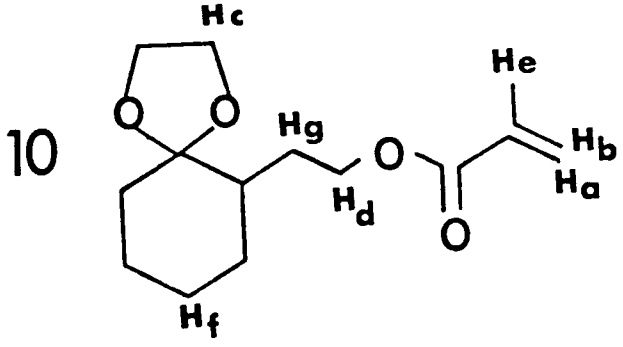


TABLE VI

2-(2-Oxocyclohexyl)ethylmethacrylate Data

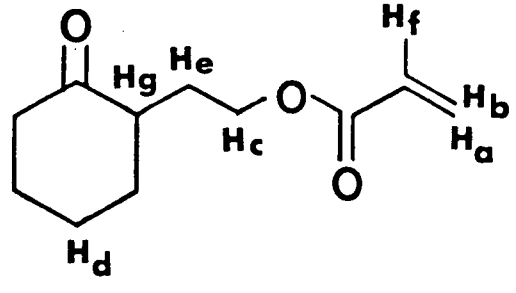
Major IR bands

Wavenumber (cm^{-1})	Shape/Intensity		Assignment
3000 - 2850	B	S	$-CH_2-$
1730 - 1700	B	S	C=O
1640	S	S	$-C=CH_2$
1200 - 1100	B	S	-C-O-

PNMR

Multiplicity	δ	Integration	Assignment
Singl.	6.2	1	a
Singl.	5.6	1	b
Multl.	4.0 - 4.5	2	c
Multl.	1.4 - 2.6	13	d, e & f
Multl.	3.6 - 4.0		g

11



89% yield (Figure 7). The material was characterized using IR and PNMR spectroscopy (Table VII).

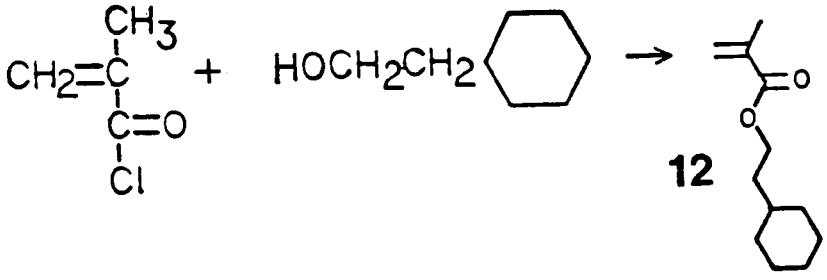


Figure 7. The synthesis of 2-(cyclohexyl)ethylmethacrylate.

Once the conditions had been worked out for the synthesis of both 2-(cyclohexyl)ethylmethacrylate and 2-(2-oxocyclohexyl)-ethylmethacrylate, and the spectral assignments were confirmed, the target monomer, 2-(2,5-dioxocyclohexyl)ethylmethacrylate (19) was successfully prepared. Figure 8 depicts the overall reaction scheme for the preparation of 2-(2,5-dioxocyclohexyl)ethylmethacrylate (19). Before the proposed synthetic pathway could be used to make the target monomer, the 1,4-cyclohexanedione had to be converted to a monoenamine derivative (14). To form a monoenamine with 1,4-cyclohexanedione, one of the carbonyl groups was converted to a ketal (13). There is, however, difficulty in preparing a monoketal of 1,4-cyclohexanedione, since the carbonyls have identical reactivities. This problem had been witnessed by a variety of authors.[69 - 73] To overcome this problem, Hyatt[74] devised a convenient method to form a monoketal of 1,4-cyclohexanedione with 1,4-butanediol (Figure 8, equation a). Using Hyatt's procedure, the

TABLE VII

2-(Cyclohexyl)ethylmethacrylate Data

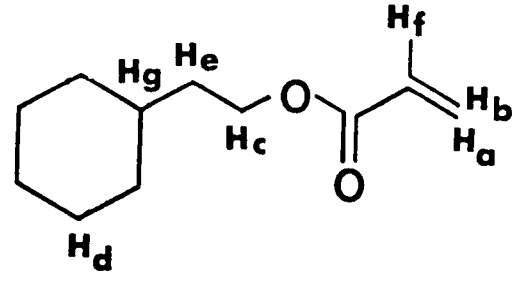
Major IR bands

Wavenumber (cm^{-1})	Shape/Intensity		Assignment
2950	B	S	$-CH_2-$
2875	B	S	$-CH_2-$
1750	B	S	C=O
1660	S	S	$-C=CH_2$
1200 - 1100	B	S	-C-O-

PNMR

Multiplicity	δ	Integration	Assignment
Singl.	6.3	1	a
Singl.	5.6	1	b
Multl.	3.9 - 3.6	2	c
Multl.	2.2 - 1.1	13	d, e, f & g

12



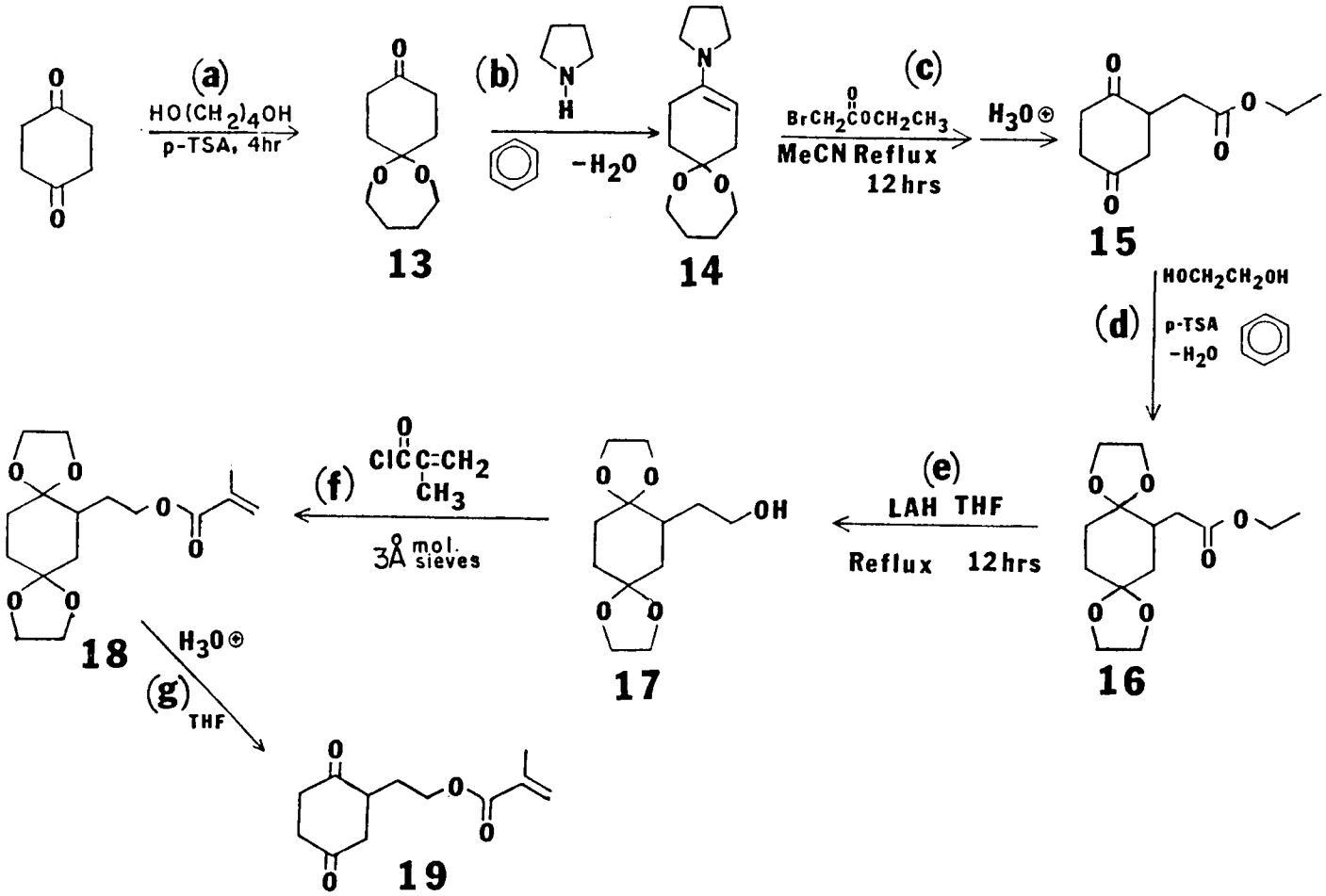


Figure 8. The overall synthesis of 2-(2,5-dioxocyclohexyl)-ethylmethacrylate.

monoketal of 1,4-cyclohexanedione (13) was prepared in a 65% yield and characterized using IR and PNMR spectroscopy (Table VIII). Once compound 13 was prepared, it was converted to the mono pyrrolidine enamine (14) and isolated in a 93% yield. The IR spectrum of compound 14, showed the carbon-nitrogen, carbon-oxygen and carbon-carbon double bond stretches, while the PNMR indicated the protons associated with the three ring systems (Table IX). Compound 14 was treated immediately with ethyl bromoacetate and after work-up, a 50% yield of ethyl(2,5-dioxocyclohexyl)acetate (15) was obtained. The characteristic ketone and ester bands were observed in the IR spectrum, the ethyl and ring protons were witnessed in the PNMR spectrum, and the carbon nuclear magnetic resonance (CNMR) spectrum indicated the presence of the ketone and ester carbonyls, along with the ring and alkyl carbons (Table X). The mass spectrum of compound 15 is shown in Figure 9 and the fragmentation assignments are presented in Table X.

Having isolated compound 15, it was then converted to the bisketal ester (16) using ethylene glycol. Compound 16 was produced in a 65% yield and characterized using IR and PNMR spectroscopy (Table XI). LAH was used to reduce the ester group, resulting in a 70% yield of the bisethylene ketal of 2-(2,5-dioxocyclohexyl)ethanol (17). The hydroxyl and ketal bands were observed in the IR spectrum, along with the loss of the carbonyl band. The PNMR showed evidence of the ring and hydroxyl protons, while the CNMR indicated the presence of the ring and alkyl carbons (Table XII). The mass

TABLE VIII

7, 12-Dioxaspiro[5.6]dodecan-3-one Data

Major IR bands

Wavenumber (cm^{-1})	Shape/Intensity		Assignment
2940	S	S	$-CH_2-$
2870	S	S	$-CH_2-$
1715	S	S	C=O
1200 - 1100	B	S	-C-O-

PNMR

Multiplicity	δ	Integration	Assignment
Tripl.	2.5	4	a
Multl.	1.7	4	b
Multl.	3.8	4	c
Tripl.	2.0	4	d

13

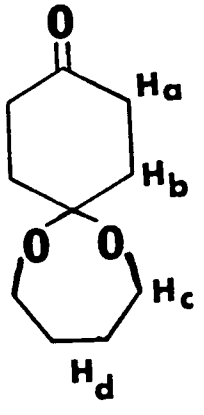


TABLE IX

Enamine of 7, 12-Dioxaspiro[5.6]dodecan-3-one Data

Major IR bands

Wavenumber (cm^{-1})	Shape/Intensity		Assignment
3020	S	M	-C=C-H
2950	S	S	$-CH_2-$
2875	S	S	$-CH_2-$
1660	S	S	-C=C-
1330	S	M	-C-N-
1175	S	M	-C-O-
1140	S	M	-C-O-

PNMR

Multiplicity	δ	Integration	Assignment
Tripl.	3.0	4	b
Broad Singl.	4.0	1	c
Broad Singl.	3.8	4	d
Multl.	1.6 - 2.4	14	a, e & f

14

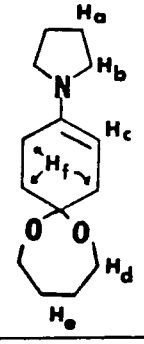


TABLE X

Ethyl(2,5-dioxocyclohexyl)acetate Data

Major IR bands

Wavenumber (cm^{-1})	Shape/Intensity		Assignment
2950	S	S	$-CH_2-$
2875	S	S	$-CH_2-$
1750 - 1715	B	S	-C=O
1175	S	M	-C-O-
1140	S	M	-C-O-

PNMR

Multiplicity	δ	Integration	Assignment
Tripl.	1.3	3	a
Quart.	4.2	2	b
Multl.	2.0 - 3.4	9	c - e

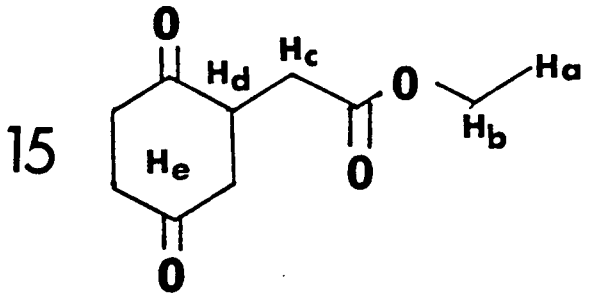
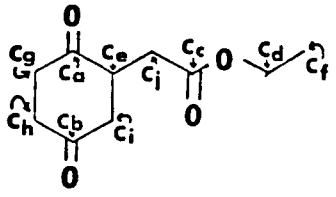


TABLE X (continued)

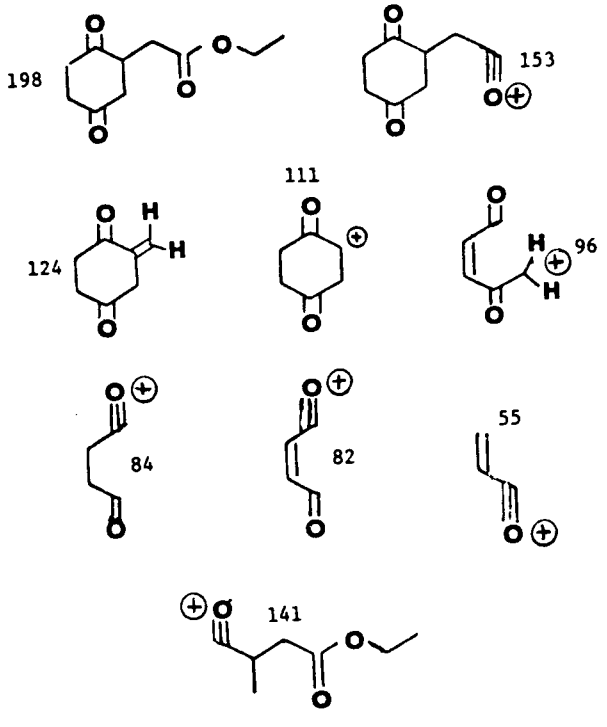
CNMR



15

δ	Assignment	δ	Assignment
208.74	a	35.76	g
207.97	b	36.82	h
171.51	c	33.59	i
60.37	d	41.87	j
42.13	e		
14.02	f		

Mass Spectral Assignments



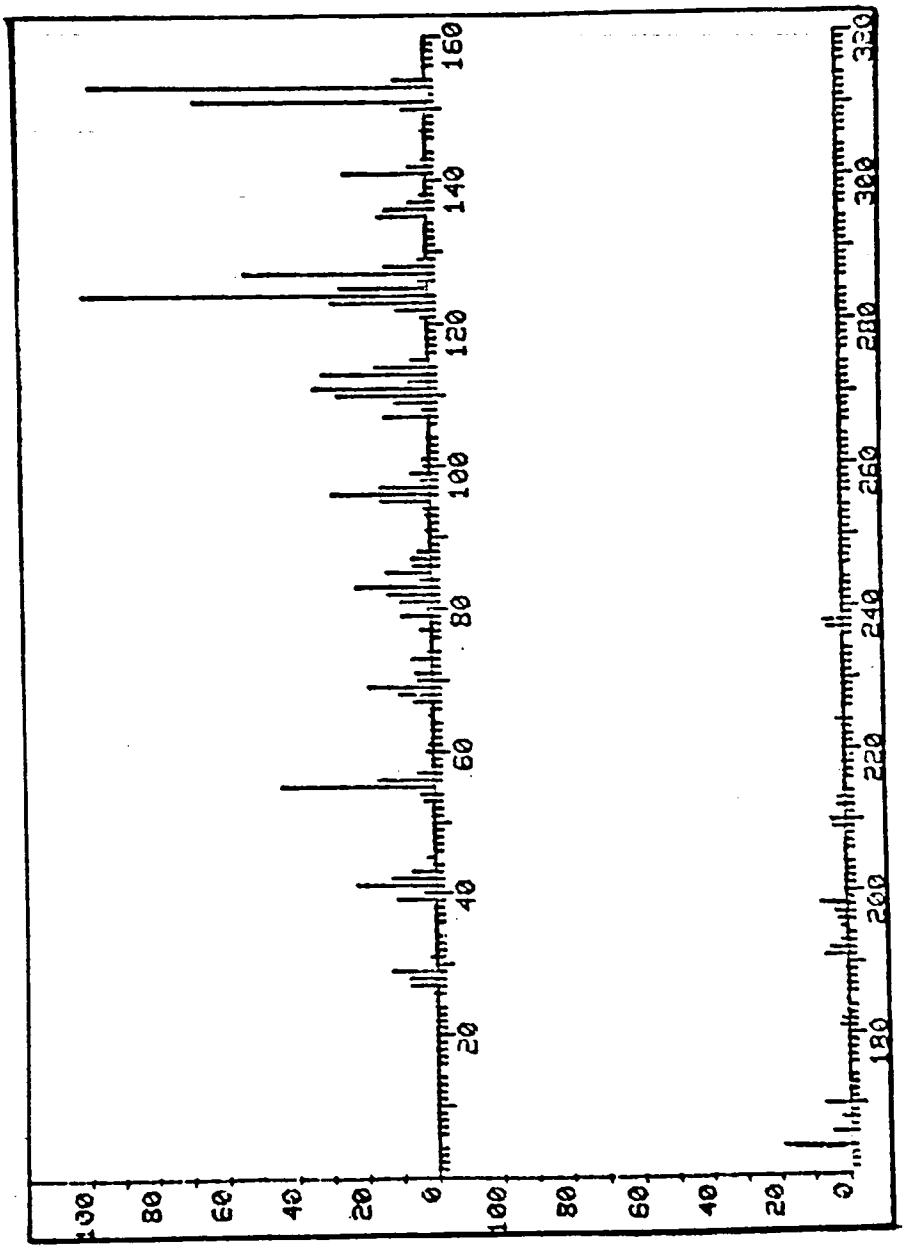


Figure 9. The mass spectrum of compound 15.

TABLE XI

Bisethylene Ketal of Ethyl(2,5-dioxocyclohexyl)acetate Data

Major IR bands

Wavenumber (cm^{-1})	Shape/Intensity		Assignment
2955	S	S	$-CH_2-$
2875	S	S	$-CH_2-$
1740 - 1730	B	S	-C=O
1200 - 1100	S	M	-C-O-

PNMR

Multiplicity	δ	Integration	Assignment
Tripl.	1.3	3	a
Part Quart.	4.1 - 4.6	10	b
Part Singl.	4.2 - 4.0		c
Split Singl.	2.0	9	d
Broad Multl.	2.2 - 3.0		e & f

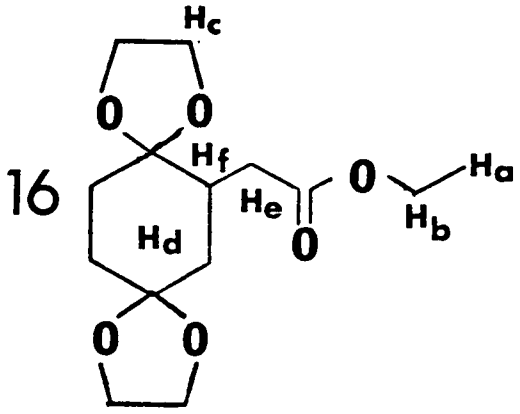


TABLE XII

Bisethylene Ketal of Ethyl(2,5-dioxocyclohexyl)ethanol Data

Major IR bands

Wavenumber (cm^{-1})	Shape/Intensity		Assignment
3600 - 3200	B	S	-O-H
2960	S	S	$-CH_2-$
2875	S	S	$-CH_2-$
1190	S	M	-C-O-
1110	S	M	-C-O-

PNMR

Multiplicity	δ	Integration	Assignment
Tripl.	3.6 - 4.0	11	a
Sharp Doubl.	3.8		b
Broad Singl.	3.0		c (D_2O exchange)
Broad Multl.	1.6 - 2.1	9	d, e & f

17

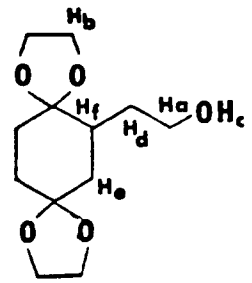
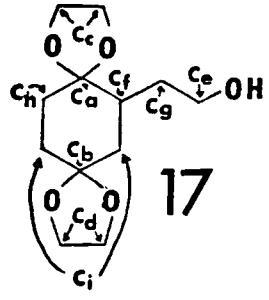


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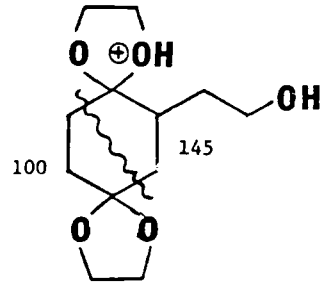
CNMR

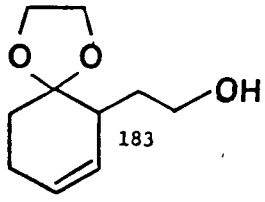


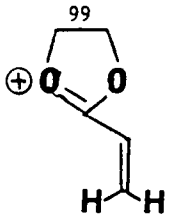
17

δ	Assignment	δ	Assignment
109.48	a	38.95	f
108.03	b	38.35	g
64.60	c	31.57	h
64.23	d	31.86	i
60.96	e		

Mass Spectral Assignments









$C_4H_7^{\oplus}$ - 55

spectrum of compound 17 can be seen in Figure 10 while the mass spectral assignments are shown in Table XII. Once the alcohol was formed it was used to form the target monomer.

Recall, that the model alcohol, compound 9, had been esterified using the method described by Banks.[80] Again using the same procedure, compound 17 was esterified with methacryloyl chloride in carbon tetrachloride along with 3Å molecular sieves. The methacrylate (18) was isolated in a 85% yield and characterized using IR and PNMR spectroscopy (Table XIII). Compound 18 was then acid hydrolized to generate the target monomer 2-(2,5-dioxocyclohexyl)ethylmethacrylate (19) in a 88% yield. The IR spectrum indicated the presence of the ketone and ester groups, and the methylene double bonds were identified in the PNMR (Table XIV). The polymerization of compound 19 will be discussed in the next section.

B. Polymer Preparation

The preparation of a poly-cyclohexanedione precursor polymer, which was to be chemically modified to generate the electroactive polymer, was attempted. It had been proposed that if the monomer, 2-(2,5-dioxocyclohexyl)ethylmethacrylate, could be polymerized, then the precursor polymer could be converted in two steps to the target TCNQ polymer as depicted in Figure 11. Before the preparation of the cyclohexanedione polymer was attempted, however, the model monomers, 2-(cyclohexyl)ethylmethacrylate and 2-(2-oxocyclohexyl)-ethylmethacrylate, were polymerized so that similar reaction

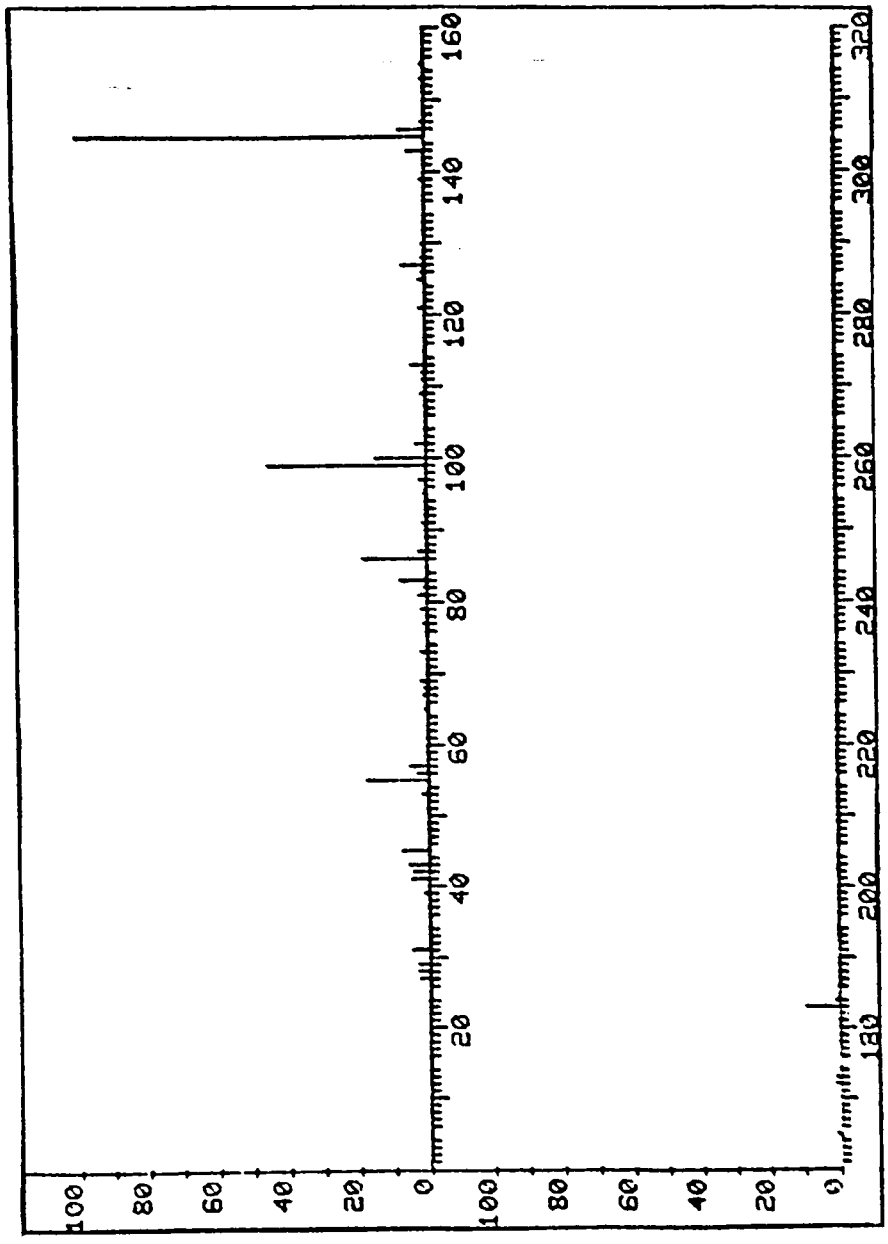


Figure 10. The mass spectrum of compound 17.

TABLE XIII

Bisethylene Ketal of 2-(2,5-dioxocyclohexyl)ethylmethacrylate Data

Major IR bands

Wavenumber (cm^{-1})	Shape/Intensity		Assignment
3000 - 2850	B	S	$-CH_2-$
1724	S	S	-C=O
1640	S	S	$-C=CH_2$
1170	S	M	-C-O-
1120	S	M	-C-O-

PNMR

Multiplicity	δ	Integration	Assignment
Singl.	6.2	1	a
Singl.	5.6	1	b
Singl.	4.0	10	c
Multl.	4.0 - 4.3		d
Singl.	2.0	12	e
Multl.	1.6 - 2.1		f & g

18

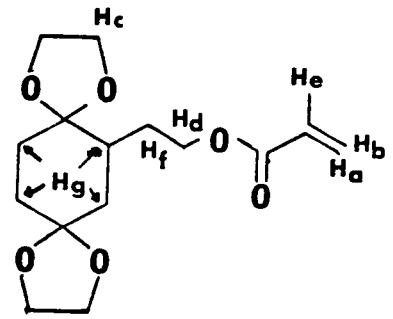


TABLE XIV

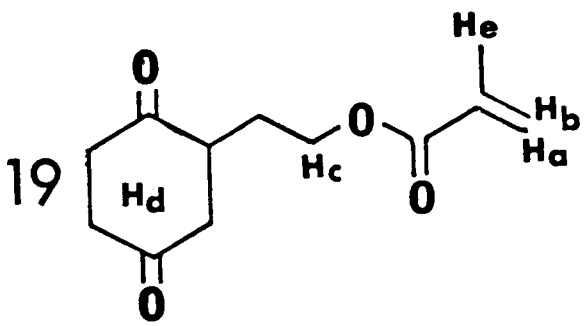
2-(2,5-Dioxocyclohexyl)ethylmethacrylate Data

Major IR bands

Wavenumber (cm^{-1})	Shape/Intensity		Assignment
3000 - 2850	B	S	$-CH_2-$
1730 - 1700	B	VS	-C=O
1640	S	S	$-C=CH_2$
1170	S	M	-C-O-
1120	S	M	-C-O-

PNMR

Multiplicity	δ	Integration	Assignment
Singl.	6.2	1	a
Singl.	5.6	1	b
Multl.	4.0 - 4.3	2	c
Singl.	2.8	12	d
Multl.	2.0		e



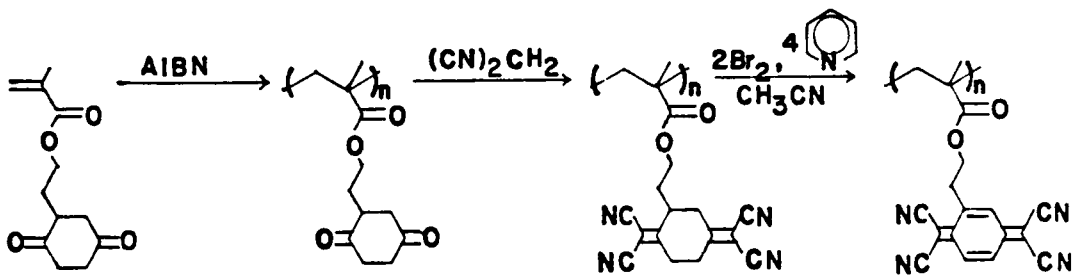


Figure 11. The proposed synthesis of poly[2-(7,7,8,8-tetracyano-p-quinodimethane)ethylmethacrylate using the chemical modification of a polymeric diketone intermediate.

conditions could be used for the polymerization of 2-(2,5-dioxocyclohexyl)ethylmethacrylate.

The synthetic routes to the preparation of the model polymers can be visualized in Figure 12. A series of four poly[2-(cyclohexyl)ethylmethacrylate] (P1) samples were prepared in THF at 60^{o} for 3 hours with different concentrations of initiator, AIBN. After the polymers were isolated, they were redissolved, reprecipitated and then cast into films to be examined by IR spectroscopy. The IR spectra for the films were identical and a representative IR spectrum for polymer P1 is shown in Figure 13 where the carbonyl (1750 - 1650 cm^{-1}) and aliphatic (3000 - 2850 cm^{-1}) bands can be seen.

After the polymerization conditions had been worked out for the preparation of polymer P1, the same procedure was used to make poly[2-(2-oxocyclohexyl)ethylmethacrylate] (P2) (Figure 12, equation b). Again, four different initiator concentrations were used to prepare polymer P2 in THF. The straw colored polymers were isolated, redissolved and then reprecipitated. Films were cast and the IR spectra were taken. Figure 14 is a representative IR spectrum of poly[2-(2-oxocyclohexyl)ethylmethacrylate] (P2), since all of the spectra were similar. The carbonyl (1750 - 1650 cm^{-1}) and aliphatic (3000 - 2875 cm^{-1}) stretches can be seen in the spectrum.

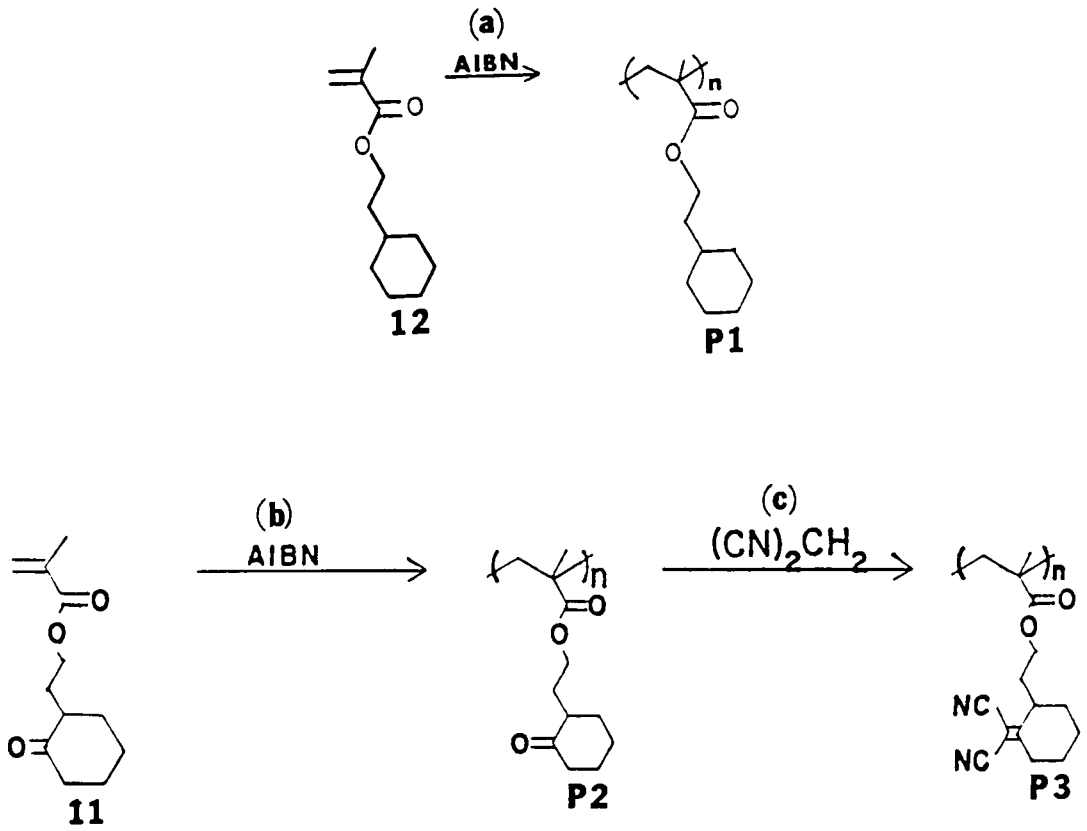


Figure 12. The preparation of the two model polymers and the chemical modification of the practice polymer intermediate.

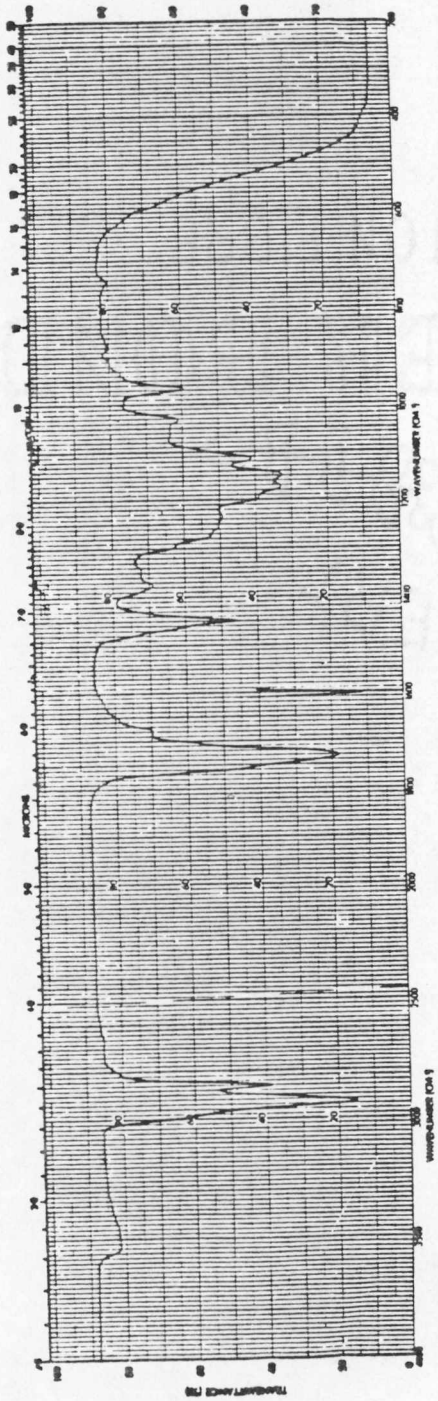


Figure 13. IR spectrum of practice polymer P1 cast as a film on a NaCl cell.

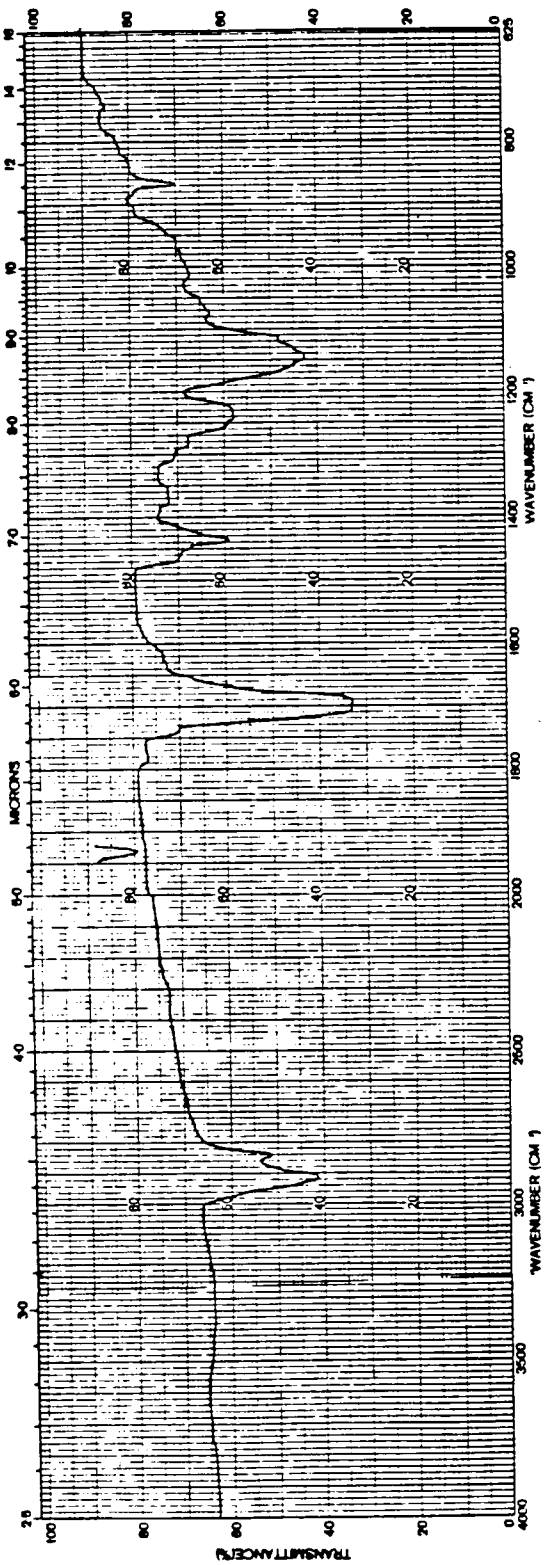


Figure 14. IR spectrum of the practice polymer intermediate polymer P2 cast as a film on a NaCl cell.

In order to determine whether chemical modifications could be performed on the target precursor polymer, the model polymer P2 was modified by condensation of the ring ketone with malononitrile, using the Knoevenagle reaction (Figure 12, equation c). Polymer P2 was first dissolved in a dioxane/benzene (5:1, v:v) mixture and malononitrile was added. After the solution became pink, β-alanine, the catalyst, was added to the reaction mixture. The red cyano polymer (P3) was isolated, redissolved and reprecipitated for purification purposes, and then cast into a film for IR analysis. The characteristic cyano stretch (between 2300 and 2200 cm^{-1}) was observed in the IR spectrum as shown in Figure 15.

Once the polymerization conditions had been determined for the two model monomers, the synthesis of the target precursor polymer, poly[2-(2,5-dioxocyclohexyl)ethylmethacrylate], was attempted using the same reaction scheme. Each time the reaction was attempted, the product quickly precipitated from solution during the course of the reaction. Following the runs, the polymers were isolated and dried, and many attempts to redissolve the materials using a variety of solvents were made. No solvent was found to dissolve the polymers, but DMF was discovered to be a good swelling solvent. Since the precursor polymer did not dissolve in any solvent, but instead formed a gel in DMF, it appeared that the polymer was highly crosslinked (Figure 16).

In this study, crosslinking is a problem because it is essential that a homogenous polymer solution be obtained for casting

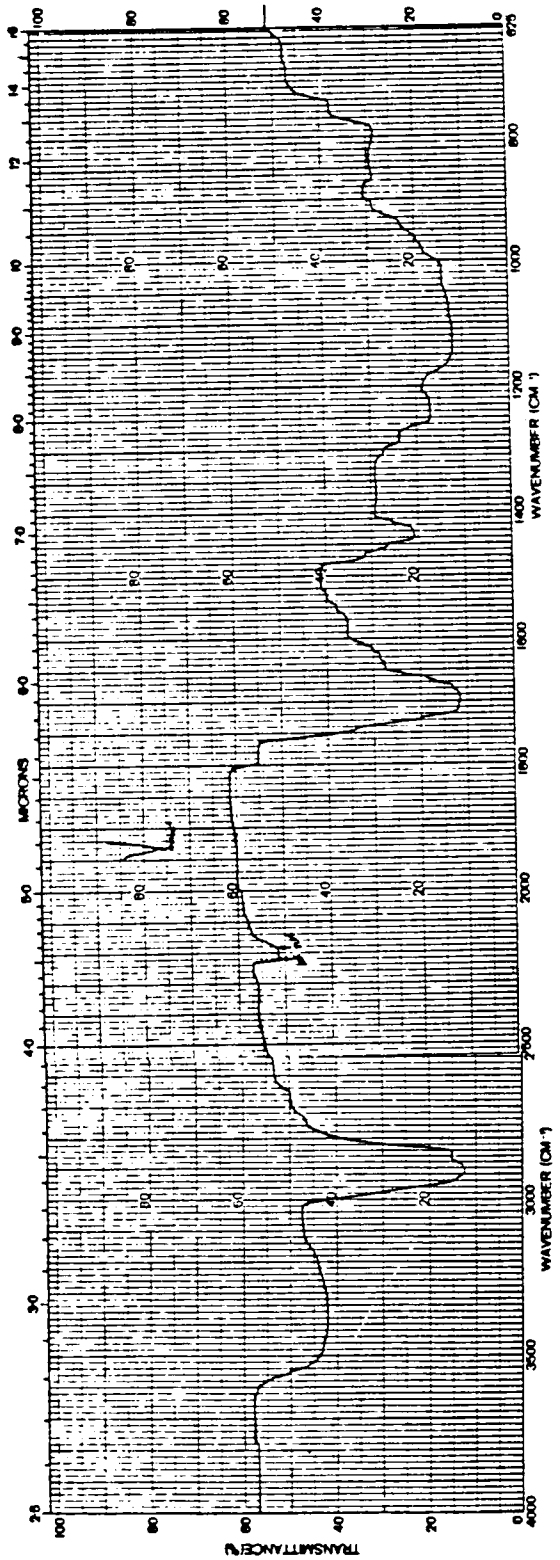


Figure 15. IR spectrum of the chemically modified polymer P3 cast as a film on a NaCl cell.

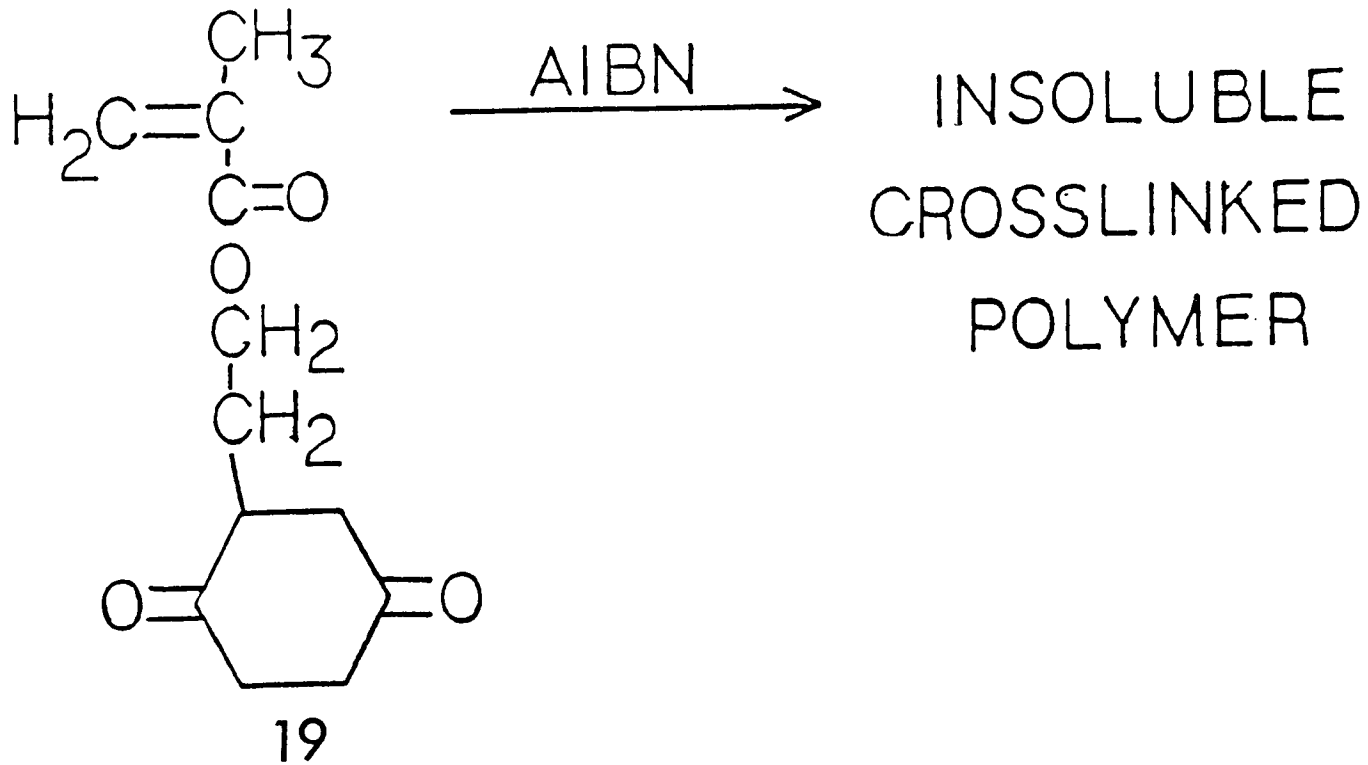


Figure 16. Attempted polymerization of 2-(2,5-dioxocyclohexyl)ethylmethacrylate.

of films and for doing further reactions on the precursor polymer. Several attempts to lower the crosslink density were made by varying the amounts of initiator, but highly crosslinked polymers were obtained whether low or high initiator concentrations were used. It is believed, by this author, that the crosslinking which occurred during the polymerization of the diketone methacrylate was either due to some form of chain transfer to the polymer, or to the presence of a small quantity of a benzoquinone impurity. Crosslinking during the polymerization of vinylbenzoquinone had been previously witnessed by Funt.[2]

In order to overcome difficulties encountered in the polymerization of the diketone methacrylate, a variation in the preparation of the diketone polymer was needed. If the linear diketone polymer could be made, then its chemical modification would be possible since the model precursor polymer, poly[2-(2-oxocyclohexyl)ethylmethacrylate], was successfully modified. The method by which the linear diketone polymer was prepared used some of the materials made in the target monomer synthesis previously described.

The grafting of electroactive moieties onto poly(methacryloyl chloride) had been successfully accomplished by Bard[56] and Miller,[55] and therefore it was believed that the grafting of a moiety on to poly(methacryloyl chloride) might be an alternative. By chemically modifying commercially available linear poly(methacryloyl chloride) (PMC), the crosslinking problem associated with the polymerization

of the diketone methacrylate could be overcome. The bisethylene ketal alcohol intermediate, compound 17 (see Figure 8, equation e), from the preparation of the diketone methacrylate, was used as the moiety for incorporation into the polymer matrix. The polymer could then be deketallized to generate the diketone polymer. An attempt was made to incorporate the alcohol into the PMC matrix using the procedure described by Miller.[55] Following work-up of the product mixture, it was obvious that little, if any, of the alcohol was incorporated into the polymer. This was due to two factors: a) the slow rate at which an alcohol was incorporated into the polymer, and b) more importantly, the size and bulkiness of the alcohol. Since the size of the alcohol could not be changed, then the reaction rate was increased by formation of an alkoxide.

The alkoxide of compound 17, which is more reactive than the alcohol, and PMC reacted smoothly to give the modified acrylic polymer. In an argon filled glove bag, n-butyl lithium was added to a dry, cold dioxane solution of compound 17 to form the alkoxide (17A). The solution was then warmed to allow for evaporation of butane. Poly(methacryloyl chloride) was added to the rapidly stirring solution in the argon atmosphere and the reaction mixture was then warmed to 50^{o}C and allowed to stir overnight (Figure 17, equation a & b1). The modified polymer P4 was isolated by pouring the polymer solution into an excess of methanol. The polymer was then redissolved and reprecipitated. A CNMR spectrum of the purified polymer sample indicated that the ring carbons were

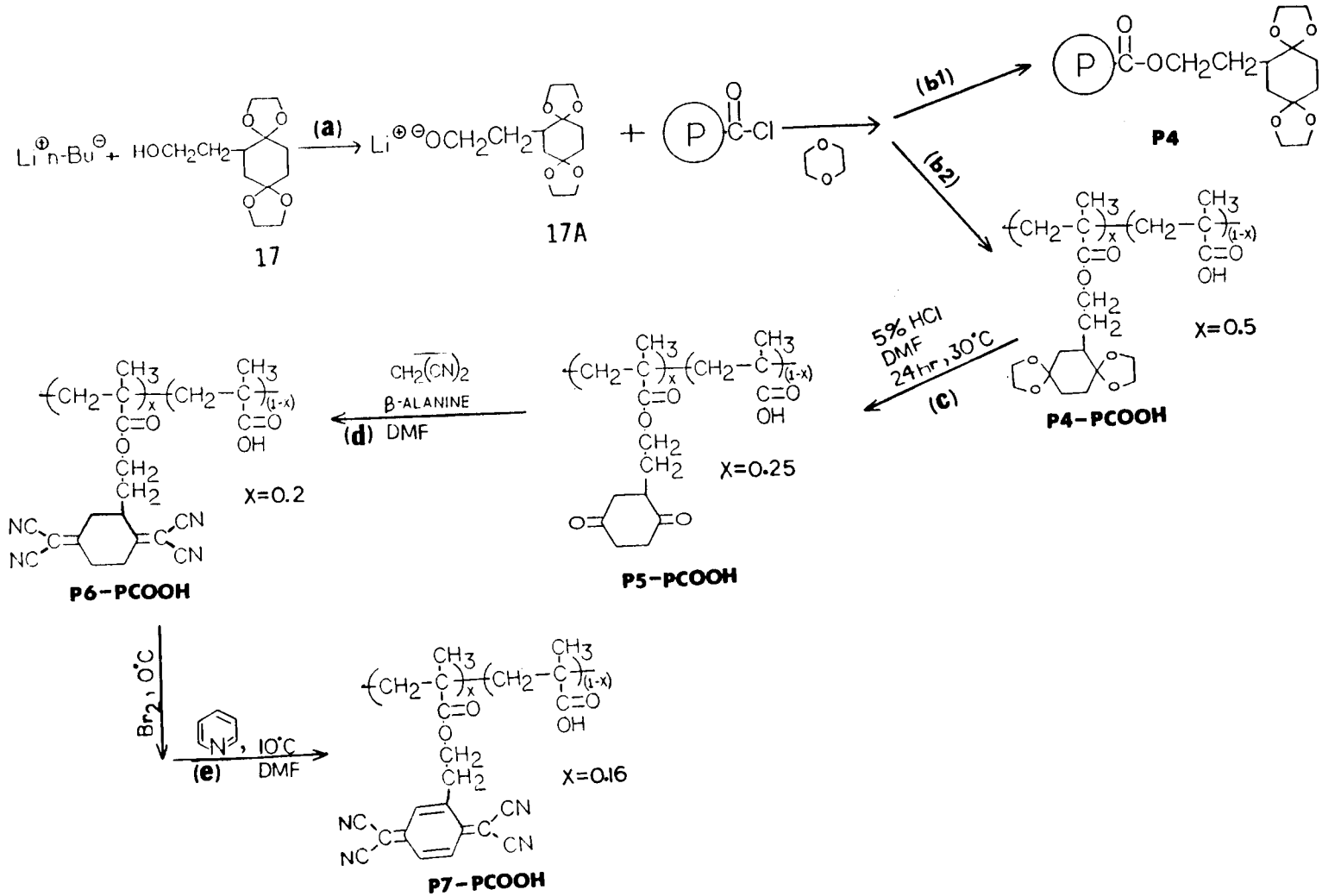


Figure 17. The overall synthesis of the TCNQ methacrylic copolymer P7-PCOOH.

present in the polymer sample (Figure 18). A KBr pellet was prepared and the IR spectrum (Figure 19) indicated that the carbonyl (1750 - 1650 cm^{-1}) and aliphatic (3000 - 2800 cm^{-1}) bands were present along with a hydroxyl stretch (3600 - 3200 cm^{-1}). Note that pure polymer P4 would not have the hydroxyl peak in its IR spectrum unless it was wet or a copolymer of P4 containing a carboxylic acid functionality. To eliminate the possibility of moisture being present in the polymer matrix, the polymer was dried at 68°C under vacuum (0.02 torr). After drying, the hydroxyl stretch remained in the IR spectrum of the polymer (Figure 19). On the basis of the elemental analysis, a copolymer repeat structure P4-PCOOH (Figure 17, equation b2), with a loading of 50% compound 17 and 50% carboxylic acid, was assigned to the product. The electrochemical behavior of this copolymer and the following chemically modified polymers will be discussed in the section on electrochemistry.

The bisketal function of the copolymer P4-PCOOH was hydrolized by dissolving it in DMF and 0.5% hydrochloric acid, and then warming the solution to 30°C (Figure 17, equation c). The diketone copolymer (P5-PCOOH) was isolated, purified, and dried under vacuum to remove any solvent or moisture which was present. A KBr pellet was prepared and the characteristic ketone (1780 - 1740 cm^{-1}), ester (1740 - 1660 cm^{-1}), aliphatic (3000 - 2850 cm^{-1}) and hydroxyl (3600 - 3200 cm^{-1}) stretches were observed in the IR spectrum (Figure 20). Elemental analysis indicated that the diketone and carboxylic acid were present in the copolymer, but the loading of the carboxylic

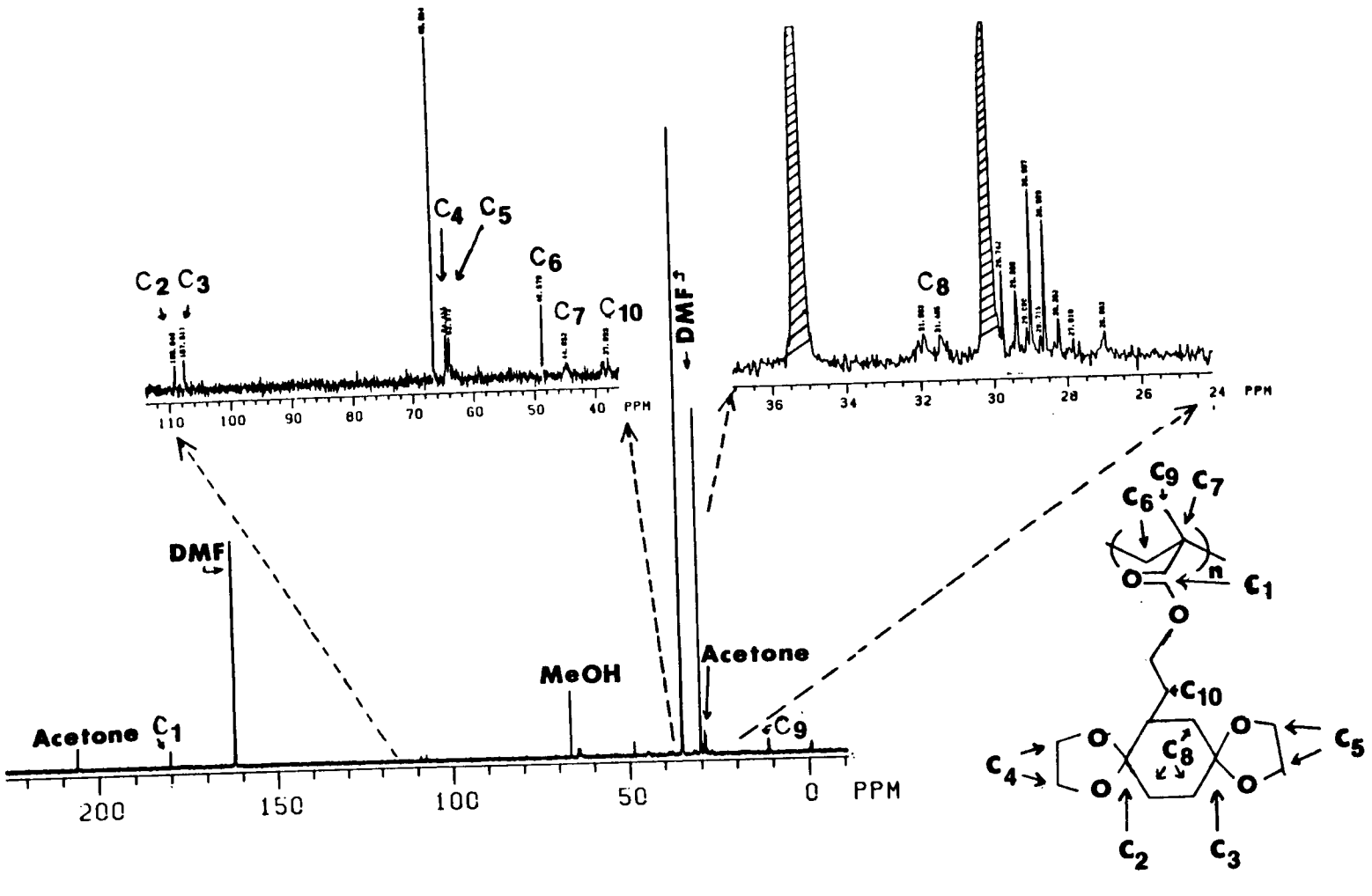


Figure 18. Carbon NMR spectrum of the reaction product of compound 17A and poly(methacryloyl chloride).

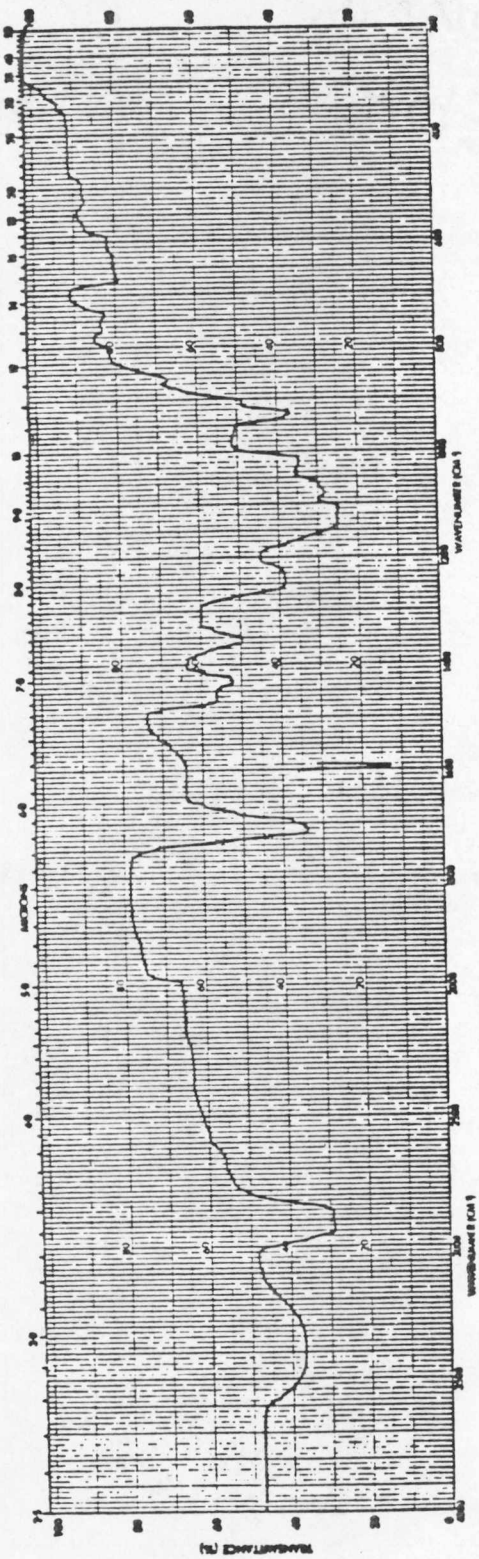


Figure 19. IR spectrum of polymer P4-PCOOH dried at 68°C under vacuum (KBr pellet).

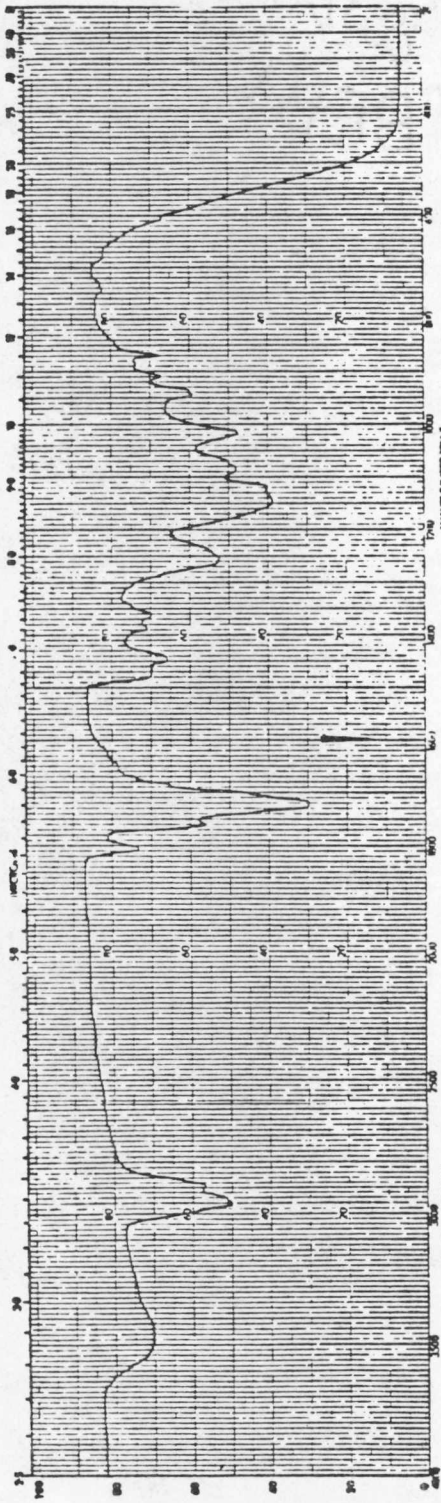


Figure 20. IR spectrum of polymer P5-PCOOH (KBr pellet).

acid had increased from 50% to 75%. The increase is presumably due to the partial hydrolysis of the diketone functionality.

The copolymer P5-PCOOH was redissolved in DMF and the Knoevenagel reaction was performed using malononitrile and the catalyst, β-alanine (Figure 17, equation d). The cyano modified copolymer (P6-POOH) was isolated and the characteristic cyano (2300 - 2200 cm^{-1}) stretch was present in the IR spectrum (Figure 21), along with the carbonyl (1750 - 1670 cm^{-1}) and hydroxyl (3600 - 3200 cm^{-1}) stretches. Nitrogen was present in the elemental analysis. The copolymer P6-PCOOH was dissolved in DMF and cooled. An argon bubbler was attached, and bromine was slowly added to the cold solution. After bromine oxidation, the cold reaction mixture was stirred under argon for an additional half hour. A solution of pyridine in DMF was slowly added to the cold copolymer P6-PCOOH solution (Figure 17, equation e). The oxidized copolymer P7-PCOOH was isolated and a KBr pellet was prepared. The IR spectrum contained the hydroxyl (3600 - 3200 cm^{-1}), carbonyl (1720 - 1670 cm^{-1}), cyano (2300 - 2200 cm^{-1}) and carbon-carbon double bond (1660 cm^{-1}) stretches as seen in Figure 22. The elemental analysis indicated that the copolymer P7-PCOOH was comprised of an 84% carboxylic acid derivative and a 16% nitrogen containing moiety.

The visible spectra for each of the polymer-DMF solutions were run. Unfortunately the spectra were inconclusive and not much information was obtained which would indicate TCNQ incorporation in the polymer. It was suspected that the solvent was possibly

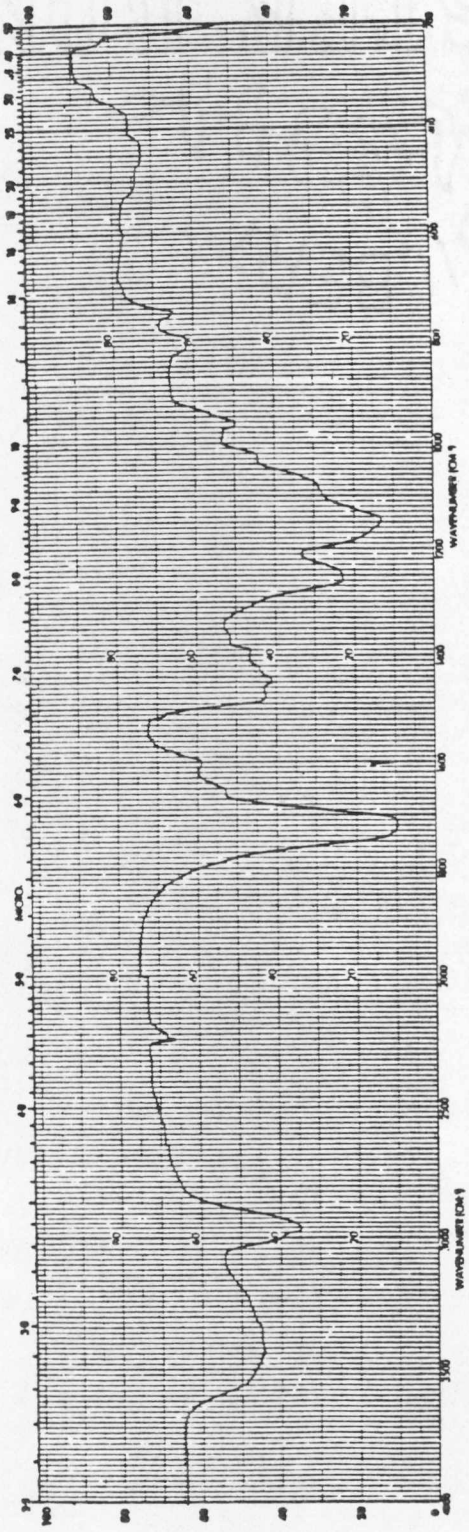


Figure 21. IR spectrum of polymer P6-PCOOH (KBr pellet).

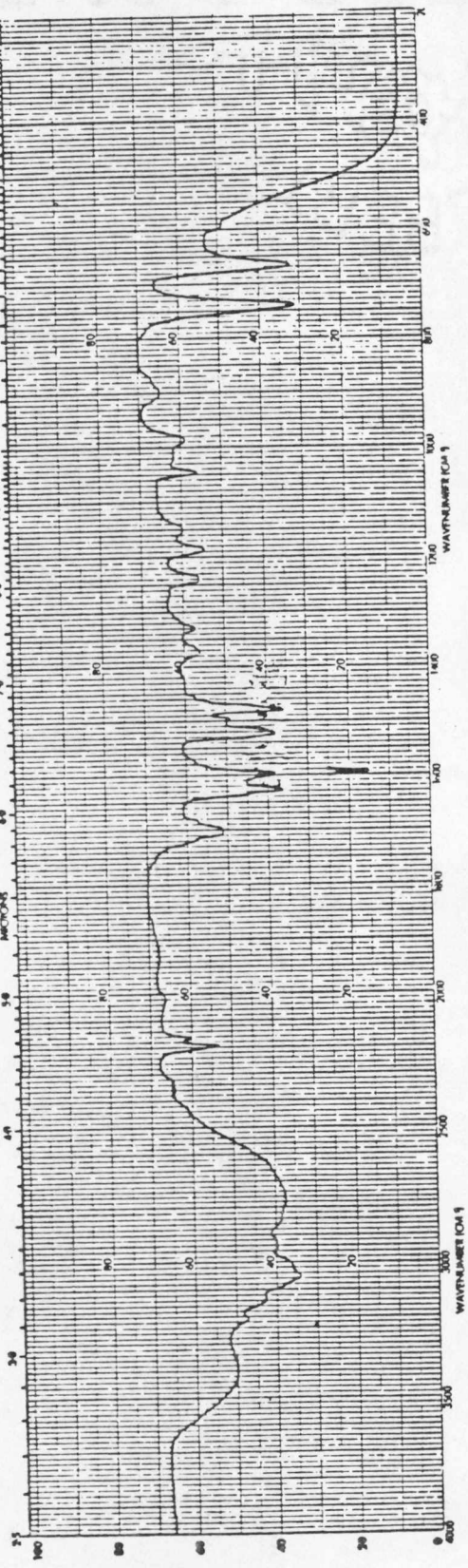


Figure 22. IR spectrum of polymer P7-PCOOH (KBr pellet).

affecting the spectra in such a manner that the peaks which were characteristic of TCNQ at 410 and 430 nm were swamped out or shifted. There was, however, a band at 480 nm for the DMF solution of P7-PCOOH which suggests the presence of a TCNQ degradation product (Figure 23). In order to remove any effects due to solvent, an alternative approach was taken where the polymers were cast as films on microscope slides. The visible spectra of the polymer intermediates and the final polymer are visualized in Figure 24. By comparing the spectra, slide by slide, one can see the differences in the polymers spectra as a result of chemical modifications. The first two polymers, P4-PCOOH and P5-PCOOH, do not have any noticeable bands in their spectra. There are, however, bands in the spectra of P6-PCOOH (480 nm) and P7-PCOOH (430 and 465 nm). At this time, it is not certain what the 480 nm absorption in the spectrum of P6-PCOOH is due to. TCNQ decomposition products such as TCNQ-H_2 have been observed in the 480 nm region of other TCNQ preparations[45] and a similar type of degradation product may be contributing to the absorption seen in the spectrum of P6-PCOOH. Recall that TCNQ has characteristic bands at 430 nm and 410 nm. Our polymer P7-PCOOH has an absorption peak at 430 nm but it is uncertain whether a band at 410 nm is present. There is also a band at 465 nm and this could possibly be attributed to some decomposition product. One must be careful in assigning the structure of P7-PCOOH on the basis of this spectrum alone, since the absorptions are broad and not well defined.



Figure 23. Visible spectrum of polymer P7-PCOOH in DMF.

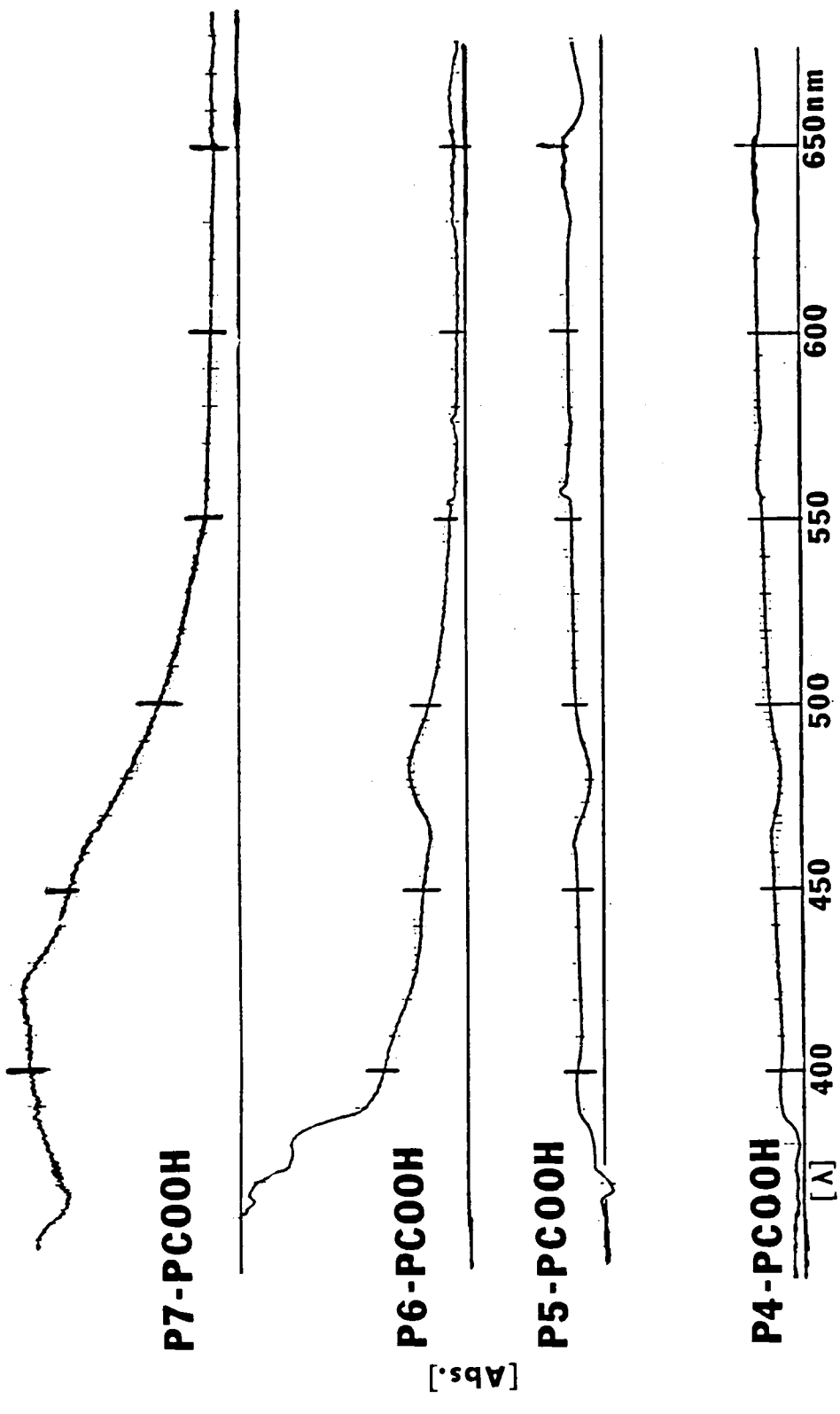


Figure 24. The composite visible spectra of the four chemically modified polymers cast as films onto microscope slides.

C. Degree of Polymerization for PMMA and the Target Polymer, obtained from the Molecular Weight of PMMA

The degree of polymerization for a polymer may be obtained by dividing the molecular weight of the polymer by the molecular weight of the repeat unit. Using this relationship, the degree of polymerization for PMMA, which was prepared by chemically modifying poly(methacryloyl chloride) (PMC), was determined from its molecular weight. Since the target polymer, P7-PCOOH, was derived from the same PMC, the degree of polymerization for PMMA would be the same as that for the target polymer, if the polymer was not degraded during the modification procedure. Therefore, in order to determine the degree of polymerization of the target polymer, the molecular weight of PMMA prepared from PMC was obtained. Before determining the molecular weight of PMMA, however, an infrared spectrum was first run in order to check its chemical structure. The IR of the PMMA prepared from PMC, cast as a film, can be seen in Figure 25. Characteristic bands between 2800 and 3000 cm^{-1}, which correspond to the methylene functionality, and at 1735 cm^{-1}, which is attributed to the ester carbonyl, were observed. Also present were additional peaks at 1760 and 1810 cm^{-1}, and the C-O stretch at 1051 cm^{-1}, which are all characteristic of anhydrides. Anhydride formation in PMMA prepared from PMC is not uncommon. Blatz indicated that anhydride formation occurred when PMC and methanol reacted to form PMMA.[83] Even though some anhydride was formed, an estimate of the molecular

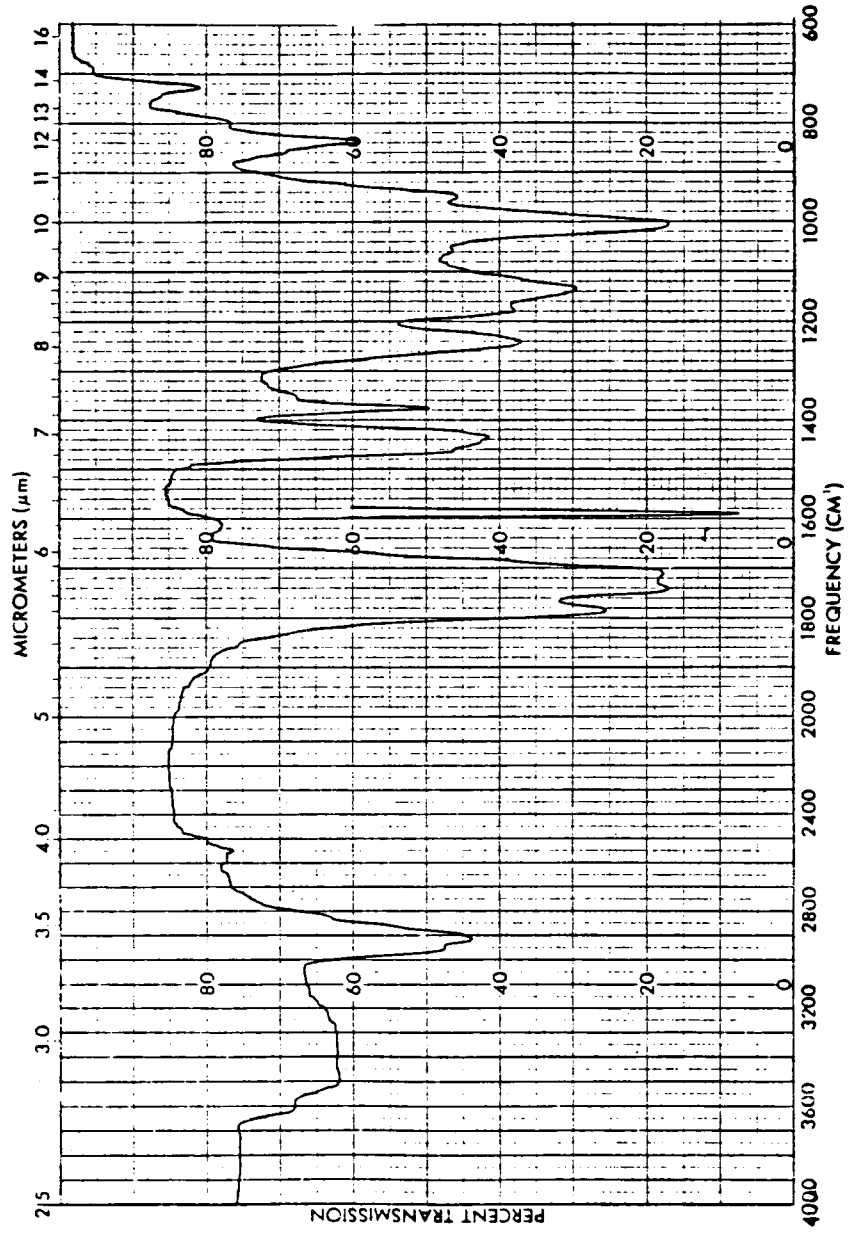


Figure 25. IR spectrum of PMMA prepared from PMC cast as a film on a NaCl cell.

weight and degree of polymerization was made using the Mark - Houwink equation. A value of 2900 was determined for the molecular weight of the polymer from the intrinsic viscosity [n] (see Figure 26, [n] = 0.035), and the Mark - Houwink constants "K" and "a" for PMMA dissolved in ethyl acetate.[84]

$$M = ([n]/K)^{1/a}$$

From the molecular weight, the degree of polymerization was estimated by assuming that the molecular weight of one PMMA repeat unit is 100. The resulting degree of polymerization for the PMMA was found to be 29. Since the target polymer P7-PCOOH was prepared from the same PMC, it also has a degree of polymerization of about 29.

D. Electrochemical Analysis

The electrochemical behavior of the four copolymers, P4-PCOOH, P5-PCOOH, P6-PCOOH, and P7-PCOOH was examined using cyclic voltammetry. For the three copolymer intermediates, as the chemical structure of the polymers changed, the electrochemical response remained constant. When the electrochemical behavior of the TCNQ containing copolymer, P7-PCOOH was examined, electroactivity was displayed. These observations will be demonstrated in the following sections.

1. Polymer film electrochemistry. The polymers were coated on a platinum electrode surface using a droplet evaporation technique by first dissolving them in a DMF:acetone (5 ml; 1:2, v:v) solution

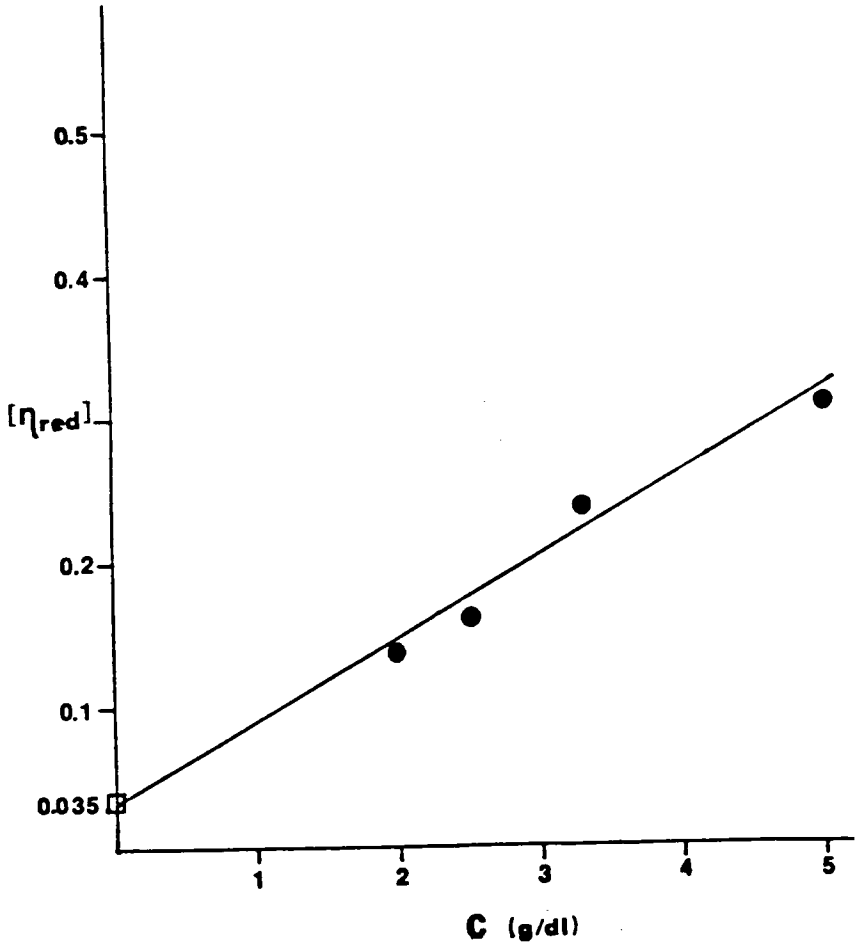


Figure 26. Plot of the reduced viscosity [n_{red}] vs concentration.

and then depositing them on the electrode surface with a dropper. The solvent was removed under reduced pressure and the polymer modified electrode was placed into a 0.1 M solution of tetrabutylammonium tetraboroflorate ($TBABF_4$) in acetonitrile. The solution was then deoxygenated and the voltammetry was recorded. As one would expect, the three copolymer intermediates, P4-PCOOH, P5-PCOOH, and P6-PCOOH displayed little electroactivity as depicted in Figure 27, while the P7-PCOOH copolymer (Figure 28) exhibited a significant electrochemical response, with a cathodic wave at -0.31 V, and an anodic wave at +1.01 V vs. a Ag/AgCl quasi-reference electrode. The reduction wave occurs within the same region as the polyester and polyurethane TCNQ's previously prepared in our laboratory.[45, 7] Unlike the previous TCNQ polymers, however, the newly synthesized poly(methacrylic)-TCNQ exhibits a very large peak separation, much larger than that observed in the other TCNQ polymers. In general, large peak separations have been attributed to slow electron transfer reactions. In this case, since our poly(methacrylic-TCNQ) is actually a copolymer composed of the TCNQ and carboxylic acid, some form of irreversible internal protonation may be occurring after electron transfer to the TCNQ group (see mechanism in Figure 29). The resulting oxidation of the protonated reduction product at the positive potentials is consistent with the cyclic voltammogram in Figure 28.

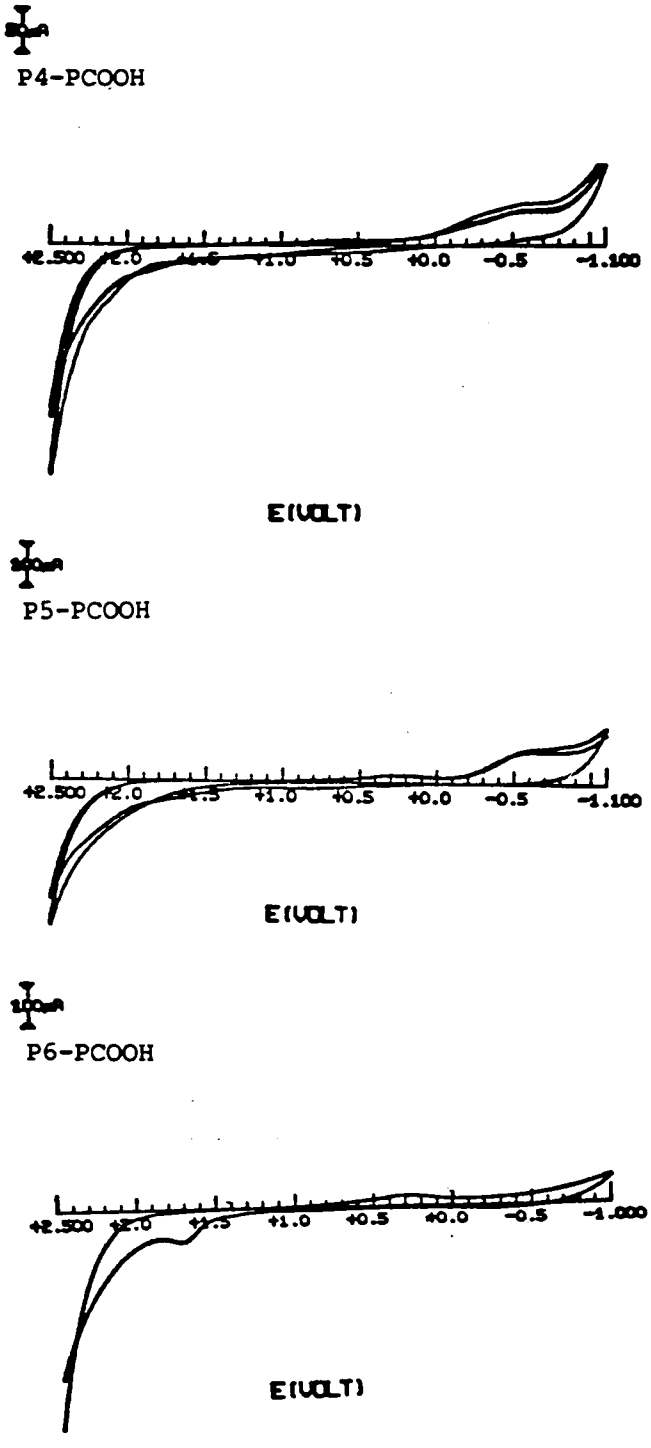


Figure 27. The composite cyclic voltammograms of polymer films P4-PCOOH, P5-PCOOH, and P6-PCOOH in 0.1M $TBABF_4$/MeCN, potential vs. Ag:AgCl, 20 mV/s .

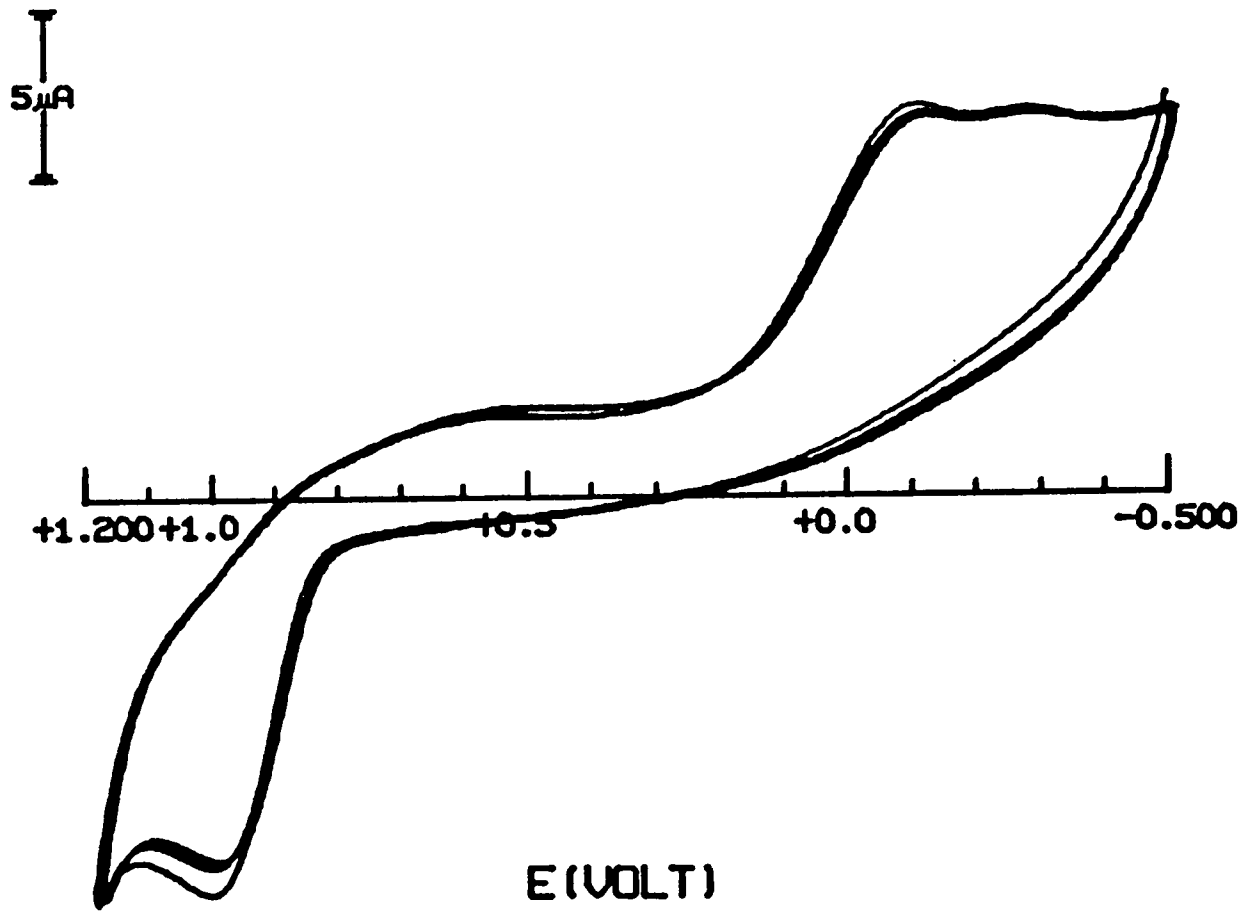


Figure 28. The cyclic voltammogram of polymer film P7-PCOOH, 0.1M $TBABF_4$/MeCN, potential vs. Ag/AgCl, 20 mV/s.

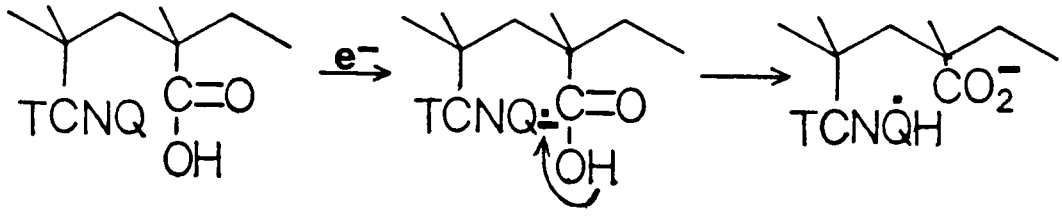
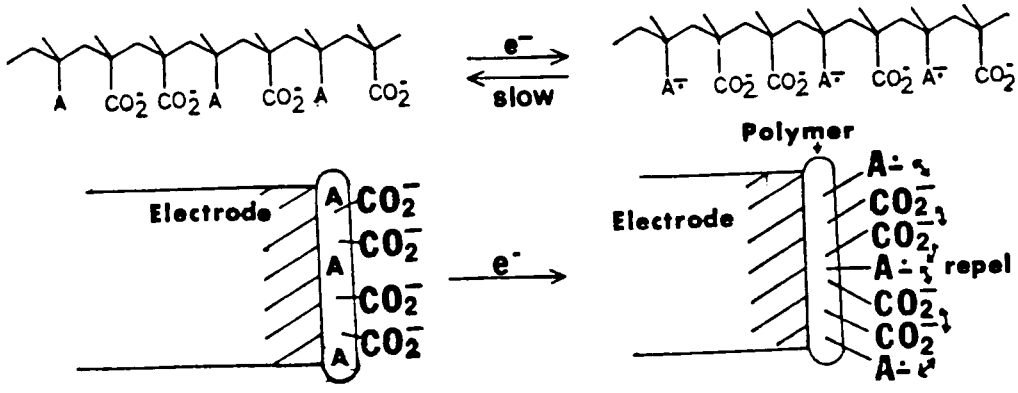
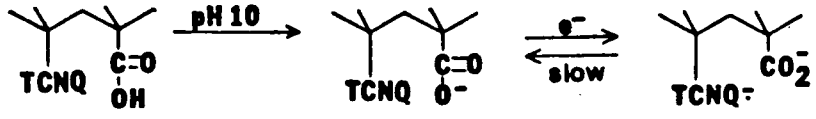


Figure 29. The proposed mechanism for the internal protonation of the TCNQ radical anion.

Another factor which may be inhibiting the rapid reversible oxidation, is chain reorientation. Prior to formation of the P7-PCOOH copolymer, the copolymer intermediate, P6-PCOOH, was treated with pyridine, and therefore, some of the acid functions in the final polymer are probably neutralized. Since the carboxylate anions are present, as the polymer begins to reduce, it becomes more polyelectrolytic in nature and the resulting polyanion will internally repel individual anions, changing the conformation of the chains. This chain reorientation or extension may result in very slow electron exchange back to the the neutral species owing to unfavorable orientations between TCNQ groups.



2. Polymer film analysis at different pH ranges. In order to eliminate the possibility of internal protonation of the radical anion, which could shut down the reversible oxidation process, the electrochemical behavior of the polymer, P7-PCOOH, film was studied at four different pH's. Again, the polymer film was cast onto the electrode surface using the polymer evaporation technique, but this time, the electrochemical response was studied in an aqueous solution of 0.5 M NaCl at pH's of 5.4, 7.8, 9.0, and 10.0 with a S. C. E. as the reference. The solution was degassed with argon, and the cyclic voltammogram was recorded between +1.0 V and -0.7 V at a scan rate of 20 mV/s. The film was recast for each pH determination, and the cyclic voltammograms were run. The four cyclic voltammograms are shown in Figure 30. The broad anodic wave did not change, but the cathodic wave, which occurred near -0.1 V vs. SCE, became sharper when the pH was increased. From the cyclic voltammograms, it appears internal protonation of the radical anion was eliminated at high pH.



3. Polymer solution electrochemical analysis. As an alternative to film electrochemical analysis, solutions of the polymers were studied in order to obtain a clearer understanding of the electrochemical process which may be occurring within the polymer matrix. Cyclic voltammograms of solutions prepared by

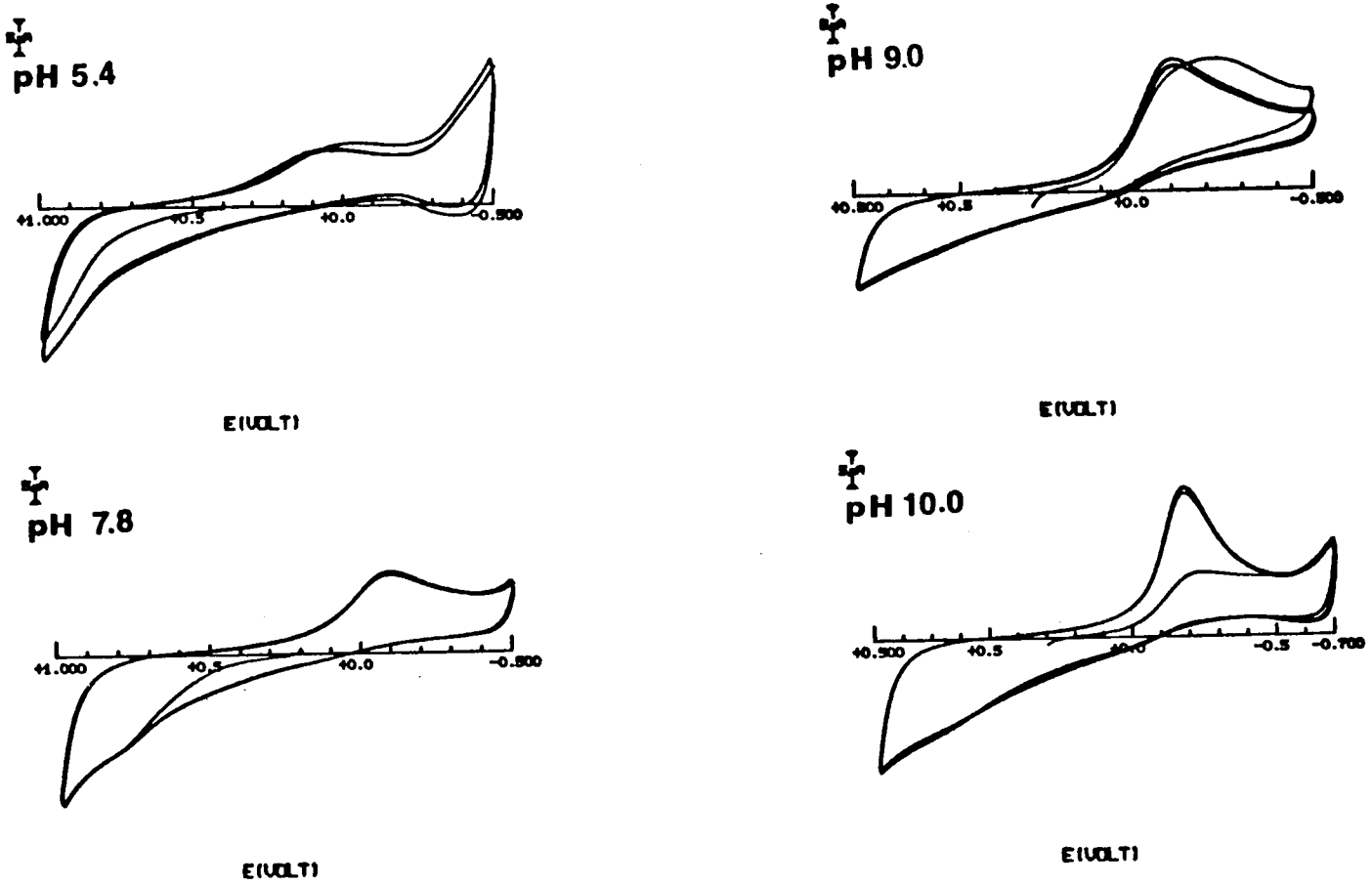
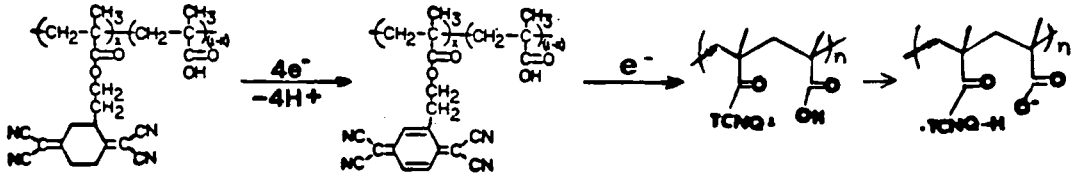


Figure 30. The composite polymer film cyclic voltammograms of P7-PCOOH at pH = 5.4, 7.8, 9.0, 10.0, in 0.5M NaCl, potential vs. SCE, 20 mV/s.

dissolving 5 mg of both P5-PCOOH and P6-PCOOH in 0.1 M of tetrabutylammonium perchlorate (TBAP)/DMF were recorded between +1.0 V and -1.0 V vs. Ag/AgCl at a scan rate of 30 mV/s using a platinum working electrode.

The voltammograms of P5-PCOOH and P6-PCOOH can be seen in Figure 31. Again, as in the polymer film voltammogram, little electrochemical behavior was seen in the voltammogram of P5-PCOOH. However, the voltammogram of P6-PCOOH does display some electrochemical behavior. At this point, it is not clear why this response is seen in solution and not as a film. It may be possible that the tetracyano moiety is undergoing reduction to form a TCNQ like intermediate which, in the presence of the carboxylic acid, is being protonated. Charge transport through a film corresponding to this process would be very slow owing to the complexity of the $4e^-$, $4H^+$ process.



If this is the case, then the solution cyclic voltammogram for the copolymer P7-PCOOH should also show a similar protonation process shutting down the reversible electrochemical oxidation. However, much to our surprise, when the solution electrochemistry was performed on the TCNQ copolymer P7-PCOOH, an oxidation wave was

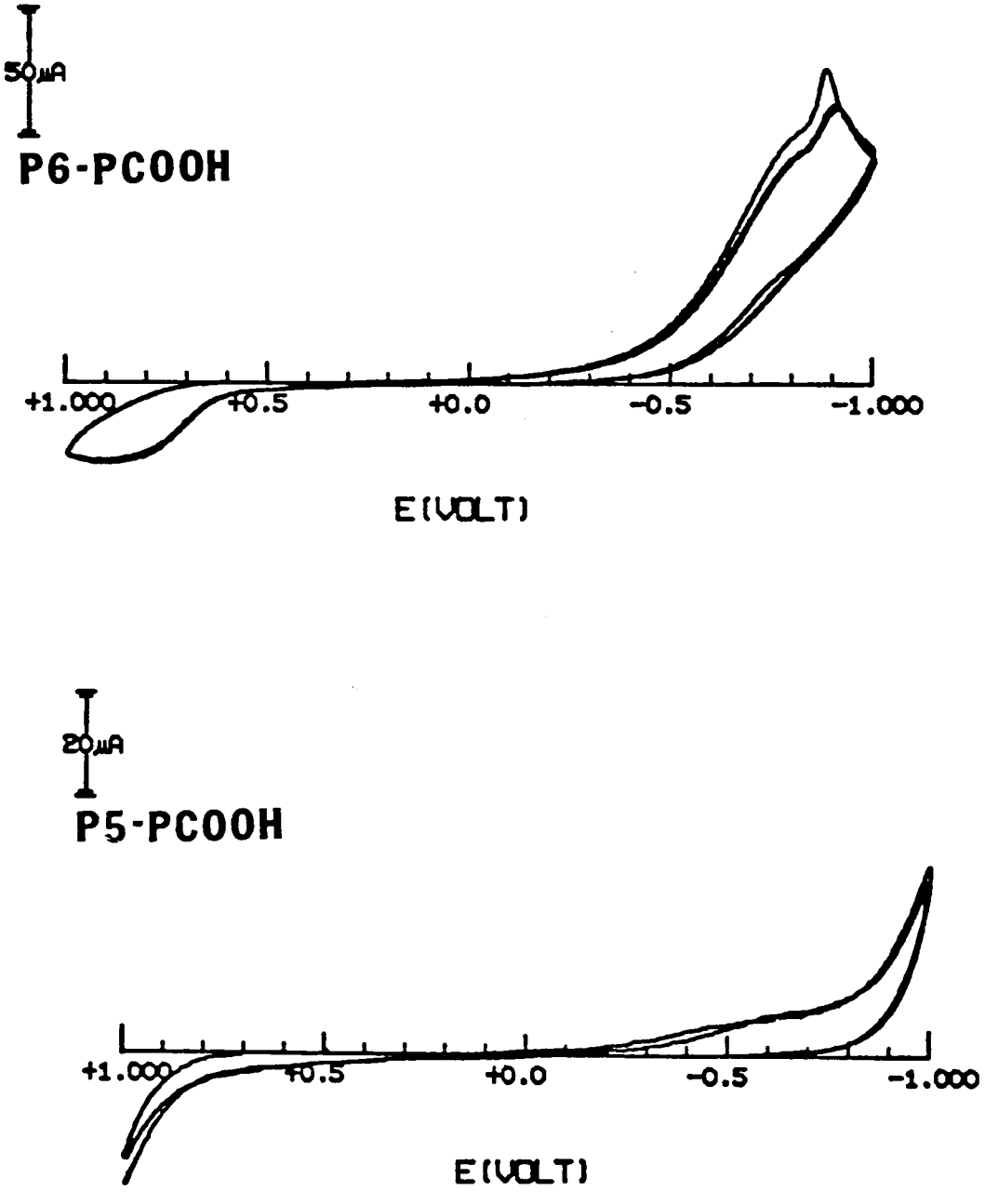


Figure 31. The solution cyclic voltammograms of P5-PCOOH and P6-PCOOH in 0.1M TBAP/DMF, potential vs. Ag:AgCl, 30 mV/s.

observed for the first time as a sharp wave near 0.0 V (Figure 32). Even though this experiment cannot explain why a response is seen in the voltammogram of P6-PCOOH, it does indicate that the copolymer, P7-PCOOH, prepared by the chemical modification process, displays a quasi-reversible oxidation - reduction wave. The reason for the unusual shape of this cyclic voltammogram compared to the previously prepared polyester and polyurethane TCNQ's is unclear.

To see whether residual pyridinium hydrobromide might be affecting the electrochemical behavior of the TCNQ copolymer, two additional electrochemical experiments were performed. The first experiment involved adding a tetrabutylammonium hydroxide solution to the polymer solution and then rerunning the voltammogram. The hydroxide would react with the pyridinium hydrobromide and carboxylic acid derivatives to form the neutral pyridine and a carboxylate anion.

$$——COOH + TBA^+OH^- \longrightarrow ——CO_2^- TBA^+ + H_2O$$

$$Pyr\text{-}H^+Br^- + TBA^+OH^- \longrightarrow Pyridine + H_2O + TBA^+Br^-$$

The resulting voltammogram showed little change in the potentials (Figure 33). During the second experiment, the voltammogram of a solution of pyridinium hydrobromide in 0.1 TBAP/DMF was run. The voltammogram, as seen in Figure 34, showed that none of the electrochemical responses related to those observed in P7-PCOOH were detected.

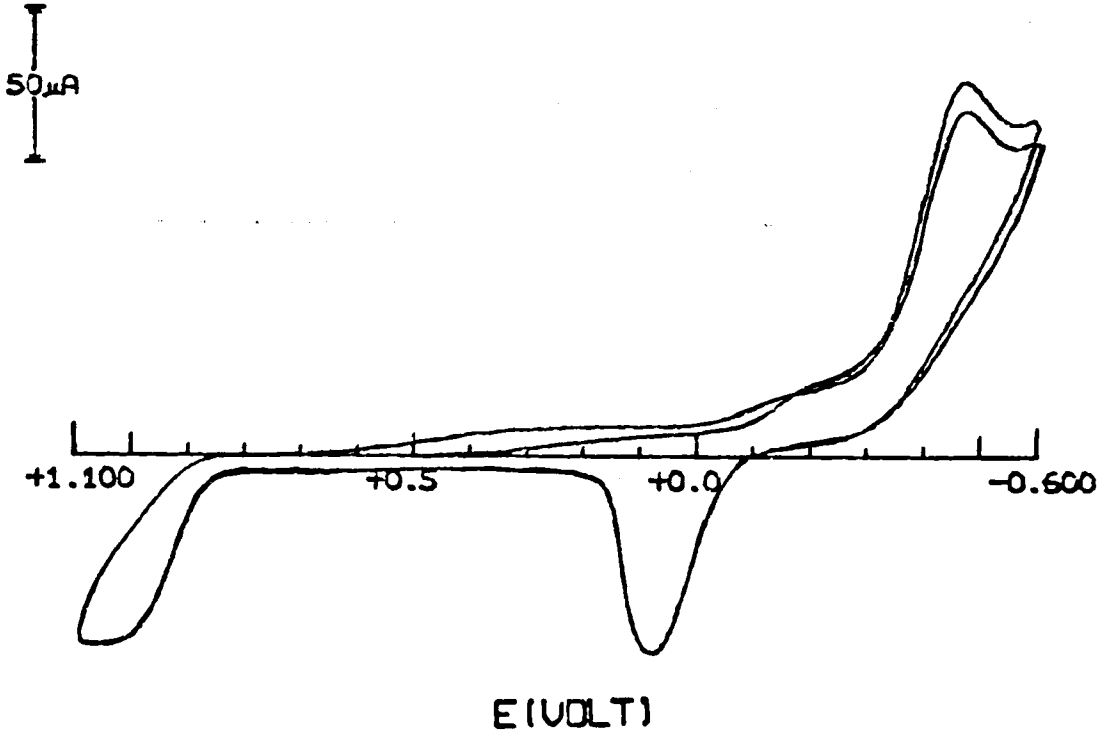


Figure 32. The solution cyclic voltammogram of P7-PCOOH in 0.1M TBAP/DMF, potential vs. Ag:AgCl, 30 mV/s.

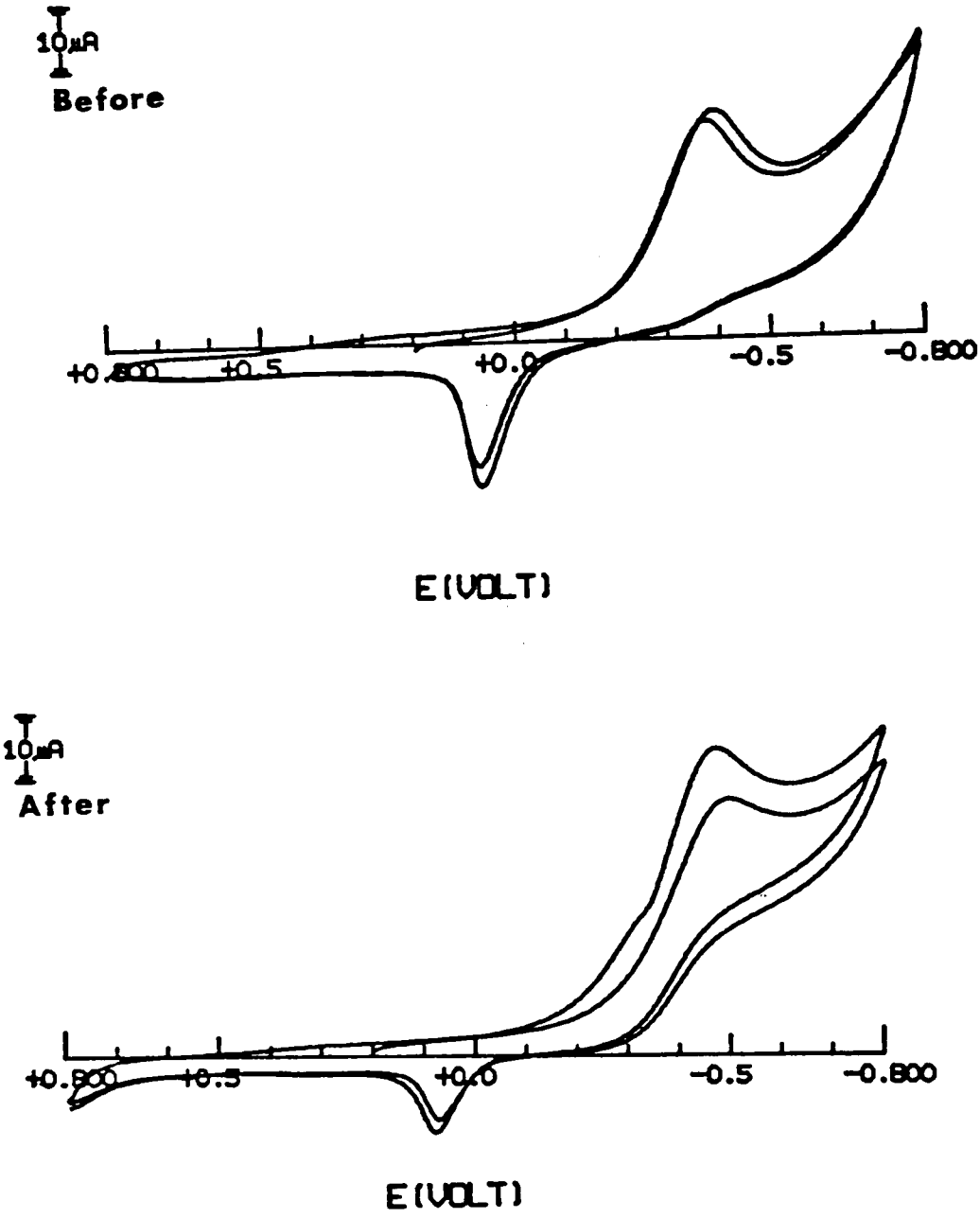


Figure 33. The effect of the addition of $TBA^{+}OH^{-}$ to the polymer solution of P7-PCOOH, in 0.1M TBAP/DMF, potential vs. Ag:AgCl, 20 mV/s.

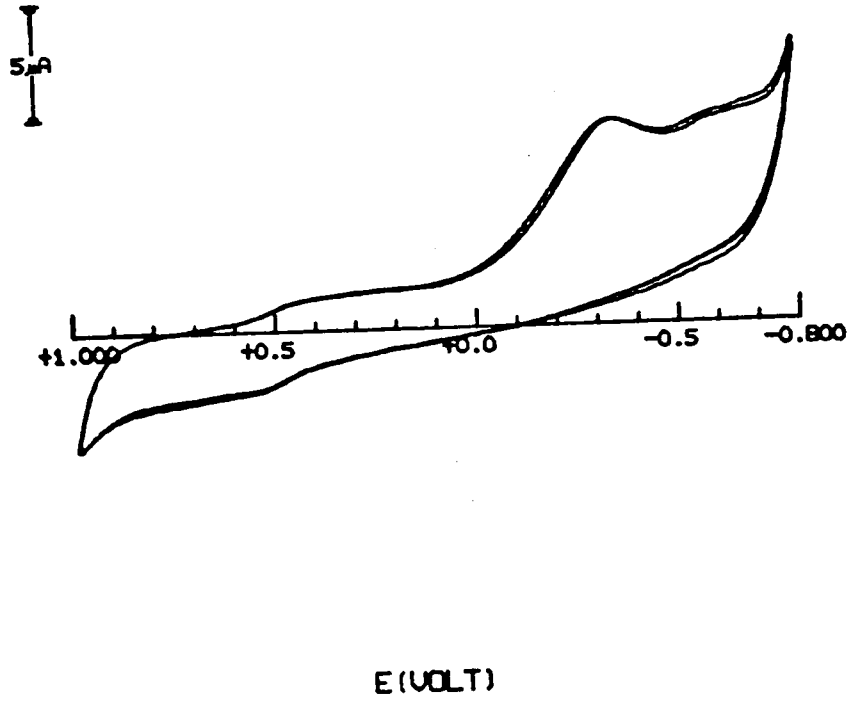


Figure 34. The cyclic voltammogram of pyridine in 0.1M TBAP/DMF after the addition of an equal portion of acid, potential vs. Ag:AgCl, 20 mV/s.

From the results of these two experiments, along with those obtained in the P7-PCOOH polymer film and solution study, it was confirmed that the electrochemical behavior witnessed in P7-PCOOH was actually produced by the chemical modification of P6-PCOOH. Even though the waves are not exactly the same as those reported for polyester- and polyurethane-TCNQs, there are similarities in the response with regard to the position of the reduction wave on the potential axis.

4. Polymer solution bulk electrolysis. As a final confirmation of the electrochemical behavior of the TCNQ copolymer P7-PCOOH, a bulk electrolysis was performed. This experiment was used to determine the number of electroactive sites contained within the material. A solution of P7-PCOOH (0.0040 g) in 0.1 M TBAP/DMF was electrolyzed to completion at 0.7 V vs. Ag/AgCl for 45 minutes.

At completion of the electrolysis, the charge (Q) is equal to the number of sites present (n) times the total number of moles of material multiplied by Faraday's constant (F):

$$Q = n \times (\text{mol of polymer}) \times F$$

The number of moles of polymer was derived from the weight of the polymer divided by its molecular weight, which was calculated from the degree of polymerization obtained from the viscosity study on PMMA. Using the degree of polymerization of 29, and the copolymer repeat structure determined by elemental analysis, a molecular weight of the polymer was calculated to be 3560. The total charge

was measured to be 1.06 coulombs. The solvent background of 0.20 coulombs was subtracted and the number of electroactive sites contained within each polymer chain was determined to be seven, assuming one electron is consumed per TCNQ group.

$$n = Q/[F \times (\text{wt. of polym})/(\text{mwt. of polym})]$$

The seven electroactive units per polymer chain is in close agreement with the repeat structure of six units per polymer chain as determined by elemental analysis. Both experimental results, therefore, confirm the formation of a polymer which contains about 20% electroactive sites.

CHAPTER IV

EXPERIMENTAL

A. Materials and Equipment

1. Materials. All materials were used as received, unless otherwise indicated.

Acetone: Fisher, ACS Certified.

Acetonitrile: Aldrich, 99% and 99+% spectrophotometric gold label grade.

β-alanine: Aldrich, 99% gold label grade.

Argon: MG Industries Scientific Gas Products.

2,2'-Azobis(2-methylpropionitrile): Aldrich, recrystalized from ethanol.

Benzene: Fisher, ACS Certified.

2-Bromoethanol: Aldrich.

Bromine: Fisher, ACS Certified.

1,4-Butanediol: Lancaster Synthesis

n-Butyl lithium: Aldrich, 1.6 M in hexane.

Calcium chloride: Fisher, 4-20 mesh.

Carbon tetrachloride: Fisher, ACS Certified.

Chloroform-d_1: Norell, Inc.

1,4-Cyclohexanedione: Lancaster Synthesis and Aldrich.

Cyclohexanone: Fisher, ACS Certified.

Diethyl ether: Fisher, ACS Certified.

Dihydropyran: Fisher, ACS Certified.

N,N-Dimethylformamide: Fisher, ACS Certified.

Dimethyl succinate: Aldrich.

1,4-Dioxane: Fisher, ACS Certified.

Ethanol: AAPER Alcohol & Chemical Co.

Ethyl acetate: Fisher, ACS Certifiied.

Ethyl bromoacetate: Aldrich, 97%.

Ethylene glycohol: Fisher, ACS Certified.

Hydrochloric acid: Fisher, ACS Reagent.

Lithium chloride: Fisher, ACS Certified.

Lithium tetrahydridoaluminate: Alfa Products, 95%.

Magnesium sulfate: Fisher, ACS Certified.

Malononitrile: Aldrich, 99%.

Methacryloyl chloride: Aldrich, distilled ($25^{\circ}C$, 20 torr).

Methanol: Fisher, ACS Reagent Anhydrous.

Methylene chloride: Fisher, ACS Certified.

Molecular sieves: Fisher, 3Å 8-12 mesh.

Nitrogen: MG Industries Scientific Gas Products.

Poly(methacryloyl chloride): Polysciences, 25% solids in dioxane.

Potassium carbonate: Fisher, ACS Certified.

Pyridine: Fisher, ACS Certified.

Pyrrolidine: Aldrich, 99%.

Silica gel: Fisher, 100-200 mesh.

Sodium bicarbonate: Fisher, ACS Certified.

Sodium chloride: Fisher, ACS Certified.

Sodium hydroxide: Fisher, ACS Certified.

Sodium sulfate: Fisher, ACS Certified.

Tetraethylammonium perchlorate, TEAP: Eastman.

Tetrabutylammonium tetraboroflorate, TBABF4: Eastman.

Tetrahydrofuran: Fisher, ACS Certified.

Triethylamine: Aldrich, 99% gold label grade.

Toluene: Fisher, ACS Certified.

p-Toluene sulfonic acid: Fisher, ACS Certified.

2. Equipment.

Cary 213 ultraviolet-visible spectrophotometer.

Hewlett-Packard mass spectrometer, Model 5980-A.

High performance liquid chromatograph: Milton Roy; Laboratory Data Control.

Mettler balance, Model P160.

Perkin-Elmer infrared grating spectrophotometer, Model 1330.

Nuclear magnetic resonance spectrometer: Varian T60 (PNMR), Nicolet NT-200 (CNMR).

BAS-100 Electrochemical Analyzer, Bioanalytical Systems Inc.

B. β-Ketoester alkylation

1. 2,5-Dicarbmethoxy-1,4-cyclohexanedione (1). A fresh solution of sodium methoxide was prepared by rapidly adding small pieces of sodium (92 g, 4 g atom) to 650 mL of absolute methanol contained in a 2-L, three neck, round bottom flask equipped with two stopers and a reflux condenser fitted with a drying tube packed with

calcium chloride and soda lime. The reaction was completed by heating the mixture under reflux for 4 h using an oil bath as the heating source. To the hot solution was added dimethyl succinate (292.28 g, 2 mol) in one portion (CAUTION: Exothermic reaction). The mixture was then heated at reflux for 24 hours.

At the end of the 24 hours, the methanol was rotoevaporated and a 2N sulfuric acid solution (1.5 L) was added to the warm residue. The mixture was stirred vigorously overnight. The solid was filtered, washed with water and then recrystallized from ethyl acetate yielding 150 g (33%) of compound 1 (mpt. = 157 - 158°C).

2. 2-Bromo-1-(2'-tetrahydropyranylhydroxy)ethane (2). In a 100 mL round bottom flask, 2-bromoethanol (25.0 g, 0.2 mol) and a catalytic amount of (0.1 g) p-toluene sulfonic acid (p-TSA) were combined and then cooled in an ice bath at 0°C. Dihydropyran (18.6 g, 0.11 mol) was added dropwise to the cold stirring mixture, and the reaction mixture was warmed to 25°C and then stirred for an hour. The mixture was distilled (70°C, 1.0 torr) to yield 24.1 g (58%) of compound 2 as a colorless liquid.

3. Alkylation of 2,5-dicarbmethoxy-1,4-cyclohexanedione (4). Into a three neck, 1-L round bottom flask, fitted with a mechanical stirrer and a reflux condenser, was placed (300 mL) anhydrous methanol and sodium metal (0.46 g, 0.02 mol). Compound 1 (4.56 g, 0.02 mol) was then added and the flask was equipped for vacuum distillation using an oil bath for heating. The methanol was removed and the stirring sodium salt of compound 1 was dried (120°C,

0.05 torr) for 3 h inside the flask. The oil bath was then cooled to 100°C and compound 2 (4.18 g, 0.02 mol) was added. The reaction mixture was stirred under dry argon at 120°C for 36 h. The reaction mixture was steam distilled yielding 3 g of a green, crystalline product. Liquid chromatography was performed on the product mixture using a C-18 reverse phase column and a 50:50 methanol/water mixture as the eluant. The chromatogram of the product indicated that it was a mixture of eight different components having similar retention volumes.

C. Practice Monomer Synthesis

1. Enamine of cyclohexanone (6). To a solution of 300 mL of benzene and cyclohexanone (98.15 g, 1.0 mole) was added pyrrolidine (71.12 g, 1.0 mole). The solution was refluxed for 24 h in a 1000 mL round bottom flask, equipped with a Dean-Stark trap, using an oil bath as the heat source. Following the reflux, the benzene was evaporated under reduced pressure, and the crude enamine was distilled under vacuum. The product compound 6 was collected as a colorless liquid (bpt. 135°C at 13 torr) in a 95% yield (143.5 g).

2. Ethyl (2-oxocyclohexyl)acetate (7). A mixture of the freshly distilled enamine, compound 6 (151 g, 1.0 mole), and 200 mL of dry acetonitrile was prepared in a three neck 1000 mL round bottom flask. A solution of ethyl bromoacetate (167 g, 1.1 mol) and 100 mL of dry acetonitrile was added dropwise to the stirring enamine solution which was kept cool using a water bath. Upon

completion of the addition, the red-orange reaction mixture was refluxed overnight using an oil bath. After cooling the reaction pot, 15 mL of water was added and the mixture was heated under reflux for an additional hour. The reaction mixture was cooled and 25 mL of 4% HCl was added. The solution was then stirred for 30 minutes at room temperature. The acetonitrile was removed on the rotary evaporator and the crude product was diluted with an equal portion of distilled water. The aqueous product mixture was extracted with diethyl ether and dried over magnesium sulfate for 24 h. The diethyl ether was evaporated, and the remaining residue was then vacuum distilled (135^{o}C, 0.3 torr) to yield 160.5 g (70%) of ethyl(2-oxocyclohexyl)acetate (7) as a colorless liquid.

3. Ethylene ketal of ethyl(2-oxocyclohexyl)acetate (8). A solution of compound 7 (114 g, 0.5 mol), ethylene glycol (45.5 g, 0.7 mol), benzene (200 mL) and a catalytic amount of p-TSA (1.5 g) was heated to reflux in a 500 mL round bottom flask. The water (8.9 mL) was removed using a Dean-Stark trap over a 12 h period. The cooled benzene solution was extracted twice (once with 10% sodium bicarbonate and then with water), dried overnight with sodium sulfate, and then evaporated to dryness. The crude product, compound 8, which was not further purified, was obtained in a 93% yield (106.2 g).

4. Ethylene ketal of 2-(2-oxocyclohexyl)ethanol (9). To a three neck 1000 mL round bottom flask, equipped with a reflux condenser and a calcium chloride tube, freshly distilled, (dried

over sodium metal) tetrahydrofuran (THF, 250 mL) was cooled to 0°C using an ice water bath. Lithium tetrahydridoaluminate (LAH) (2:1; LAH:ester; 25 g) was slowly added to the cold stirring THF. After forming the LAH/THF slurry, a mixture of dry THF (250 mL) and compound 8 (114.2 g, 0.5 mol) and was added dropwise to the cold LAH/THF solution with the aid of a 500 mL pressure-equalizing funnel. The addition was completed after 2 h, and the mixture was then heated under reflux overnight. After cooling, the excess LAH was carefully destroyed using dropwise additions of a 15% sodium hydroxide solution. The gel-solution was filtered and washed with a large excess of THF. The THF solution was dried overnight using sodium sulfate. The THF was removed using the rotary evaporator and the residue was then distilled under vacuum. Compound 9 was collected as a colorless liquid (bpt. 110-115°C at 0.5 torr) in an 81% yield (75.0 g).

5. Ethylene ketal of 2-(2-oxocyclohexyl)ethylmethacrylate (10). In a 100 mL round bottom flask equipped with a reflux condenser and a calcium chloride tube, freshly distilled methacryloyl chloride (2.61 g, 25 mmol) was added to a stirring mixture of powdered 3Å molecular sieves (4.0 g, dried at 60°C at 0.5 torr for 24 h), compound 9 (3.68 g, 20 mmol) and carbon tetrachloride (50 mL). The solution was then refluxed overnight using an oil bath. The cooled reaction mixture was filtered using a medium pore frit buchner funnel and then washed with 50 mL of carbon tetrachloride. The carbon tetrachloride was evaporated under vacuum

yielding 3.65g (77%) of compound 10 as a yellow oil. No further purification was performed.

6. 2-(2-oxocyclohexyl)ethylmethacrylate (11). Compound 10 (3.65 g, 15 mmol) was placed in a 500 mL round bottom flask, and 50 mL of 3N HCl was added along with enough THF to bring the total volume to 200 mL. The solution was refluxed for 4 h and then allowed to stir at room temperature overnight. The reaction mixture was extracted with diethyl ether and the ether extract was washed with a saturated sodium chloride solution and water, dried over magnesium sulfate, filtered, and then evaporated under reduced pressure resulting in 2.4 g (75%) of 2-(2-oxocyclohexyl)ethyl-methacrylate (11) as a yellow oil.

7. 2-(Cyclohexane)ethylmethacrylate (12). Freshly distilled methacryloyl chloride (2.61 g, 25 mmol) was added to a 100 mL round bottom flask containing carbon tetrachloride (50 mL), 2-(cyclo-hexane)ethanol (2.56 g, 20 mmol), and powdered 3Å molecular sieves (4.0 g; dried at 60°C and 0.05 torr, for 24 h). The flask was equipped with a reflux condenser and drying tube, and the mixture was allowed to reflux for 12 h. The cooled solution was filtered to remove the 3Å molecular sieves and the sieves were then washed with an additional 50 mL of carbon tetrachloride. The extract was combined with the filtrate, and the carbon tetrachloride was removed to yield 3.49 g (89%) of compound 12.

D. Target Monomer Synthesis[85]

1. 7,12-Dioxaspiro[5.6]dodecan-3-one (13). A mixture of 1,4-cyclohexanedione (112.0 g, 1.0 mol), 0.5 g of p-toluenesulfonic acid (p-TSA) and 1 L of toluene was stirred at reflux. 1,4-Butanediol (90.0 g, 1.0 mol) was added dropwise over a 3.5 h period, during which time 18.2 mL (1.0 mol) of water was collected. The mixture was cooled, washed with 10% sodium bicarbonate solution, and dried with a 1:5 potassium carbonate:sodium sulfate mixture. The toluene was evaporated and the yellow oil residue was triturated with ethyl acetate at 0°C. The solution was filtered to remove the bisketal, and the solvent was evaporated. The residue was distilled (vigeraux column) yielding compound 13 (120.6 g, 65 % yield) as a clear liquid (bp 85-90° at 0.5 torr).

2. Pyrrolidine enamine of 7,12-dioxaspiro[5.6]dodecan-3-one (14). To a solution of compound 13 (138.5 g, 0.75 mol) and 300 mL of benzene, pyrrolidine (71.1 g, 0.8 mol) was added. The solution was refluxed for 12 h and the water (13.5 mL, 0.75 mol) was then removed using a Dean-Stark trap. The benzene was evaporated and the crude enamine was distilled yielding compound 14 (166 g, 93.3 % yield) as a colorless liquid (bp 135-140°C at 0.3 torr). The pure enamine must be used quickly in order to minimize discoloration and water contamination.

3. Ethyl(2,5-dioxocyclohexyl)acetate (15). To a mixture of the freshly distilled pyrrolidine enamine (14) (118.6 g, 0.5 mol) and 200 mL of dry acetonitrile, a solution of ethyl bromoacetate

(83.5 g, 0.5 mol) in 50 mL of dry acetonitrile was added dropwise. The red-orange reaction mixture was refluxed overnight. After cooling, 20 mL of water was added and the mixture was refluxed for an additional hour. The reaction mixture was then cooled and 25 mL of 4% hydrochloric acid was added. The reaction mixture was stirred for a half hour and then the acetonitrile was removed. An equal volume of water was added and the mixture was extracted with diethyl ether. The diethyl ether extract was washed with water, dried with magnesium sulfate overnight, and evaporated. The residue was distilled (collecting the fraction between 125 and 150^{o}C at 0.03 torr) yielding 49.5 g (50 % yield) of compound 15 as a colorless liquid.

4. Bisethylene ketal of ethyl(2,5-dioxocyclohexyl)acetate (16). A solution of compound 15 (49.5 g, 0.25 mol), ethylene glycol (31.0 g, 0.50 mol), p-TSA (0.5 g) and benzene (200 mL) was heated to reflux and the water formed (9.1 mL, 0.5 mol) was removed over a 12 h period. The cooled benzene solution was extracted with saturated sodium bicarbonate and water, dried with sodium sulfate, and evaporated yielding 47.0 g (65% yield) of compound 16.

5. Bisethylene ketal of 2-(2,5-dioxocyclohexyl)ethanol (17). Freshly distilled THF (250 mL) dried over sodium metal, was added to a flask, equipped with a reflux condenser and drying tube, and cooled to 0^{o}C. Lithium tetrahydridoaluminate (LAH) (10.0 g) was slowly added to the cold THF while stirring. Compound 16 (57.2 g, 0.2 mol) which was diluted with 100 mL of the dry THF was then

slowly added dropwise to the cold LAH/THF slurry, the mixture was allowed to warm to room temperature and then heated to reflux for 12 h. The reaction mixture was cooled, and the remaining LAH was killed off using 5M potassium hydroxide. The gelatinous solution was filtered and washed with a large excess of THF. The THF was then evaporated under reduced pressure and the residue was distilled resulting in a 70% yield (34.16 g) of compound 17, as a colorless liquid (bp 115 - 130°C at 0.3 torr).

6. Bisethylene ketal of 2-(2,5-dioxocyclohexyl)ethyl-methacrylate (18). Freshly distilled methacryloyl chloride (2.61 g, 25 mmol) was added to a flask containing carbon tetrachloride (50 mL), compound 17 (4.88 g, 20 mmol), and 4.0 g of powered 3Å molecular sieves (dried at 60°C at 0.5 torr, for 24 h). The flask was equipped with a reflux condenser and drying tube, and the mixture was allowed to reflux for 12 h. The cooled solution was filtered to remove the 3Å molecular sieves, and the sieves were then washed with an additional 50 mL of carbon tetrachloride. The extracts were combined and the carbon tetrachloride was removed to yield 5.3 g (85%) of compound 18 as a yellow oil.

7. 2-(2,5-dioxocyclohexyl)ethylmethacrylate (19). Compound 18 (5.3 g, 17 mmol), 3N hydrochloric acid (25 mL), and enough THF to bring the total solution to 125 mL, was stirred at reflux for four hours and then at room temperature overnight. The solution was extracted with diethyl ether, washed with saturated sodium chloride and then with water, dried with magnesium sulfate and evaporated

under reduced pressure to yield 3.4 g of compound 19 (88%) as a light yellow oil.

E. Polymerization

1. Polymerization of 2-(cyclohexane)ethylmethacrylate (P1). A series of four polymerization tubes containing compound 12 (1.96 g, 10 mmol) and THF (10 mL) were prepared. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was then added to the tubes in the following quantities: 4.1 mg, 0.25 mol %; 8.2 mg, 0.5 mol %; 16.4 mg, 1.0 mol %; and 41.0 mg, 2.5 mol %. The tubes were sealed with a septum and a freeze-thaw cycle was performed three times. The tubes were heated at 60°C in a constant temperature water bath for 3 h and then cooled to room temperature. The polymers were isolated in methanol and dried yielding an average of 1.80 g of polymer P1.

2. Polymerization of 2-(2-oxocyclohexyl)ethylmethacrylate (P2). Four polymerization tubes containing compound 11 (0.21 g, 1 mmol), THF (5 mL) and different quantities of AIBN (0.41 mg, 0.25 mol %; 0.82 mg, 0.5 mol %; 1.64 mg, 1.0 mol %; and 4.10 mg, 2.5 mol %) were prepared. The tubes were sealed with a septum and frozen in a dry-ice acetone bath. A vacuum was pulled on the tubes and a freeze-thaw cycle was performed thrice on each tube. The tubes were frozen once more and sealed under partial vacuum. The tubes were removed and warmed to 60°C in a constant temperature

water bath. After a period of 3 h, the tubes were removed and cooled to room temperature. The ampoules were opened and the polymers were precipitated in methanol and then dried yielding an average of 0.2 g of polymer P2.

3. Knoevenagel reaction of poly[2-(2-oxocyclohexyl)ethyl-methacrylate] (P3). Polymer P2 (0.1 g) was dissolved in a dioxane/benzene mixture (5:1, 25 mL) and malononitrile (0.06 g, 0.9 mmol) was added. The pink stirring solution was warmed to 50°C and β-alanine (0.5 mL of a 0.12% soln. in water) was then added. The reaction mixture was stirred for an additional hour and the polymer was precipitated in methanol. The red polymer (P3) was dried in vaco yielding 0.09 g.

4. Polymerization of 2-(2,5-dioxocyclohexyl)ethylmethacrylate. Four polymerization tubes containing compound 19 (0.2 g, 1 mmol) and THF (5 mL) were prepared. AIBN was then added to the tubes in the following quantities: 0.41 mg, 0.25 mol %; 0.82 mg, 0.5 mol %; 1.64 mg, 1.0 mol %; and 4.10 mg, 2.5 mol %. The tubes were sealed with a septum and a freeze-thaw cycle was performed three times on each tube. The tubes were heated in the constant temperature water bath at 60°C for 3 h. The tubes were broken open and the glassy polymers were removed. A variety of solvents, such as THF, dioxane, diethyl ether, benzene, hexane, and DMF, were used in an attempt to dissolve the insoluble material.

F. Polymer Modification

1. Polymer modification of poly(methacryloyl chloride) (P4-PCOOH). In a 100 mL round bottom flask, a solution of freshly distilled dioxane (15 mL), dried over sodium metal, and compound 17 (3.50 g, 0.015 mol) was cooled to 0°C. n-Butyl lithium (10 mL) was slowly added to the dioxane solution using a syringe and the alkoxide solution was stirred and allowed to warm to room temperature in a glove bag under argon atmosphere. An ampoule containing poly(methacryloyl chloride) was opened in the glove bag and (4.16 mL) the polymer was added to the alkoxide solution using a syringe. The reaction flask, equipped with a reflux condenser and drying tube, was heated to 50°C overnight. The mixture was cooled and poured into absolute methanol (20 mL), and the polymer was isolated. The polymer P4-PCOOH was redissolved in dry dioxane, reprecipitated, and dried in the drying pistol yielding 2.50 g of polymer P4-PCOOH.

2. Poly(2-(2,5-dioxocyclohexyl)ethylmethacrylate) (P5-PCOOH). Polymer P4-PCOOH (2.5 g) was dissolved in N,N-dimethylformamide (DMF), and 0.5% hydrochloric acid (5 mL) was added. The solution was stirred at 30°C for 24 h, cooled, and the polymer was then precipitated in methanol. The material was reprecipitated and dried in a drying pistol resulting in 2.1 g of polymer P5-PCOOH.

3. Poly[2-(2,5-bis(dicyanomethylene)cyclohexyl)ethyl-methacrylate] (P6-PCOOH). Polymer P5-PCOOH (1.0 g) was dissolved in DMF (25 mL), and malononitrile (0.60 g, 9 mmol) was added. The pink solution was warmed to 40°C and stirred for 30 minutes, and β-alanine (5 mL of a 0.12% soln. in water) was then added. The reaction mixture was stirred at room temperature for an additional hour, and the polymer was precipitated in methanol. The red-brown polymer was reprecipitated and dried yielding 0.85 g of polymer P6-PCOOH.

4. Poly[2-(7,7,8,8-tetracyano-p-quinodimethane)ethyl-methacrylate] (P7-PCOOH). Polymer P6-PCOOH (0.3 g) was dissolved in DMF (25 mL) and cooled to 10°C while stirring under argon. Bromine (0.25 g, 1.6 mmol) was added dropwise and the mixture was stirred for an additional half hour at 10°C. Pyridine (0.30 g, 3.8 mmol) in DMF (5 mL) was then added over a 15 minute period. After completion of the addition, the mixture was stirred at 0°C for a half hour and then warmed to room temperature. The solution was poured into 35 mL of methanol, filtered, and washed with an additional 50 mL of methanol. The material was dried, and 0.25 g of polymer P7-PCOOH was formed.

G. Spectrometric Analysis

1. Analysis by ultraviolet / visible spectroscopy. The chemically modified polymers were scanned in a Cary 213 ultraviolet / visible spectrophotometer as a polymer solution in

DMF, and as films cast on microscope slides. The polymer solutions were run with the autobaseline recorded for the reference solvent. The samples were scanned between 350 - 700 nm under the following instrument settings a) a balance of 6.0, b) an original gain of 3.0, c) a chart display setting of 10.0, d) a scan rate of 0.5 nm/sec, and e) a period of 1.0 sec. After running the visible spectra of the polymer solutions, the polymer films were run. In order to compensate for the microscope slide absorptions, an autobaseline was obtained. Clean microscope slides were taped to both the reference and sample holders, and then scanned between 350 - 700 nm with the autobaseline turned on. The reference microscope slide was kept constant and the polymer film samples were run at the same wavelength range using the same instrument settings previously described for the polymer solution analysis.

2. Infrared spectroscopy of the chemically modified polymers. The chemically modified polymers were first ground in a mortar with a pestle. A 1:10 mixture of the polymer in KBr was then prepared and pressed into pellets. The polymer-KBr pellets were scanned between 200 and 4000 cm^{-1} in a Perkin - Elmer infrared grating spectrophotometer.

H. Molecular Weight Determination of PMMA, used to estimate the Degree of Polymerization of the Target Polymer

1. Preparation of poly(methylmethacrylate) (PMMA). A solution of freshly distilled dioxane (15 mL), dried over sodium metal,

anhydrous methanol (3.2 g, 0.1 mol), and triethylamine (1.5 mL) was prepared in a glove bag under an argon atmosphere. An ampoule of poly(methacryloyl chloride) was opened in the glove bag and 4.16 mL of the polymer was added to the methanol solution using a syringe. The reaction flask was equipped with a reflux condenser and drying tube, and the mixture was then heated at 50°C for 12 h. The solution was cooled and poured into 25 mL of anhydrous methanol, and the precipitated polymer was isolated. The polymer was redissolved, reprecipitated and dried yielding 2.1 g of PMMA.

2. Viscosity determination of PMMA. The intrinsic viscosity of PMMA dissolved in ethyl acetate was determined using a Ubbelohde viscometer. The times (T_1 to T_4) at which four different concentrations (2.0. 2.5, 3.3 and 5.0 g/dl) of PMMA in ethyl acetate flowed through the viscometer's capillary was measured along with the flow time (T_o) of pure solvent. The flow times were determined in a constant temperature water bath at 20°C. The relative viscosity (n_{rel}) was then determined by dividing the measured flow time (T_1 to T_4) for each concentration by the flow time at zero concentration (T_o). From the relative viscosity, the reduced viscosity (n_{red}) was calculated using the following equation: $[n_{red}] = (n_{rel} - 1)/C$; where C = concentration (g/dl). A plot of the reduced viscosity vs. the concentration was made and extrapolated to zero concentration. The intercept or intrinsic viscosity [n] was used in the Mark - Houwink equation, along with

the constants "K" (21.1 x 10^{-3} ml/g) & "a" (0.64) for ethyl acetate,[84] to determine the molecular weight of the polymer.

I. Electrochemical Analysis

1. Polymer film preparation. Dried polymer sample (5 mg) was dissolved in a DMF/acetone (5 mL; 1:2, v:v) solution and stirred for 5 minutes. Using a droplet evaporation coating technique, the clean platinum electrode surface was covered with a few drops of the polymer solution. The electrode was placed in a desiccator and a vacuum was pulled. The solvent was removed and the electrode was then used in the cyclic voltammetry analysis.

2. Cyclic voltammetry analysis of a polymer film. The polymer film modified platinum working electrode was placed in the electrolyte solution containing a reference and counter electrode. Depending on whether the solution was aqueous or nonaqueous, either a saturated calomel electrode (aq), or a silver:silver chloride electrode (nonaq) was used as the reference. The solution (0.1M in electrolyte) was degassed with argon for five minutes prior to electrochemical analysis. The potential limits were set within the range of +1.0 and -1.0 V, and the initial potential was set such that no initial current would be detected. Depending upon the sample, the scan rate was set between 10 and 50 mV/sec. After completion of the electrochemical experiment, the platinum surface was polished using 1.0 and 0.3 micron lapping compound, and cleaned in an ultrasonic bath.

3. Cyclic voltammetric analysis of a polymer solution. A solution was prepared containing 5 mg of the polymer in 25 ml of a 0.1M DMF electrolyte solution. The polymer solution was degassed for five minutes with argon, and the platinum working electrode, counter electrode, and silver/silver chloride reference electrode were placed in the solution. The potential limits were set between a +1.0 and -1.0 V range. The initial potential was set such that no initial current was detected, and depending upon the sample, the scan rate was between 10 and 50 mV/sec in either the positive or negative direction. After completing the analysis, the electrodes were washed with DMF and acetone, and cleaned in the ultrasonic bath.

CHAPTER V

CONCLUSION

The main objective of this research project was to prepare a polymer containing a TCNQ group pendant to the polymer chain. It was hoped that a synthetic procedure could be devised that was more convenient than the schemes followed by Day[45] and Francis[7] in their preparations of TCNQ polyesters and polyurethanes, and that the resulting material would have equivalent or superior properties. The initial idea for synthesizing the target TCNQ polymer was to prepare a TCNQ-monomer, and then polymerize it. Since the reaction conditions used to prepare the monomer would probably destroy the double bond needed for chain growth polymerization, and the quinone like nature of the TCNQ would most likely resist radical or ionic polymerization, this approach was not performed. Instead two other methods, as depicted in Figures 35 and 36, were attempted.

The first approach (Figure 35) involved the polymerization of 2-(2,5-dioxocyclohexyl)ethylmethacrylate (19), which had been successfully prepared via a series of reactions using the monoalkylated cyclohexanedione (15) formed by an enamine alkylation reaction. This approach resulted in a precursor polymer which was highly crosslinked. Further modification of the precursor polymer using this method of forming the target polymer was not attempted due to the problems associated with crosslinking. Instead, the second scheme (Figure 36), which involved the chemical modification

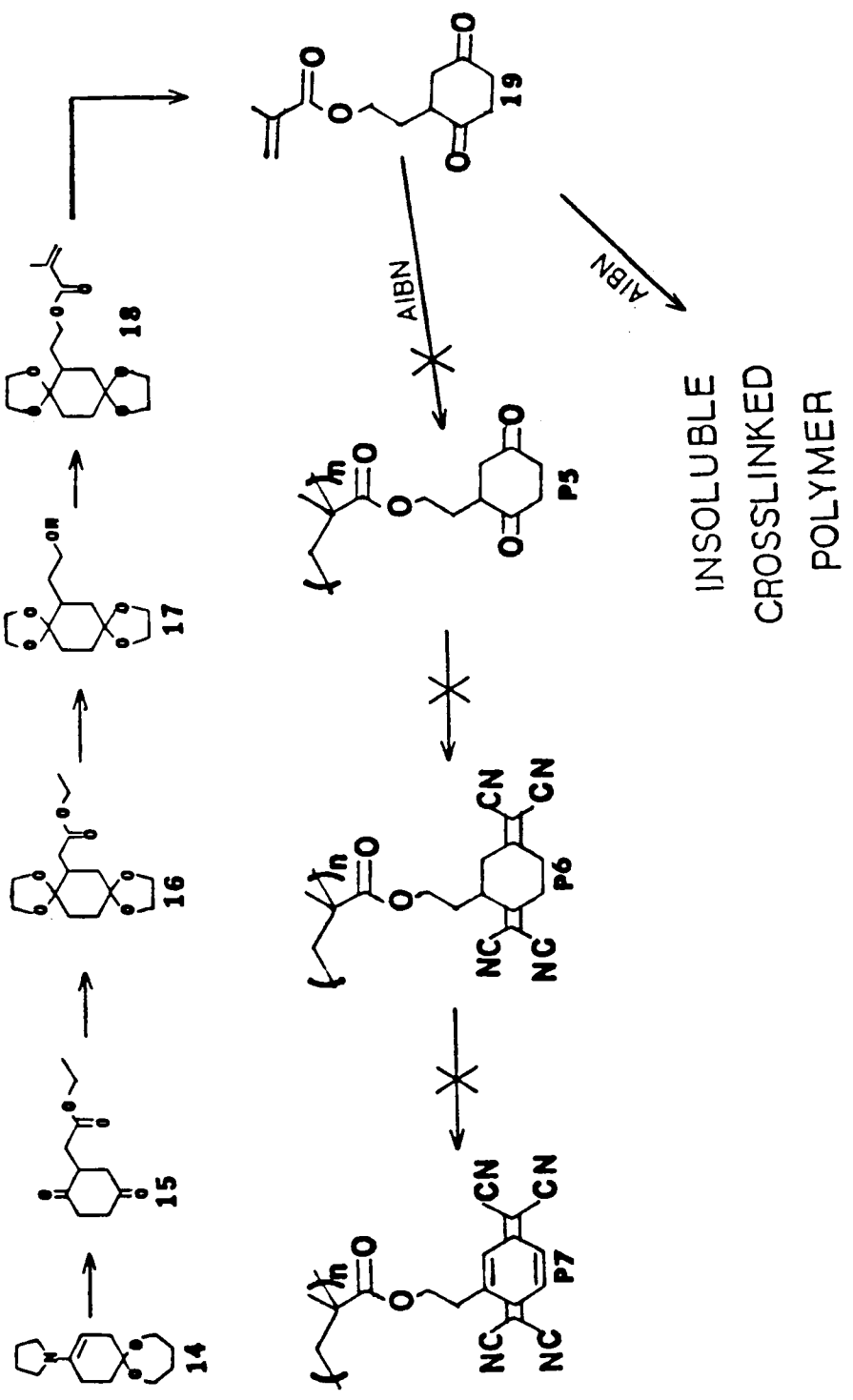


Figure 35. The attempted synthesis of a TCNQ methacrylate polymer.

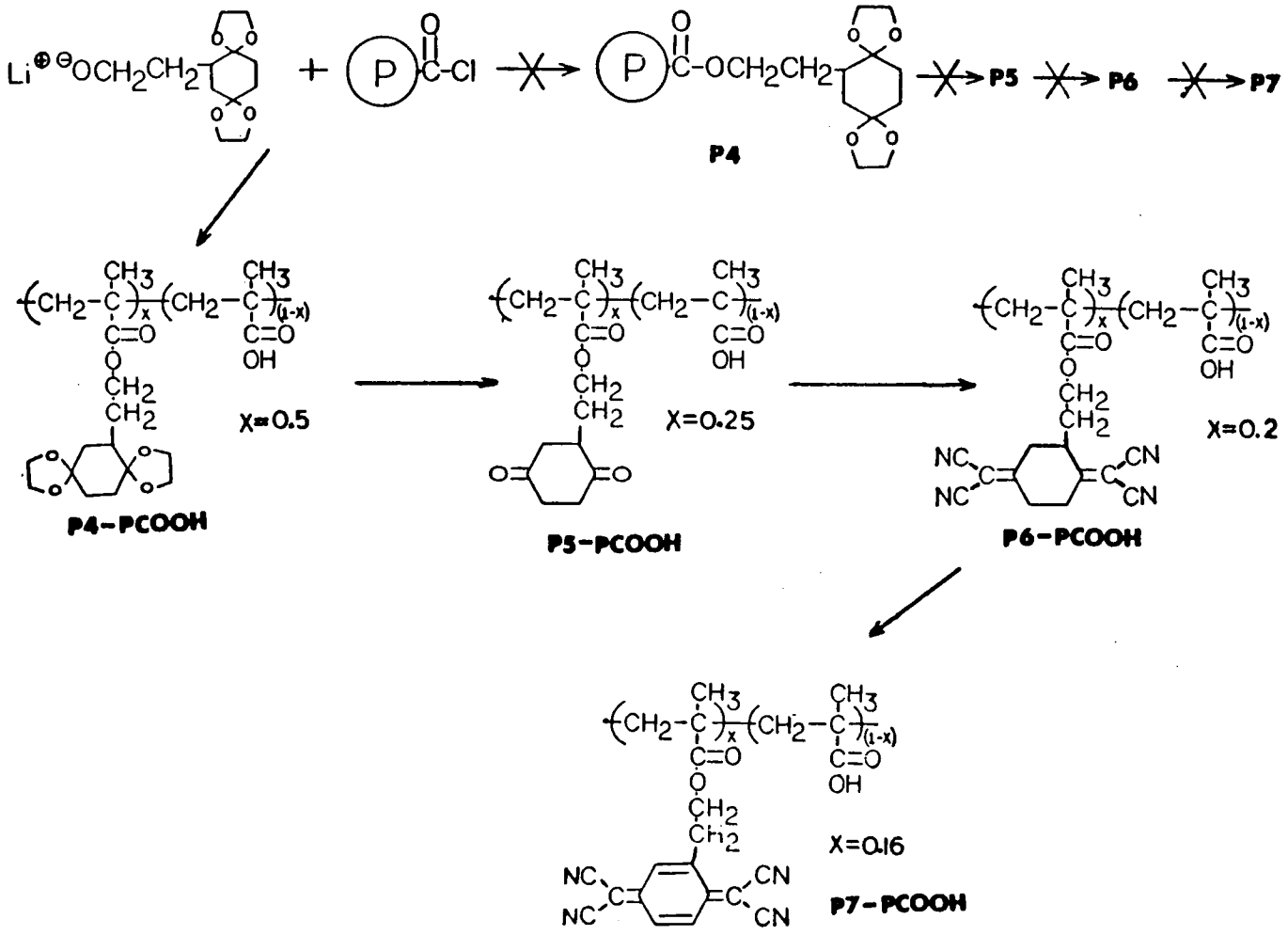


Figure 36. The successful preparation of a methacrylic TCNQ - methacrylic acid copolymer (P7-PCOOH), by the chemical modification reactions on methacrylic polymer intermediates (P4-PCOOH, P5-PCOOH, and P6-PCOOH).

of poly(methacryloyl chloride) to form a precursor polymer, was found to be more successful. In the first step of the scheme, alkoxide (17A) formation of the bulky alcohol (17) was essential to successful incorporation of the alcohol into the poly(methacryloyl chloride) polymer matrix. Infrared spectroscopy and elemental analysis showed that the homopolymer, P4, was not actually made, but instead, a copolymer, P4-PCOOH, which was comprised of P4 units and poly(methacrylic acid), was formed. From the P4-PCOOH copolymer, the other copolymers, P5-PCOOH, P6-PCOOH, and P7-PCOOH were successfully prepared and confirmed by elemental analysis and infrared spectroscopy. From the elemental analysis, the % incorporation of the substituted cyclohexyl ring moiety for the copolymers P4-PCOOH, P5-PCOOH, P6-PCOOH, and P7-PCOOH were calculated to be 50%, 25%, 20%, and 16% respectively. The degree of polymerization was estimated from the molecular weight of PMMA and found to be around 29.

Also, the visible spectra of the copolymers, cast as films, were obtained. Copolymers P4-PCOOH and P5-PCOOH had no absorptions in the visible region, copolymer P6-PCOOH had an absorption peak at 465 nm which is possibly due to some type of degradation product, and the copolymer P7-PCOOH had an absorption peak at 430 nm which is characteristic of TCNQ. A peak at 410 nm, which is also representative of TCNQ, was not well defined in the visible spectrum of P7-PCOOH.

The electrochemical behavior of the copolymers (P4-PCOOH through P7-PCOOH) cast as films and in solution was also examined using cyclic voltammetry. Films of copolymers P4-PCOOH through P6-PCOOH showed no evidence of electroactivity, but P7-PCOOH on the other hand, was shown to exhibit electrochemical behavior. The voltammetry of the P7-PCOOH film, however, was influenced by the formation of a polyanion, which resulted in slow electron transfer back to the neutral TCNQ species. Also, the electron transfer was shown, in a pH study, not to be solely influenced by internal protonation due to residual carboxylic acid residues. The solution electrochemistry exhibited quasi-reversible behavior which is not fully understood.

It appears that the carboxylic acid functionality plays a role in the electrochemical behavior of the TCNQ polymer. The fact that a carboxylic acid functionality is present, can be used advantageously since the polymer has the property of being both an electron exchange and ion exchange material at the same time. For example, by fully titrating the residual carboxylic acid functions with an alkaline base, the counter ions are present within the neutral polymer matrix, thus eliminating the need for a "breakin-in-step" as reported by Day[45] and Francis.[7] On the other hand, since the carboxylic acid functionality may be responsible for the quasi-reversible behavior, it might be better to explore a polymer system where the formation of the carboxylic acid would be either eliminated or reduced. One such polymer system might be

poly(chloromethyl styrene) which could be modified using the reactions described within this dissertation. In this case the unreacted chloromethyl groups of poly(chloromethyl styrene) could be deactivated by treatment with the alkoxide (17A) to form an ether and the resulting polymer deketalized in the fashion described. Also an advantage of studying the styrene polymer as opposed to the copolymer P7-PCOOH, is that the anchimeric assistance, which results in loss of the incorporated moiety within the methacrylic polymer, would be eliminated.

LIST OF REFERENCES

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1. Sulzberg, T.; Cotter, R. J. Macromolecules **1969**, 2, 146.

2. Funt, B. L.; Hoang, P. M. J. Electroanal. Chem. **1983**, 154, 229.

3. Murray, R. W.; in Bard, A. J. (Ed.), "Electroanalytical Chemistry," Vol. 13, Marcel Dekker, N. Y., 1984.

4. Kaufman, K. B.; Schroeder, A. H.; Patel, V. V.; Nichols, K. H. J. Electroanal. Chem. **1982**, 132, 151.

5. Melby, L. R.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mochel, W. E. J. Am. Chem. Soc. **1962**, 84, 3374.

6. Day, R. W.; Inzelt, G.; Kinstle, J. F.; Chambers, J. Q. J. Am. Chem. Soc. **1982**, 104, 6804.

7. Francis, C. V., Ph D Thesis, University of Tennessee, Knoxville, 1985.

8. Inzelt, G.; Chambers, J. Q.; Kinstle, J. F.; Day, R. W. J. Am. Chem. Soc. **1984**, 106, 3396.

9. Joo, P.; Chambers, J. Q. J. Electroanal. Chem. **1985**, 132, 1345.

10. Odian, G. G., "Principles of Polymerization," 2nd Ed., Wiley Interscience, N. Y., 1981, p. 295.

11. Simione, C. I.; Perce, V.; Natansohn, A. J. Polym. Sci., Polym. Chem. Ed. **1982**, 20, 63.

12. Oshima, R.; Biswas, M.; Wada, T.; Uryu, T. J. Polym. Sci., Polym. Lett. Ed. **1985**, 23, 151.

13. Herweh, J. E. J. Polym. Sci., Polym. Chem. Ed. **1985**, 23, 2767.

14. Stevens, M. P., "Polymer Chemistry an Introduction," Addison - Wesley Publishing Co. Inc., Mass., 1975, p. 203.

15. Lane, R. F.; Hubbard, A. T. J. Phys. Chem. **1973**, 77, 1401.

16. Lane, R. F.; Hubbard, A. T. J. Phys. Chem. **1973**, 77, 1411.

17. Watkins, B. F.; Behling, J. R.; Kariv, E.; Miller, L. L. J. Am. Chem. Soc. **1975**, 97, 3549.

18. Evans, J. F.; Kuwana, T.; Henne, M. T.; Royer, G. P. J. Electroanal. Chem. **1977**, 80, 409.

19. Moses, P. R.; Wier, L.; Murray, R. W. Anal. Chem. **1975**, 47, 1882.

20. Kaufman, F. B.; Engler, E. M. J. Am. Chem. Soc. **1979**, 101, 547.

21. Merz, A.; Bard, A. J. J. Am. Chem. Soc. **1978**, 100, 3222.

22. Van De Mark, M. R.; Miller, L. L. J. Am. Chem. Soc. **1978**, 100, 3223.

23. Cassidy, H. G. J. Am. Chem. Soc. **1949**, 71, 402.

24. Cassidy, H. G.; Kun, K. A., "Oxidation - Reduction Polymers," Interscience Publishers, N. Y., 1965, p. 1.

25. Ezrin, M.; Updegraff, I. H.; Cassidy, H. G. J. Am. Chem. Soc. **1953**, 75, 1610.

26. Reynolds, D. D.; Catheart, J. A.; Williams, J. L. J. Org. Chem. **1953**, 18, 1709.

27. Stern, R.; English, J.; Cassidy, H. G. J. Am. Chem. Soc. **1957**, 79, 5797.

28. Kun, K. A.; Cassidy, H. G. J. Polym. Sci. **1962**, 56, 83.

29. Spinner, I. H.; Yannopoulos, J.; Metanomski, W. Can. J. Chem. **1961**, 41, 483.

30. Etienne, A.; Le Berre, A.; Brun, J. J. Bull. Soc. Chim. de France **1962**, 7, 1496.

31. Cathers, G. I.; Fuoss, M. R. J. Polym. Sci. **1949**, 4, 121.

32. Kamogawa, H.; Larkin, J. M.; Toei, K.; Cassidy, H. G. J. Polym. Sci., A-2 **1964**, 3602.

33. Rodd, E. H., "Pyridine and Its Derivatives," in Chemistry of Carbon Compounds, Vol. IV, Part A, Elsevier, N. Y., 1957, Chpt. VII.

34. Green, D. C.; Allen K. W. J. Chem. Soc., Chem. Commun. **1978**, 832.

35. Kaplan, M. L.; Haddon, R. C.; Wudl, F.; Feit, E. D. J. Org. Chem. **1978**, 43, 4642.

36. Pittman, C. U.; Ueda, M.; Liang, Y. F. J. Org. Chem. **1979**, 44, 3639.

37. Kropa, E. L.; Welcher, R. P.; US Patent 2,703,792; 1955.

38. Manecke, G.; Bauer, C. Z. Elektrochem. **1958**, 62, 311.

39. Izoret, G. Compt. Rend. **1961**, 253, 274.

40. Parini, V. P.; Kasakova, S. Z.; Okorokova, M. N.; Berlin, A. A. Uysokomole. Soedin. **1961**, 3, 402.

41. Pittman, C. U.; Liang, Y. F.; Ueda, M. Macromolecules **1979**, 12, 541.

42. Pittman, C. U.; Liang, Y. F.; Ueda, M. Macromolecules **1979**, 12, 355.

43. Pittman, C. U.; Narita, M.; Liang, Y. F. Macromolecules **1976**, 9, 360.

44. Watanabe, M.; Iida, T.; Sanui, K.; Ogata, N.; Kobayashi, T.; Ohtaki, Z. J. Polym. Sci., Polym. Chem. Ed. **1984**, 22, 1299.

45. Day, R. W., Ph D Thesis, University of Tennessee, Knoxville, 1984.

46. Rao, M. L.; Mukerjee, B.: Palit, S. R. Chem. Ind. **1961**, 145.

47. Sansoni, B.; Sigmund, O. Angew. Chem. **1961**, 73, 299.

48. Sansoni, B.; German Patent 1,005734; 1957.

49. Kun, K. A.; US Patent 3,173,892; 1965.

50. Kun, K. A.; Belgium Patent 631,811; 1963.

51. Kaufman, F. B.; Engler, E. M.; Green, D. C.; in Carrener, C. E. (Ed.) "Modification of Polymers," ACS Symposium Series 121, ACS Washington, D. C., 1980, p. 435.

52 Okawara, M.; Oiji, Y.; Imoto, E. Kogyo Kagaku Zasshi **1962**, 65, 1.

53. Etienne, A.; Izoret, G. Compt. Rend. **1961**, 252, 2111.

54. Izoret, G. Compt. Rend. **1962**, 254, 671.

55. Degrand, C.; Miller, L. L. J. Am. Chem. Soc. **1980**, 102, 5728.

56. Itaya, K.; Bard, A. J. Anal. Chem. **1978**, 50, 1487.

57. Du Bois, D. Inogr. Chem. **1984**, 23, 2047.

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

59. Anderson, J. R.; Jorgensen, O. J. J. Chem. Soc., Perkin Trans. I **1979**, 3095.

60. Baghdadchi, J.; Panetta, C. A. J. Org. Chem. **1983**, 48, 3852.

61. Russkikh, V. S.; Abashev, G. G. J. Org. Chem. USSR **1983**, 19, 742.

62. Nielsen, A. T.; Carpenter, W. R. Org. Synth. **1974**, 5, 288.

63 March, J., "Advanced Organic Chemistry," 2nd Ed., Mc Graw Hill, N. Y., 1981, p. 419.

64. Green, T. W., "Protective Groups in Organic Synthesis," Wiley Intersience, N. Y., 1981, p.21.

65. Witiak, D. T.; Poochikian, G. K.; Feller, D. R.; Kenfield, N. A.; Newman, H. A. J. Med. Chem. **1975**, 18, 992.

66. Segre, A.; Viterbo, R.; Parisi, G. J. Am. Chem. Soc. **1957**, 79, 3503.

67. House, H. O., "Modern Synthetic Reactions," W. A. Benjamin, Inc.; Calf., 1972, p. 72.

68. Ref. 64, p. 123.

69. Gardner, P.; Hayes, R.; Brandon, R. J. Org. Chem. **1957**, 22, 1206.

70. Courtot, P. Bull. Soc. Chim. Fr. **1962**, 1493.

71. Lambert, J. J. Am. Chem. Soc. **1967**, 89, 1836.

72. Haslanger, M.; Lawton, R. G. Synth. Commun. **1974**, 4, 155.

73. Marshall, J.; Flynn, G. Synth. Commun., **1979**, 9, 123.

74. Hyatt, J. A. J. Org. Chem. **1983**, 48, 129.

75. Morrison, R. T.; Boyd, R. N., "Organic Chemistry," 4th Ed., Allyn & Bacon, Inc.; Boston, 1983, p. 821.

76. Padias, A. B.; Hall, H. K. Macromolecules **1982**, 15, 217.

77. Herweh, J. E. J. Polym. Sci., Polym. Chem. Ed. **1985**, 23, 2767.

78. Ohya, T.; Otsu, T. J. Polym. Sci., Polym. Chem. Ed. **1983**, 21, 3169.

79. Chu, S. C.; Butler, G. B. J. Polym. Sci., Polym. Lett. Ed. **1977**, 15, 277.

80. Banks, A. R.; Fibiger, R. F.; Jones, T. F. J. Org. Chem. **1977**, 42, 3965.

81. Ref. 64. p. 121.

82. Cook, A. G. "Enamines: Synthesis, Structure and Reactions," Marcel Decker, N. Y., 1969, Chpt. 8

83. Blatz, P. C. J. Polym. Sci. **1962**, 58, 755.

84. Brandrup, J.; Immergut, E. H. "Polymer Handbook," 2nd Ed., Interscience, N. Y., 1975, p IV-13.

85. Muschelewicz, K. J.; Binkley, J. A.; Chambers, J. Q. Org. Prep. Proc. Int. (submitted 1987).

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During his course of studies at UAB the author met Adana Ocak, and they were married in November of 1980. They have two children; a daughter, Aliya, born July 16, 1984, and a son, Adil, born June 5, 1986.