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Synthesis, Characterization, and Diels-Alder Reactivity of Polymers Containing the 2,3,6,7-Anthracenetetracarboxyl Unit.

James Larry Morris

Louisiana State University and Agricultural & Mechanical College

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SYNTHESIS, CHARACTERIZATION, AND DIELS-ALDER REACTIVITY OF POLYMERS CONTAINING THE 2,3,6,7-ANTHRACENETETRACARBOXYL UNIT

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College
in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by

James Larry Morris
B. A. University of North Alabama, 1988
May 1995
For My Father

Yesterday I stood in the shadow of a tree
More tall and magnificent than the eye could see

Though winds would come and others might fall
The love of this tree sheltered us all

One faithless day brought a violent storm
And the most beautiful tree began to change form

As cold winds blew limbs withered away
While he fought so hard with us to stay

Flood waters rose yet still he stood brave
The hopes and dreams in our hearts to save

Alas the wise tree thought he might die
So he turned to face us and bid us good-bye

With bright light in my eyes on the morn I awaken
And find with the flood the great tree was taken

For the waters carried him across the sea
Where he stands with those as beautiful as he

In memory of my beloved father

James Curtis Morris
March 25, 1934 - April 18, 1991
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Anthracene is a fluorescent molecule that undergoes chemical reactions as a Diels-Alder diene. Incorporation of the anthracene nucleus into a polymer system imparts upon it the characteristics of anthracene. This work in concerned with the synthesis of a suitable 2,3,6,7-anthracenetetracarboxylic acid based monomer. The monomer is then polymerized and the resultant polymer is crosslinked in a Diels-Alder reaction.

The synthesis of 2,3,6,7-anthracene derivatives is underdeveloped. The difficulty in the synthesis of these compounds has probably precluded their development. Herein is described the synthesis of 2,3,6,7-anthracenetetracarboxylic acid in three simple steps inexpensively and in high yield. Older methods required more steps and costly reagents.

The solubility of monomer precursors was generally quite low causing great difficulty. An ester/acid chloride monomer was developed that was soluble, purifiable and polymerizable. Polymers derived from this monomer were thermally stable, fluorescent, and active as Diels-Alder dienes.

The polymeric Diels-Alder reaction was successful with N-phenylmaleimide leading to the desired polymeric adduct. Crosslinking and concomitant formation of an intractable network was observed when a difunctional maleimide was used in the reaction.
CHAPTER ONE.

A Review of the Study of Condensation Polymers Containing the Anthracene Nucleus.

1.1 Introduction.

Anthracene containing polymers are well known in the open literature. The polymer systems are diverse, but the polymers are based on a limited monomer set. Polymers containing anthracene show some of the chemical and physical properties of anthracene, 1.I, such as fluorescence, and the tendency of the anthracene nucleus to undergo 4 + 2 cycloaddition reactions across the 9,10 positions of the anthracene ring.

The peculiar polymerization of 9-vinyl anthracene has been the subject of a review article. Anthracene containing polymers have been shown to form charge transfer complexes with electron acceptors leading to the potential for new high strength materials. Studies of anthracene containing polymers have contributed to a greater understanding of
physical macromolecular chemistry. Polarized fluorescence of anthracene nuclei incorporated by either 9,10 enchainment or by pendant substitution provides a very sensitive probe of macromolecular diffusion. The phenomenon of spinodal decomposition was studied by the photochemical 4+4 cycloaddition of anthracene pendant styrene based polymers. Examples of polymers incorporating anthracene in the backbone have been shown to exhibit interesting photophysical characteristics and allowed photochemical crosslinking.

As the interests of this project are centered about the synthesis of condensation polymers containing the anthracene moiety, we will not consider addition polymers containing the anthracene moiety further. Anthracene containing condensation polymers can be divided into two main categories which include those with the anthracene group pendant to the polymer backbone, and those with the anthracene incorporated into the backbone. Further subclassifications can be made considering the substitution pattern of the anthracene. For instance, one class may contain polymers having pendant anthracene groups attached at the 9 position while another may contain polymers having anthracene in the backbone attached through the 2 and 6 positions.
1.2 Polyanthrylenes and Polymethyleneanthrylenes.

Anthracene analogs of poly(p-phenylene) or poly(9,10-anthrylene), 1.II, reaction 1.1, have been prepared in many ways. The simplest method is the low temperature pyrolysis of anthracene by Berlin.⁸ Other methods are the Wurtz-Fittig reaction,⁹ transition metal catalyzed coupling¹⁰ oxidative polymerization with AsF₃¹¹, by coupling and subsequent aromatization of the anthracene radical anion,¹² and by electrochemical methods.¹³ In all cases, polyanthrylenes are very insoluble and number average molecular weights range from 1,200 to 2,000. These methods depend on free radical processes for polymerization and polymeric products are usually separated into a soluble fraction and an insoluble fraction. The insoluble fractions are crosslinked due to radical hydrogen abstraction and subsequent branching. The soluble component is not really a polymer but an oligomer with DP of 8 to a maximum of 20 or so.

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

Solubility of the oligomers presents a problem. Even when linear products are obtained, the rigid rod like polymers are insoluble when any
moderate molecular weight is reached. To combat this problem, Müller et. al. synthesized poly(2,6-di-t-butyl-9,10-anthrylene).\textsuperscript{14} This was accomplished by the coupling of the dilithiated derivative of the 2,6-di-t-butyl-9,10-anthrylene trimer with 2,6-di-t-butylanthraquinone and subsequent aromatization with hydriodic acid. The method yielded soluble oligomers of $M_n$ 3,100 and MWD 1.2. Investigation of the structure by NMR yielded evidence of a highly regular structure as opposed to crosslinked products in previous methods.

The spacing between anthracene units can be easily extended by any desired number of methylene groups. Many different polymethyleneanthracenes have been prepared. We will describe different strategies to achieve polymers containing from one to five methylene groups per anthracene repeating unit.

Polyanthrylenemethylene, \textbf{1.III}, was synthesized by Montaudo, et. al.\textsuperscript{15} via Friedel-Crafts reaction of \textit{bis}-9,10-(dichloromethyl)anthracene with anthracene in the presence of $\text{SnCl}_4$, \textbf{reaction 1.2} $\text{Ar} = 9,10$ Anthryl. $M_n$ by VPO were determined to be 2500.

This method allows for the formation of copolymers containing the anthracene methylene unit. The authors prepared various copolymers of anthracene with variously substituted benzenes and dibenzyls according to \textbf{reaction 1.2}, and \textbf{reaction 1.3}, with comonomers listed in \textbf{table 1.1}. Molecular weights for the copolymers ranged from 1400 to 6250 by VPO in o-dichlorobenzene at 130°C. Polymers of type A had predominately 9,10-
anthracene linkages while polymers of type B had both 9,10-and 1,4-anthracene linkages. The distribution of the different linkages were attributed to steric effects associated with the arylating agent.

\[
\begin{align*}
\text{C}_6\text{H}_2\text{Cl} + \text{H-Ar-H} & \xrightarrow{\text{SnCl}_4, \text{EtNO}_2} \text{Polymer A} \quad \text{Reaction 1.2} \\
+ \text{ClCH}_2\text{-Ar-CH}_2\text{Cl} & \xrightarrow{\text{SnCl}_4, \text{EtNO}_2} \text{Polymer B} \quad \text{Reaction 1.3}
\end{align*}
\]

Table 1.1 Comonomers used to make polyanthrylenemethylenes.

<table>
<thead>
<tr>
<th>Chloromethylated Comonomers</th>
<th>Aromatic Comonomers</th>
</tr>
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<tbody>
<tr>
<td>ClH\text{C} - CH\text{Cl}</td>
<td>ClH\text{C} - CH\text{Cl}</td>
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<td>ClH\text{C} - CH\text{Cl}</td>
<td>ClH\text{C} - CH\text{Cl}</td>
</tr>
</tbody>
</table>
Jones and Larson\textsuperscript{16} synthesized the same polymer two ways. By reaction 1.4 and by the reaction of chloromethylethyl ether with anthracene, reaction 1.5. Regiochemistry of the linkages was verified by IR, \textsuperscript{1}H NMR, and \textsuperscript{13}C NMR. The polymers showed good thermal stability in the region of 380 to 495°C.

An interest in conducting polymers led to the unsuccessful attempted synthesis of poly(9,10-dimethyleneanthracene), 1.IV, by the pyrolysis of 9,10-dimethylanthracene.\textsuperscript{17} Later, two strategies for the synthesis of this polymer were realized by Golden\textsuperscript{18} who prepared it by the coupling of 9,10-di(chloromethyl)anthracene with phenyl lithium, reaction
1.6 and by the solid state or solution polymerization of bi(anthracene-9,10-dimethylene), reaction 1.7.

Poly(9,10-dimethylene anthracene), 1.IV, is a lemon yellow, insoluble, amorphous solid which decomposes above 360°C. These materials were later studied for their thermal stability in air. At temperatures above 300°C, the isothermal weight loss resembled an autoacceleration, whereby the rate of decomposition increased with exposure to the high temperature environment.

Bender et. al. synthesized poly(anthralenemethylene) polymers, reaction 1.8, by reductive alkylation of anthracene with 1,n-dibromoalkanes. Anthracene was reduced by lithium in ammonia and alkylated with a 1,n-dibromoalkane. In general, a 90% yield of the
dihydroanthracene polymers were obtained. Using 1,2-dibromoethane, however, the cyclic dimer 9,9',10,10'-tetrahydro-9,9'-bianthryl is formed exclusively. Larger dibromoalkanes (N = 6,8) gave appreciable amounts of unimolecular cyclization products.

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{(CH}_2\text{)}_N & \\
\end{align*}
\]

\[
\begin{align*}
\text{Li} + \text{NH}_3 & \rightarrow \quad \text{S} \\
200^\circ \text{C} & \\
\end{align*}
\]

\[
\begin{align*}
\text{N} = 1, 4, 6, 8
\end{align*}
\]

The dihydroanthracene polymers had a molecular weight of between 1200 and 3500 depending on the synthesis conditions such as mixing rate and concentration of reagents. The molecular weight was verified by GPC and FD mass spectroscopy.

The dihydroanthracene polymers proved to be soluble precursors to polyanthracenes. Aromatization was achieved by reaction of the dihydroanthracene polymer with sulfur at 200°C. The solubility of the aromatized polymer was dependent on the molecular weight of the material and the degree of aromatic conversion. Aromatics polymers with higher molecular weights were insoluble. Since the poly(9,10-
dihydroanthrylenetrimethylene) polymer was generated in the highest yield with the least by products, it was studied further.\textsuperscript{21} NMR data was used to confirm the structure of the polymer and conditions were determined to maximize molecular weight. Also, the polymers poly(9,10-dihydroanthrylenedecamethylene) and poly(9,10-dihydroanthrylene-2-butynylene) were prepared. Both polymers had $M_n$ of 2200. The aromatized dihydroanthracene polymers were reacted with Li in THF to give a polyanion in which each anthracene had been reduced with two electrons.\textsuperscript{22} Quenching of this mixture with water gave back the dihydroanthracene polymer cleanly.

Though poly(9,10-dihydroanthrylenemethylenes) were more soluble as precursors, the aromatized polymers were not very soluble in organic solvents. To obtain greater solubility, alkyl groups were placed on the anthracene nucleus.\textsuperscript{23} The monomer 2,3-di-n-heptyl anthracene was prepared via Diels-Alder reaction of naphthoquinone with 2,3-di-n-heptylbutadiene. From this monomer, poly(2,3-di-n-heptyl-9,10-dihydroanthrylenetrimethylene) was synthesized by reductive alkylation with 1,3-dibromopropane and Na in ammonia. The total sample was found to be soluble in chloroform; an insoluble fraction as observed in previous syntheses, was not detected. The initial $M_n$ was reported to be 3100, though further reaction with an excess of both reducing agent and 1,3-dibromopropane resulted in a material with $M_n$ of 9700 by VPO. The higher molecular weight sample remained soluble in chloroform.
not as of yet reported, the polymer may be aromatized to the anthracene form as in previous experiments.

1.3 9,10-Anthracene Polymers.

The synthesis of analogs of poly(9,10-anthrylene) was undertaken. From 9,10-anthracenedicarboxylic acid was synthesized a polyanhydride by dehydration with acetic anhydride reaction 1.9. A polyester from octane-1,8-diol and 9,10-dimethoxycarbonylanthracene was synthesized by transesterification, reaction 1.10. A polycarbonate could be prepared from 9,10-anthracenediol and phosgene, reaction 1.11, but it decomposes at a relatively low 185°C.

The resultant physical properties of these materials were disappointing as compared to polyanthralenes. The polyester proved to be difficult to synthesize and offered low thermal resistance (dec. 140°C) as well as being of low molecular weight ($M_n$ of 1100 by VPO). The polyanhydride is insoluble and decomposed at 300°C. The polycarbonate forms viscous solutions but decomposes at a relatively low 185°C.

Bender and Müllen synthesized the monomers 2,3,6,7-tetra-n-heptyl-9,10-anthracenediol and 2,3-di-n-heptyl-9,10-anthracenediol and reacted them with 1,10-decanedioic acid dichloride, reaction 1.12.
The polyesters were soluble in common organic solvents and had $M_n$ by VPO of 3900-4500 for the 2,3-dialkyl monomer and 7900 for the 2,3,6,7-tetraalkyl monomer.
Gorda, et al.\textsuperscript{26} prepared polyesters connected through the 9 and 10 positions of the anthracene nucleus for the purpose of studying their macromolecular charge transfer behavior. Anthracene-9,10-diatomic acid dimethyl ester was polymerized under reduced pressure in the melt with a diol in the presence of Ti(OBu)\textsubscript{4} as a catalyst, reaction 1.13. \(M_n\) and degree of polymerization were determined by high field (360 or 400 MHz) NMR to be from 7780 to 9181 and 18 to 26 respectively depending on the alcohol used. Molecular weights were relatively low, but this insured that the polymers were soluble in chloroform. The effect of the R group, reaction 1.13, on the charge transfer properties of the anthracene ring were studied by the comparison of the formation of the charge transfer complex with chloranil among the derivatives.\textsuperscript{27}

\[
\text{Reaction 1.13}
\]

\[R = \text{HO-(CH}_2\text{)}_5\text{-OH, HO-(CH}_2\text{)}_{10}\text{-OH, or HO-(CH}_2\text{CH}_2\text{O)}_3\text{-H}
\]

A thiol ester ene polymer has been developed by Kobayashi et al.\textsuperscript{28} for the purpose of studying its conductive behavior. 9,10-Diethynyl anthracene was condensed with 9,10-anthracenedithiol in the presence of UV light or a free radical initiator in THF, reaction 1.14. The polymer was
extracted to obtain both soluble and insoluble fractions. The soluble fraction had $M_n$ of 3800 by a method based on copper acetylide. The insoluble fraction had $M_n$ of from 19,000 to 42,000 by the same method. The polymer decomposed rapidly at 300°C in air. The undoped polymer had a conductivity of about $10^{-11}$ S/cm and about $10^{-6}$ S/cm when doped with iodine.

A side reaction in the synthesis of polyethers, phase transfer polymerization was found to form poly(p-xylidine). Later, this technique was used to give a polymer of poly(9,10-anthrylidine), reaction 1.15. Bis-9,10-(chloromethyl)anthracene was coupled in the presence of quaternary ammonium salts in benzene or THF/DMSO/aqueous NaOH solution to give the anthrylidine polymer. The polymer flowed between 235 and 253°C dependent upon reaction conditions, while TGA showed a 10% weight loss between 260 and 305°C.

\[ \text{Reaction 1.14} \]
Following an interest in the synthesis of π-conjugated polymers and their conductive behavior, the above polymer and derivatives was later synthesized by the palladium catalyzed Heck coupling. These authors found that Pd catalyzed coupling of 9,10-divinyl anthracene did not produce the desired polymer with a dihalogenated aromatic compound. However, reversing the substituents so that 1,4-divinyl benzene is coupled with 9,10-dibromoanthracene leads to polymer in quantitative yields, reaction 1.16. If the anthracene ring is substituted with a t-butyl group in the 1 or 2 position, the molecular weights are higher than in the unsubstituted case. The unsubstituted derivative precipitates at an earlier stage in the reaction. Premature precipitation of the unsubstituted polymer abbreviates the $M_n$ to about 1000 while the solubility of the t-butyl substituted polymer helps it to remain in solution.

Since an anthracene containing homopolymer was not possible due to steric constraints associated with 9,10-divinylanthracene it was decided to move the reaction center away from the anthracene nucleus. Bis-9,10-(1,3-butadienyl)anthracene was synthesized and coupled with the Pd catalyzed Heck reaction with 9,10-dibromoanthracene to give
polyanthralenedivinylene, 1.V. Molecular weights were generally higher than the monovinyl derivative and conditions were developed to achieve a $M_w$ of 2800.

\[ R \quad \text{Br} + \quad \text{Heck coupling} \quad \text{Reaction 1.16} \]

\[ R = \text{H or t-butyl} \]

An acetylene containing anthracene analog to the polymer was prepared in a series of polyacetylenes by the CuI catalyzed coupling of acetylenes by oxygen, reaction 1.17.\textsuperscript{31} $M_n$ of a polymer containing 0.4:3:1 ratio of anthracene:4-amonophenyl:1,3-disubstituted benzene based monomers was 9300 by GPC while MWD was 4.81. This polymer lost less than 5% of its mass at a temperature of up to 550°C under nitrogen. An exotherm in the DSC indicates thermal crosslinking of this material at 257°C.
Palladium catalyzed C-C coupling\textsuperscript{32} was employed to synthesize an ethynyl bridged p-phenylene/9,10-anthracene polymer, reaction 1.18. 1,4-Diethynyl benzene was coupled with 9,10-dibromoanthracene in the presence of Pd(PPh\textsubscript{3})\textsubscript{4}, CuI, and triethylamine. M\textsubscript{n} of the polymer was 1550 by halogen end group analysis. Degradation of the polymer starts at about 380°C under nitrogen.

A phenyl substituted derivative of this polymer was later synthesized by Solomin, et. al., reaction 1.19\textsuperscript{33} An anthracene containing diyne diol was heated with 2-phenyl-1,4-dibromobenzene to yield the polymer below.

This oligomer was soluble in toluene and chloroform and had a molecular weight by GPC of 1400. The DSC showed a decomposition at
around 340°C while TGA demonstrated that the polymer retained 63% of its mass at 800°C.

A thermotropic liquid crystalline polymer was obtained by Memeger, 1.VI, by condensing 9,10-anthracenedicarboxaldehyde with 2-chloroterephthaldehyde and 4-4’bis-[(tributylphosphonio)methyl]-bibenzylidine in a Wittig reaction. The polymer had an inherent viscosity, \( \eta_{inh} \), of 0.35 dl/g in a \( o \)-dichlorobenzene/chlorobenzene solvent system at 270°C. The polymer melted at 300°C to form an anisotropic liquid crystalline phase. The polymer decomposed at 450°C under nitrogen retaining 50% of its mass at 700°C.
For purposes of assessing the $X^{(2)}$ non-linear optical and conductive behavior, anthracene containing polycarbosilanes were synthesized, reaction 1.20.\textsuperscript{35,36}

\[
\begin{align*}
\text{Polycarbodisilane 1} & - R_1 = R_2 = \text{Ph} \\
\text{Polycarbodisilane 2} & - R_1 = \text{CH}_3, R_2 = \text{n-octyl}
\end{align*}
\]

The reaction proceeds under catalysis from $(\text{PPh}_3)_2\text{PdCl}_2$, $\text{Et}_3\text{N}$, CuI, and $\text{P(Ph)}_3$. Anthracene containing polycarbosilane 1 was a solid and had $M_w$ of 23,543 with MWD of 3.15 while polycarbosilane 2 was a viscous oil and had $M_w$ of 11,020 with MWD of 2.80. Polycarbosilane 1 when doped with $\text{FeCl}_3$ showed an increase in conductivity of $10^{-7} \text{S/Cm}$ from $10^{-10} \text{S/Cm}$.\textsuperscript{37}

1.4 Pendant Anthracene Polymers.

Anthracene pendant polymers based on 4,5-dihydro-2-[2-(9-anthryl)ethyl]-1,3-oxazole were synthesized by Simionescu, et al, reaction 1.21.\textsuperscript{38} The polymers were initiated by a number of tosylates including methyl tosylate, ethylene ditosylate, and penta(ethyleneoxide) ditosylate.
Both methodologies give low molecular weight polymers having a maximum number average degree of polymerization of 23. The polymers are white, amorphous powders soluble in CHCl₃, DMSO, THF, DMF, acetone, and dioxane. The polymers are hydrolytically unstable and tend to degrade during work-up. They are insoluble in ethyl ether, petroleum ether, and methanol. Characterization included analysis by IR, ¹H NMR, and UV spectroscopy.

David, et. al. have synthesized 9-anthracene pendant polymers from 2-oxazolines. These polymers are spontaneously formed upon mixing 2-(9-anthrylethyl)-2-oxazoline and 7,7,8,8-quinodimethane, reaction 1.22.
2-(9-Anthrylethyl)-2-oxazoline, 1.VII was included in a series of charge transfer copolymers studied by Simionescu et. al.\textsuperscript{40} The anthracene moiety functions as an electron acceptor while the dinitro phenyl substituent functions as an acceptor. This group found that the anthracene monomer did not polymerize by itself, but copolymerized with the dinitrophenyl monomer to form polymers that decreased in molecular weight with increasing proportion of anthracene containing monomer.

Anthracene containing pyrrole monomers have been prepared and electropolymerized.\textsuperscript{41} 1-[2-(9-Cyanoanthracene-10-ylmethylamino)ethyl]-pyrrole, 1.VIII, was synthesized and polymerized on a spherical Pt microelectrode at 1.2 V vs. satd. NaCl calomel electrode. Cyclic voltametry studies indicated that the thin coherent films were electroactive and capable of holding 4 positive charges per anthryl group.
A series of electroinitiated anthracene containing pyrrole copolymers were synthesized from the monomers shown in Figure 1.1. The homo and copolymers formed flexible films. By selective integration of waves of the corresponding homopolymer, the concentration of the different monomers could be determined in the copolymer.

![Figure 1.1 Pyrrole based anthracene containing monomers.](image)

A later study determined that the conductive character of the chain structure has little effect on the chain structure of the compounds.
Polyions containing anthracene have been prepared by the Menschutkin reaction, reaction 1.23. A series of polyionenes were synthesized from monomers shown in table 1.2. These polymers were soluble in water, and formed macromolecular charge transfer complexes. These CT complexes were disrupted due to chain expansions and contraction caused by a polyelectrolyte effect with the addition of salt. The polymers formed thermally reversible 4+4 cycloaddition dimers upon irradiation with 340 nm light. Fluorescence and absorption spectroscopy suggested that the anthracene groups associated via hydrophobic interactions in water and salt solutions.

A series of anthracene pendant oligomers have been synthesized by Tazuke, et al., reaction 1.24 and their photoreactive and spectral properties both in solution and in the solid state have been evaluated. The oligomers are based on 2-(9-anthryl)methylpropane-1,3-diol, 1.IX. The
monomers are reacted with an acid chloride or ester to achieve the corresponding oligoesters; only degrees of polymerization of between 2 and 7 for all the systems investigated were achieved. Polymerization of the ester containing monomers was done in the melt under vacuum using hydrated calcium acetate and Sb$_2$O$_3$ as catalysts. Polymerization using acid chlorides was accomplished in the same manner except using no catalyst. HCl was removed by bubbling nitrogen through the mixture.

These systems were studied for their fluorescence properties\textsuperscript{49}, their charge transfer interactions with acceptor polymers\textsuperscript{50} and their tendency to photodimerize and thermally dissociate the dimers.\textsuperscript{51} An intramolecular charge transfer oligomer\textsuperscript{52} was then synthesized by this group from the previous diol and diethyl (4-N,N-dimethylaminobenzyl)malonate to give the cooligomer 1.X.

**Table 1.2** Monomers employed to form anthracene containing polyionenes.

<table>
<thead>
<tr>
<th>Ditertiary amine components</th>
<th>Dialkylhalide components</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Ditertiary amine components" /></td>
<td><img src="image2.png" alt="Dialkylhalide components" /></td>
</tr>
</tbody>
</table>
The DP of 1.9 was estimated to be 4-5 by GPC. The exiplex formation as well as its concentration dependence was characterized by absorption and fluorescence spectroscopy.

Later, the method of transthiolation was used to improve the molecular weight of these polymers. The thiol ester of the acid component was heated with the diol. In all cases, the molecular weight of the
polymers synthesized by this method increased from a factor of 2.1 to 5.5 over those synthesized previously.

A polyurethane elastomer\textsuperscript{54} was then fashioned from 1,1X and polyoxypropylene glycol (PPG), ethylene bis (4-cyclohexyl diisocyanate) and 2-ethyl-2-()-1,3-propane diol. The reaction mixture consisted of 20\% of hydroxyl units coming from the cross linker, 20\% from 1,1X, and the rest from PPG. The mechanical properties of the material in its natural as well as photochemically crosslinked state were compared. The crosslinked material exhibited a higher Young's modulus.

Anthracene containing glycidyl esters were synthesized for potential use in the information storage industry, reaction 1.25.\textsuperscript{55} 9-Anthracenyl-glycidyl ester was oligomerized cationically by BF\textsubscript{3} and anionically in the presence of alkali or alkoxides. Molecular weights were obtained ebulliscopically and found to be on the order of 1000 for cationic oligomerization and from 800-930 for anionic polymerization.

\[
\begin{align*}
\text{Anthracene} & \xrightarrow{\text{Base or Lewis acid}} \text{Anthracene glycidyl ester} \\
\text{Reaction 1.25}
\end{align*}
\]

Copolymers with β-naphthanenylglycidyl ester were synthesized and used in the study of the photoconduction of these polymers.\textsuperscript{56}
9-Carboxylanthryl glycidyl ester was also synthesized and oligomerized via BF$_3$ to a molecular weight of 1000-2000, reaction 1.26.$^{57}$

![Reaction 1.26](image)

1.5 Anthracene Containing Polypeptides and Polyglutamates.

The polypeptides poly(β-9-anthrylmethyl L-aspartate) and statistical copolypeptides with γ-benzyl L-glutamate were synthesized from their N-carboxyanhydrides.$^{58}$ The series of polypeptides had feed ratios of 0.2, 0.4, 0.6, and 0.8. They all showed almost identical elution diagrams having a molecular weight of around 2,000. CD studies on these polymer indicate that while poly(γ-benzyl L-glutamate) forms a right handed helix, poly(β-9-anthrylmethyl L-aspartate) forms a left handed one.

Standard solution phase peptide synthesis was used to synthesize a block copolypeptide that consisted of two N-(benzyloxycarbonyl)-L-lysine units and one L-9-anthrylalanine unit in succession throughout the chain.$^{59}$ The resulting copolypeptide had a molecular weight exceeding 10,000. CD studies of this polymer suggest that the copolypeptide forms a
right handed helix having regularly spaced anthracene units. The absorption and fluorescence of this copolypeptide suggests that it does not form ground state dimers or higher aggregates.

2% 8-11-(9-Anthryl)undecyl-L-glutamate units were included in a copolymer consisting of 28% 8-n-octadecyl-L-glutamate and 70% 8-methyl-L-glutamate. The $M_w$ of this terpolymer was determined to be 460,000. This material was used to study Langmuir-Blodgett films.

1.6 Polymers Containing Anthracene in the Backbone.

A series of polyesters and polyamides containing the 2,6(7)-disubstituted anthracene unit were synthesized by thermal elimination of ethylene from the ethyl bridged 2,6(7)-disubstituted dihydroanthracene polymer, reaction 1.27.6 The inherent viscosities of the aromatized polyamides in $H_2SO_4$ ranged from .32 to .92 while the polyesters in tetrachloroethane/phenol solvent system ranges from .31 to .82. The polymers were characterized by NMR, IR, and DSC. These polymers were thermally stable, degrading at or near 400°C.

Anthracene endcapped oligomers have been linked together by the action of 1,4,5,8-tetrahydro-1,4:5,8-diepoxyanthracene, reaction 1.28. The Diels-Alder adduct formed then undergoes thermal dehydration to yield an anthracene containing subunit. The dehydration was monitored by NMR.
The resulting aromatized polymers are thermally stable, the onset of thermal decomposition being in excess of 600°C by TGA.

\[
\begin{align*}
\text{Z} &= \text{NH or O} \\
\text{R} &= (\text{CH}_2)_4 \\
&\quad (\text{CH}_2)_6 \\
&\quad (\text{CH}_2)_{10}
\end{align*}
\]

Reaction 1.27

A study was then conducted to find the condition of maximum thermal stability and processing ease for application as a composite matrix resin.\(^{64}\) The result was that the polymer was made easier to process without loss of thermal stability by modifying the polyimide portion of the polymer. The study was extended by Scola\(^{65}\) who improved properties of the system by modifying the polyimide portion of the molecule.

Anthracene containing polythiazoles, imidazoles, and oxazoles were synthesized by displacement of phenol from the diphenyl ester of 1,5-anthracenedicarboxylic acid reaction 1.29.\(^{66}\) Inherent viscosities ranged from 0.6 to 0.8 for all polymers in a 2% solution of H\(_2\)SO\(_4\). The polymers had good thermal stability by TGA with the onset of decomposition above 500°C.
Another anthracene containing imidazole polymer was synthesized via a poly(azomethine) intermediate. The poly(azomethine) intermediate was prepared by the condensation of 9,10-
anthracenedicarboxaldehyde with 3,3',4,4'-tetraaminodiphenyl ether in DMAc. The resulting product had an inherent viscosity in DMAc of 0.3 at 0.2% concentration (w/v).

\[ \text{Reaction 1.30} \]

The cyclodehydrogenation reaction, reaction 1.30, to form the imidazole polymer was carried out in DMAc to which iron(III)chloride had been added. Dry air was then bubbled through the solution for eight hours. The conversion was monitored by IR spectroscopy. The imidazole polymer had a higher inherent viscosity (0.5 under the same conditions as previous).

As a part of a study of the effect of structure on thermal stability, a pyromellitic acid based polyimide with 1,4-diaminoanthracene was synthesized, 1.XI.68 This study was limited to the thermal stability in air of the polymer as well as a general characterization of the films. The polyimide was a powder that lost mass at a rate of 1.94%/Hr. at 400°C in air.

Poly(1-aminoanthracene) was electrochemically prepared, reaction 1.31.69 1-Aminoanthracene was dissolved in an acetonitrile/tetra-n-butylammonium hexafluorophosphate solution. An electronically
conductive purple film formed on the Pt electrode. Its conductivity was then estimated using scanning tunneling microscopy.

![Chemical structure of a compound](image)

Poly(1-aminoanthracene) was also later synthesized by chemical oxidative polymerization.\textsuperscript{70} Acid and Fe catalyzed oxidation of 1-aminoanthracene was accomplished in acetonitrile by hydrogen peroxide. \(M_n\) by GPC using a polystyrene standard is 45,000 with MWD of 1.23. TGA shows these materials start to lose mass at 300°C but retain 72% of their mass at 900°C.

A oligoisoidoxazine based on diaminophenyl anthracene was prepared\textsuperscript{71} by condensation of 1,2,4,5-tetracyanobenzene with 9,10-(4,4'-diphenyl)anthracene and \(m\)-chlorophenol to form the oligomer, 1.XII. The
product of this reaction precipitates early in the reaction and by elemental analysis, the product is on average only a dimer.

Vinogradova, et. al.$^{72}$ synthesized aromatic polyamides based on 9,10-bis(4'-aminophenyl)anthracene, reaction 1.32. Aromatic and aliphatic copolymers were also investigated.

Various organic moieties were employed in the diacid chloride. Among them were adipic, sebacic, tere- and iso-phthaloyl chlorides. Also acid chlorides of 2,2-bis-(4-carboxylphenyl)hexafluoropropane, and 3,3-bis-(4"-carboxyphenyl)phthalide were used. Diamines used in the copolymer included p-phenylene diamine, 9,9-bis-4'-aminophenyl)fluorene, and 5(6)-amino-2-(4'-aminophenyl)benzimidazole. The best solvent system for the synthesis of these materials was 2:1 NMP : hexamethylphosphoramide at a concentration of 12% solids. From this solvent system, inherent viscosities of polymers in H$_2$SO$_4$ ranged from 0.53 to 1.91.
Polyimides, 1.XIII, have been prepared from 9,10-bis-(4'-aminophenyl)anthracene. The interest in these systems were purely for their spectral properties and no information concerning thermal stability or molecular weights were given.

Luminescent polymeric Schiff bases, 1.XIV, were prepared by condensation of a dialdehyde with a diamine. Only M_n's from ultracentrifugation for the ethylene bridged polymer, ~10,000, were given as the terephthaloyl derivative is insoluble. The polymers are not
as the terephthaloyl derivative is insoluble. The polymers are not stable to hydrolysis and were synthesized for the study of their spectral properties.

The AlCl$_3$ catalyzed Friedel-Crafts polymerization of 4,4'-bis(2,6-dimethylphenoxy-4-phenyl) sulfone using CH$_2$Cl$_2$ as both comonomer and solvent was reported by Percec and Tingerthall, reaction 1.33. The polymer yield was 87% and the M$_n$ was 4059 with polydispersity of 1.31 by GPC. The polymer was determined to be a polymeric Diels-Alder diene reacting with tetracyanoethylene to produce bridged dihydroanthracene units in the main chain, 1.XV.

![Chemical Structure](image)

Tingerthall(Bruss), et. al. later reported that products of the same synthesis were soluble and film forming. The aromatization is complete by 20 hr. yielding approximately the decamer by $^1$H NMR. By DSC it was reported to have a T$_g$ of around 280°C and T$_m$ of between 421 and 428°C.
1.7 Synthetic Goals: the Statement of Intended Research.

The literature search yielded no examples of polymers containing the 2,3,6,7-tetrasubstitution pattern. This is specifically the unit that we wished to study. The research project directed toward the end of synthesizing polymers containing the 2,3,6,7-anthracene fragment that was pursued consisted of three parts. First, as will be elaborated in chapter two, a reactive monomer based on 2,3,6,7-anthracenetetracarboxylic acid was developed. Second, as detailed in chapter three, the synthesis of 2,3,6,7-
anthracenetetracarboxyl containing homo- and copolymers was advanced. Lastly, described in chapter four, we studied the Diels-Alder reactivity of the anthracene moiety in the polymer backbone. This study included not only the addition of dienophiles to the polymer backbone, but the crosslinking and concomittant gelation of solutions of 2,3,6,7-anthracenetetracarboxyl containing polymers using a difunctional maleimide based bis-dienophile.
2.1 Introduction.

The synthesis of 2,3,6,7-tetrasubstituted anthracene derivatives has not been widely studied. Perhaps this is because the 2,3,6,7 positions of anthracenes are less active than 1,4,5,8 and 9,10 positions toward electrophilic aromatic substitution. Until our research in the field, the literature revealed six methods for the synthesis of 2,3,6,7-tetrasubstituted anthracenes. Our method, which culminates with a reactive monomer based on 2,3,6,7-anthracenetetracarboxylic acid, comprises a seventh. The seven methods are described in the following sections.

2.1.1 Early Syntheses of 2,3,6,7-Tetramethylanthracene.

The first three syntheses of 2,3,6,7-tetramethylanthracene were reported by Morgan and Cousson\textsuperscript{78} who were studying components of coal tar, scheme 2.1. Their first method was the pyrolysis of 2,4,5,3',4'-pentamethylbenzophenone followed by oxidation to the anthraquinone and reduction to 2.1. This method is low yielding, scheme 2.1, route A. The second method developed by this group was the Friedel-Crafts condensation of 2 moles of 3,4-dimethylbenzoyl chloride to the 2,3,6,7-
tetramethylanthraquinone and subsequent reduction to 2.1, scheme 2.1, route B. Their third synthesis started with the Diels-Alder reaction of p-benzoquinone with 2,3-dimethyl-1,3-butadiene. 2.1 was obtained after subsequent reduction of the anthraquinone followed by aromatization of the anthracene nucleus, scheme 2.1, route C.

Scheme 2.1 Routes toward the synthesis of 2,3,6,7-tetramethylanthracene.

Barnett, Goodway, and Watson later refined this chemistry and added their own synthesis of 2.1. Their method consisted of the Friedel-Crafts
reaction of methylene chloride with \( \alpha \)-xylene. 2.1 was obtained by recrystallization from xylene, scheme 2.1, route D.

2.1.2 The Synthesis of 2,3,6,7-Anthracenetetracarboxylic Acid.

The first published synthesis of 2,3,6,7-anthracenetetracarboxylic acid was by Marschalk, whose 5 step synthesis started with 2,3,6,7-tetramethylnanthracene, scheme 2.2. Oxidation of the methyl substituents (a) was accompanied by anthraquinone formation. The synthesis entailed (b) reduction to 9,10-dihydro-2,3,6,7-anthracenetetracarboxylic acid. Aromatization required (c) conversion of the tetraacid to the bis-anhydride followed by (d) dehydrogenation of the 9,10 positions with sulfur. Hydrolysis of the resultant anhydride (e) gave 2,3,6,7-anthracenetetracarboxylic acid. This synthesis is impractical because of the time requirement to get to product as well as the total yield over all steps from basic starting materials is quite low (less than 5%).

2.1.3 The Method of Luo and Hart.

The sixth method based upon a benzo-[1,2-c:4,5-c']difuran intermediate was developed by Luo and Hart scheme 2.3. Reaction of anthracene diendoxide with tetraphenylcyclone (a) produced an adduct which liberated benzo-[1,2-c:4,5-c']difuran upon heating in decalin. If the
thermolysis is conducted in the presence of dienophiles such as dialkyl maleates or fumarates (b) followed by dehydration with sulfuric acid, *tetrakis- 2,3,6,7-(alkyloxycarbonyl)anthracenes* are formed along with carbon monoxide and tetraphenyl benzene (c). This is a very elegant synthesis but rather expensive reagents are required.

![Scheme 2.2 The method of Marshalk.](image)

2.2 Synthesis of a Reactive Monomer Based on 2,3,6,7-Anthracene-tetracarboxylic Acid.

We have developed an attractive alternate method for the synthesis of 2,3,6,7-tetrasubstituted anthracenes. The general methodology was developed by Cava, Drana, and Muth. This group published a synthesis of 2,3-disubstituted naphthalenes via a tandem Diels-Alder rearomatization reaction. α,α,α',α'’-Tetabromo-ι-xylene is reacted with a
dienophile such as N-phenylmaleimide or maleic anhydride to give the corresponding naphthalene derivative. This reaction proceeds through a quinodimethane intermediate which undergoes a Diels-Alder reaction. This sequence is followed by spontaneous dehydrohalogenation yielding the 2,3 disubstituted naphthalene derivative, scheme 2.4.

Scheme 2.3 The method of Luo and Hart.

The synthetic utility of this reaction is that it can be used to generate mono and bis 2,3-disubstituted naphthalenes using \( \alpha,\alpha,\alpha',\alpha' \)-tetrabromo-o-xylene or 2,3,6,7-tetrasubstituted anthracene molecules using tetrais-1,2,4,5-dibromomethylbenzene also called octabromodurene (OBD), scheme 2.5. OBD undergoes a bis tandem Diels-Alder rearomatization reaction with N-phenylmaleimide to give N,N'-bis(phenyl)-2,3,6,7-anthracene-tetracarboxylic-2,3:6,7-diimide.
Tetrakis-1,2,4,5-(dibromomethyl)benzene, 2.III, was synthesized according to Soyer et. al. All photochemical brominations were carried out in a quartz reaction vessel. A solution of 1,2,4,5-tetramethylbenzene, 2.II, was brought to reflux and irradiated with 3000Å light. Brominations were attempted using tungsten flood lamps as the light source, but the quality of the product was not as high and caused some problems with the solubility of intermediates later in the synthesis. Liquid bromine was added over a period of 4 hours and the solution irradiated under reflux for 2 days. During this time a large amount of HBr was liberated. An off-white powder was isolated by filtration, washed with boiling chloroform, and dried. This powder was used without further purification as its melting point matched that of the literature.

Our first attempts to synthesize the 2,3,6,7-tetrasubstituted anthracene nucleus were based on the reaction of ester and anhydride
derivatives of maleic or fumaric acid. In the example below, 2.III was allowed to react with maleic anhydride in the presence of sodium iodide in dimethyl formamide (DMF) solvent at 80°C overnight.

\[ \text{Br}_2\text{CH} \cdot \text{CHBr}_2 + 2 \text{maleic anhydride} \rightarrow \text{Reaction 2.1} \]

The reaction mixture was poured into water and decolorized with sodium bisulfite. Products of the reaction of 2.III with maleic anhydride, diethyl malonate and dimethyl fumarate respectively were difficult to isolate by filtration. Attempts at using celite 545 as a filter aid failed as the particles simply passed through. Rather than try to isolate products from the above reaction, dienophiles other than those mentioned above were then tried as an alternative.

The product from the reaction of 2.III with N-phenyl maleimide, N,N'-bis(phenyl)-2,3,6,7-anthracenetetracarboxylic-2,3:6,7-diimide, 2.IV, precipitated from the reaction mixture and was filtered directly from the reaction mixture. An insoluble yellow amorphous powder was obtained. This powder was triturated with boiling water and with p-dioxane. The HBr liberated from the reaction apparently forms a salt with the solvent. After triturating the crude 2.3 with p-dioxane and drying, a portion of the
sample is soluble in water. Evaporation of the aqueous solution then yields white crystals which give the correct NMR spectrum for DMF when dissolved in water, and form a precipitate upon addition of a solution of silver nitrate. Thus the crystals were apparently N,N-dimethylformamide hydrobromide. p-Dioxane removes unreacted 2.II in which it is recrystallizable. 2.IV is insoluble in solvents ranging from hexane to methanesulfonic acid. It darkens slightly on heating to 300°C in air. The thermal stability in air of this compound showed promise as a model for the polymer system, but its insolubility limited the methodology with which it could be characterized. We were able to collect a FAB mass spectrum and an IR spectrum containing bands at 1773 and 1724 cm⁻¹ consistent with the imide structure.

The anthracene diimide is resistant to hydrolysis by acids but will hydrolyze in 10 to 25% sodium hydroxide solution to yield a brown solution that gives a noticeable blue fluorescense. Neutralization of the basic solution yields the tetracarboxylic acid, 2.V, which is a finely divided bright yellow powder. The powder may be filtered and dried and will dissolve with evolution of gas in a solution of potassium carbonate. Unfortunately, 2.V is also quite insoluble and attempts to directly characterize the solution were difficult. Again, reasonable FAB mass spectral and IR data were obtained, and since the tetrapotassium salt was quite water soluble, ¹H and ¹³C NMR data from D₂O solution gave expected results.
Scheme 2.5  Synthesis of 2,6(7)-di-n-butyloxycarbonyl-3,7(6)-dichlorocarbonylanthracene.
Indications at this point in the research were that we were successful in synthesizing 2.IV and 2.V. The insolubility of these compounds, however, was hindering our study of them. To break up the presumed solubility limiting microcrystallinity characteristic of flat polynuclear aromatic compounds and dimerization of organic acids, we decided to form a soluble ester. *Tetrakis-2,3,6,7-(methoxycarbonyl)anthracene* was prepared by a modified procedure of Grundy, et al.\(^4\)

\[
\begin{array}{c}
\text{OCH}_3 + 4 \text{acetone} \\
\text{H}_3\text{CO} - \\
\text{COH} + 3 \text{acetone}
\end{array}
\]

**Reaction 2.2**

The tetracarboxylate salt is methylated by the action of dimethyl sulfate in acetone. The crude product was sublimed under vacuum and recrystallized from acetonitrile to yield x-ray quality pale yellow rhombohedral crystals. The resulting x-ray structure verified that our new synthesis of 2,3,6,7-tetrasubstituted anthracenes gave the correct product, **figure 2.1**. The structure indicates that the molecule lies on an inversion center. In **table 2.1** the fractional atomic coordinates are given for the structure in **figure 2.1**. The structural features of bond distances, bond angles and the coordinates assigned to hydrogen atoms are given in **tables 2.2 through 2.4** respectively.
Figure 2.1 ORTEP drawing of 2.X.

Table 2.1 Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²) for 2.X Beq = \((8p^2/3)\text{Si}_j\text{U}_i^*\text{aj}^*\text{aj}\text{aj}\).

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>0.64815(8)</td>
<td>0.5178(2)</td>
<td>1.0978(1)</td>
<td>6.38(4)</td>
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<tr>
<td>O2</td>
<td>0.78773(7)</td>
<td>0.4111(2)</td>
<td>1.0473(1)</td>
<td>4.16(2)</td>
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<tr>
<td>O3</td>
<td>0.90891(7)</td>
<td>0.5269(2)</td>
<td>0.7697(1)</td>
<td>4.47(3)</td>
</tr>
<tr>
<td>O4</td>
<td>0.85021(7)</td>
<td>0.7126(2)</td>
<td>0.9157(1)</td>
<td>3.94(2)</td>
</tr>
<tr>
<td>C1</td>
<td>0.6667(1)</td>
<td>0.5043(2)</td>
<td>0.8551(2)</td>
<td>3.31(3)</td>
</tr>
<tr>
<td>C2</td>
<td>0.73494(9)</td>
<td>0.5408(2)</td>
<td>0.7619(2)</td>
<td>3.21(3)</td>
</tr>
<tr>
<td>C3</td>
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Table 2.2 Table of bond distances (Å) for 2.X.

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Table 2.3 Bond angles in degrees for 2.X.

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Table 2.4 Fractional atomic coordinates and isotropic thermal parameters for H atoms (Å²) for 2.X.

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Since methyl esters are relatively stable compounds, the use of tetraakis-2,3,6,7-\((\text{methoxycarbonyl})\)anthracene as a monomer was discounted. Attention was then focused on ways to make the presumably more reactive 2,3,6,7-anthracenetetracarboxylic acid dianhydride. Pyromellitic dianhydride can be synthesized by sublimation of the acid, so an attempt at direct vacuum sublimation of 2.V was made. All attempts failed due to extensive decomposition even at pressures of 10 millitorr.

March\textsuperscript{85} describes the synthesis of acid anhydrides by the action of phosgene on triethylamine salts of 1,2-disubstituted carboxylic acids in methylene chloride. A successful attempt to dissolve 2.V in a methylene chloride solution of triethylamine led us to believe that a route to the dianhydride could be found using solution phase chemistry. Since phosgene is poisonous, a similar method was used substituting acetyl bromide for phosgene. The premise was that the acetyl bromide would form a mixed anhydride with 2.V which would spontaneously decompose to the more stable anhydride of 2.V and acetic acid. This reaction yields a yellow-orange precipitate which gives the expected IR spectrum for a cyclic acid anhydride. This compound suffers again from poor solubility. It is partially soluble in hexamethyl phosphoramide. The solubility characteristics of 2.VI again limited the characterization of this compound. The IR spectrum, had a significant peak for free carboxylic acid, though, and shows that the sample is not sufficiently pure for polymerization.
It became clear that if a high quality polymer were to be obtained, a soluble, reactive monomer would have to be formulated. Our attention then focused on the synthesis of derivatives readily soluble in conventional low boiling solvents. One way to do this would be to add to the molecule a hydrocarbon tail. The most convenient way to do this for our systems was to formulate an ester from the crude anhydride product of 2.VI. Crude 2.VI was heated with n-butanol at 90°C until dissolved giving a red solution. Excess n-butanol was evaporated and the reaction product was chromatographed on a silica column using 1:1 ethyl acetate-THF. In this manner, a mixture of 2,6(7)-di-n-butyloxycarbonyl-3,7(6)-anthracene, 2.VII, without impurities was isolated. 2.VII is soluble in conventional solvents and is pure. This method fails to separate the syn and anti isomers of the product as seen by the proton NMR. The apparent triplet at 8.79 ppm is comprised of a two singlets corresponding to the inequivalent protons in the 9,10 positions of the syn diester and a central singlet corresponding to the equivalent protons in the 9,10 positions of the anti diester. The apparent 1:2:1 triplet at 8.79 ppm suggests that the syn to anti ratio is close to 50:50.

The final step to a highly reactive monomer is easy due to the newfound solubility of 2.VII. Reactive monomers can be synthesized from 2.VII according to Volksen. The acid-ester, 2.VII, was suspended in dry ethyl acetate and excess oxalyl chloride was added. Carbon mono- and dioxide were evolved on heating. After evolution of gas had ceased,
evaporation of ethyl acetate and recrystallization from cyclohexane gave the pure acid chloride-ester monomers in a 50:50 syn to anti ratio as estimated by NMR figure 2.2 and figure 2.3.

Figure 2.2 $^1$H NMR of 2.VIII.

Our naming of monomer systems differ slightly from some articles in the literature. In much of the literature concerning reactive ester monomers to date, diacid chloride diesters based on pyromellitic acid are called "ortho" or "meta" isomers. While this is sufficient for pyromellitic acid based compounds it is not for fused linear aromatic acids such as 2,3,6,7-naphthalene or anthracene tetracarboxylic acids. We therefore recommend "syn" and "anti" as the more appropriate nomenclature. In the case of other tetracarboxylic acids, such as $3,3',4,4'$-biphenyltetra carboxylic acid, the diesters are most appropriately described using IUPAC nomenclature.
2.3 Experimental.

2.3.1 Materials and Methods.

Dichloromethane, triethylamine, and ethyl acetate were dried by distillation from calcium hydride. Anhydrous, N,N-dimethylacetamide and N,N-dimethylformamide and reagents were purchased from Aldrich Chemical Co. and were used without further purification. NMR spectra were taken on Bruker AC series machines of the specified field. FAB mass
spectra were taken on a Finnigan TSQ-70 mass spectrometer. FT/IR spectra were taken on a Perkin Elmer 1760X spectrometer.

2.3.2 Synthesis of *tetrakis*-1,2,4,5-(Dibromomethyl)benzene (2.III).

The general procedure of Soyer, Kerfanto, and Raphalen was used. 1,2,4,5-tetramethylbenzene (87.5g, 0.65 moles) was dissolved in 3.5L of carbon tetrachloride in a 4L quartz vessel. The solution was heated to reflux and irradiated by 3000Å light in a Rayonette® chemical reactor. Bromine (280 mL, 5.44 moles) was added over a period of 6 hours. After 2 days, the product was filtered and washed with boiling chloroform. Average yields were 78%. The crude product was used without further purification. An analytical sample was prepared by recrystallization from p-dioxane, mp. 305°C (dec.); lit. mp. 305°C (dec.).

2.3.3 Synthesis of N,N'-bis(Phenyl)-2,3,6,7-anthracene-tetracarboxylic-2,3:6,7-diimide (2.IV).

*Tetrakis*-1,2,4,5-(dibromomethyl)benzene, (20g, 0.026 moles), N-phenyl maleimide (9g, 0.052 moles), NaI (45g, 0.300 moles), and N,N-dimethylacetamide (300 mL) were charged into a capped Erlenmeyer and maintained at 80°C with stirring. After 10 hours, a yellow precipitate had formed. The precipitate was filtered, trititated once with boiling water, three times with boiling p-dioxane, and dried. The resulting bright yellow
solid, 3.32g (47%), is highly insoluble in organic solvents. It is resistant to methanesulfonic and polyphosphoric acids. The bis-imide, 2.IV, gradually darkens on heating in air to 300°C. IR(KBr cm\(^{-1}\)) 1773.2, 1724.2, 1504, 1373.4, 1128.7; FAB Mass Spec. [M\(^{+}\)] = 468.4.

### 2.3.4 Synthesis of 2,3,6,7-Anthracenetetracarboxylic Acid (2.V)

Bis-imide, 2.IV, (2g, 4.3 mmoles), NaOH (10g, 0.25 moles), and water (40g) were charged into a round bottomed flask and refluxed under nitrogen for 12 hours. The resulting solution was decolorized with charcoal and extracted with 2x50 mL portions of ether. The aqueous solution was acidified and the resulting yellow precipitate was isolated by centrifugation, washed with distilled water, recentrifuged and dried in-vacuo. Tetraacid, 2.V, is a pale yellow amorphous solid which dissolves in 5% potassium carbonate solution with evolution of carbon dioxide. Dec. >300°C in air, IR(KBr cm\(^{-1}\)) 3044.1, 2663.3, 1707.4, 1483.3, 1408.7, 1304.1, 1251.8, 1139.6, 1035.3, 938.2. FAB Mass Spec. [M+H\(^{+}\)] = 355.4. \(^1\)H NMR (ppm) (200 MHz, D\(_2\)O) (as potassium salt) 8.65 (s, 2H) and 8.20 (s, 4H); \(^{13}\)C NMR 180.0, 138.9, 134.0, 130.2, 129.8.
2.3.5 Synthesis of tetrakis-2,3,6,7-(Methoxycarbonyl)anthracene (2.10).

Tetraacid, 2.10, (1.00 g, 2.82 mmole) was converted to the tetrapotassium salt with excess potassium carbonate (3.15 g, 0.0124 moles) in 45 mL of water. The resulting brown salt solution was filtered into a RB flask. The water was removed and the residue dried in-vacuo. To this were added 50 mL of dry acetone and a 1.5 molar excess (2.14 g, 0.0169 moles) of dimethyl sulfate. The solution was allowed to reflux overnight. The resulting suspension was filtered and the acetone evaporated. The residual oil was diluted with about 3 mL of acetonitrile and refrigerated. Crystals of the tetraester were isolated by filtration, sublimed in-vacuo, and recrystallized from acetonitrile to yield 0.360 g (0.877 mmole) of crystals suitable for x-ray analysis (31% from the tetraacid). Mp 226-228°C. 1H NMR (ppm) (200 MHz, DMSO-d6) δ 9.01 (s, 2H), 8.59 (s, 4H) 3.91 (s, 12H); 13C NMR (ppm) δ 52.7, 128.4, 129.9, 131.0, 131.4, 167.0; GC/MS single peak (m/z) 410.

2.3.6 Synthesis of 2,3,6,7-Anthracenetetracarboxylic 2,3:6,7-dianhydride (2.11).

Finely ground 2,3,6,7-anthracenetetracarboxylic acid, 7 1.0 g (0.00283 mol), was dissolved in a mixture of 1.95 mL (1.42 g, 0.0141 mol) of dry triethylamine in 100 mL of dry dichloromethane and the solution was treated with 0.627 mL (1.04 g, 0.00846 mol) of acetyl bromide. A green
precipitate formed immediately. The reaction was allowed to stir for 15 min. The resulting precipitate was filtered, washed with dichloromethane and dried in-vacuo. The yield of bis-anhydride was 0.72g, (79%), dec. >300°C in air, IR(KBr) 3446.3, 3036.6, 1838.1, 1792.6, 1724.4, 1238.9, 912.7 cm⁻¹.

2.3.7 Synthesis of 2,6(7)-Di-n-butyloxycarbonyl-3,7(6)-anthracene dicarboxylic Acid (2.VII)

Dianhydride, 2.VI, 1.0 g (0.00314 mol) was warmed with 25 mL of dry n-butanol to 90°C until a homogeneous solution was obtained (≈ 1.5 h). The excess n-butanol was removed from the filtered solution under reduced pressure and the residue was chromatographed on silica gel (ethyl acetate:THF, 1:1). The product obtained, 1.12 g (76%), is a mixture of the syn and anti isomers; ¹H NMR (ppm) (200 MHz, acetone-d₆) δ 8.98 (t, 2H), 8.67 (d, 2H), 8.50 (d, 2H), 4.33 (t, 4H), 1.75 (m, 4H), 1.47 (m, 4H), 0.96 (t, 6H); ¹³C NMR (ppm) (400 MHz, THF-d₈) δ 168.21, 168.03, 133.23, 133.04, 133.00, 132.80, 132.14, 132.06, 131.84, 131.73, 130.90, 130.82, 130.44, 130.33, 130.02, 129.64, 65.77, 31.58, 20.11, 14.12; IR(KBr) 3447.4, 2970.6, 2879.7, 2645.1, 1714.1, 1630.8, 1479.4, 1275.1, 1131.2, 934.4 cm⁻¹; LC/MS, (m/z) 466 (M⁺).

2.3.8 Synthesis of 2,6(7)-Di-n-butyloxycarbonyl-3,7(6)-dichlorocarbonylanthracene (2.VIII).

Diester diacid 2.VII, 4.10 g (0.00880 mol) was suspended in 50 mL of dry ethyl acetate. Oxalyl chloride, 1.8 mL (2.619 g, 0.0206 mol) was added
and the mixture was warmed to 40°C; dissolution of the product was accompanied by evolution of gases. When gas evolution ceased, the ethyl acetate was stripped in-vacuo and the residue recrystallized from cyclohexane to which 2 drops of oxalyl chloride was added. The product was recovered by centrifugation and dried in-vacuo, 3.81g (86%) of a yellow solid was obtained; $^1$H NMR (ppm) (200 MHz, CDCl$_3$) $\delta$ 8.71 (t, 2H), 8.57 (d, 2H), 8.55 (d, 2H), 4.27 (t, 4H), 1.80 (m, 4H), 1.50 (m, 4H), 1.00 (t, 6H); $^{13}$C NMR (200 MHz, CDCl$_3$) $\delta$ 167.4, 165.9, 133.9, 132.5, 132.3, 131.9, 131.8, 130.9, 130.5, 130.1, 128.1, 127.9, 66.4, 30.5, 19.2, 13.7.
CHAPTER THREE.

Synthesis and Properties of Copolymers Containing 2,3,6,7-
Tetrasubstituted Anthracene.

3.1 Introduction.

Instead of the synthesis of copolyamic esters, as presented in this chapter from the diester diacid chlorides synthesized as in the last chapter, it might have been simpler to produce polymers if we had been able to purify the dianhydride of the anthracene tetracarboxylic acid. The synthesis of the polymer would simply have resulted from mixing the purified monomers in dry polar aprotic solvents. In that case, we would have obtained polyamic acids, which have been studied extensively. Polyamic acids, however, are susceptible to hydrolysis if the normally hygroscopic polar aprotic solvents absorb water from the atmosphere. Through the process of anchiomeric assistance of the ortho carboxylic acid group, the polymer is effectively cleaved over time leading to materials with decreased mechanical properties.

Since the dialkyl ester diacid chlorides of the anthracene tetracarboxylic acid are soluble and purifiable, we may synthesize ester analogs of polyamic acids. These polymers are called polyamic esters. Since the carboxylic acid group is blocked by the alkyl ester group, anchiomeric assistance is not possible and the resultant polymer is less affected by changes in the concentration of water in a solution of the
polymer. Thus, the viscosity of a polyamic ester solution should remain constant while the viscosity of a polyamic acid solution will decrease in time if not stored properly.

One of the goals in the synthesis of 2,3,6,7-anthracenetetracarboxyl containing polymers was to determine whether polymers incorporating the anthracene derived unit have advantages in thermal stability. If so, would there be benefits in the synthesis of copolymers. Another goal was to determine the Diels-Alder reactivity of the anthracene moiety in the polymer to strong dienophiles such as N-phenyl maleimide. The crosslinking of the polymer was then possible by reaction with bis-maleimides resembling N-phenyl maleimide in structure. The synthesis of the anthracene derived diester dicarboxylic acid requires much time, effort, and resources. Since crosslinking requires only one or two links per chain, copolymers are also an attractive solution since the concentration of anthracene derived monomer in the polymer need not be high.

It was decided that since most of the 2,3,6,7-anthracenetetracarboxyl containing monomer precursors were insoluble, that the diamine component should be selected so that the polymer would have the highest solubility. 4-Aminophenyl ether was selected as the diamine component because the oxygen of the ether linkage causes a pronounced "kink" in the polymer. Such structures in a polymer inhibit crystallization of the polymer thereby insuring solubility. A suitable analog of the anthracenetetracarboxylic acid component is pyromellitic acid. Toward this
end, a simpler method for the synthesis of pure diester diacid chlorides was
developed.

3.2 Synthesis of a Pyromellitic Acid Derived Comonomer and Purification
of the Diamine Component.

The comonomer 2,5-dicyclohexyloxycarbonyl-1,4- benzenedicarbonyl
dichloride was prepared in a similar manner to that of the anthracene
based monomer. The diester-diacid was synthesized by heating the
inexpensive and readily available pyromellitic dianhydride with excess
cyclohexanol, dried by distillation from calcium hydride. NMR showed the
presence of both a small amount of pyromellitic acid, and an appreciable
amount of the monosubstituted ester. The diesters are easily purified on a
column using methyl acetate as the eluent. NMR of the chromatographed
material indicates a pure 50:50 mixture of syn to anti dicyclohexyl ester,
figure 3.1.

The two peaks at 7.95 and 8.24 ppm are due to the inequivalent
protons from the syn diester. The central peak at 8.09 ppm is due to the
equivalent protons of the anti diester. The ester mixture is then reacted
with oxalyl chloride in an exactly analogous fashion as with the anthracene
derived monomer in chapter two. The resultant mixture is then
recrystallized from hexanes. Only the anti isomer recrystallizes as white
needles while the syn isomer remains in solution, figure 3.2.
Figure 3.1 'H NMR of syn and anti dicyclohexyl esters of pyromellitic acid.

Figure 3.2 'H NMR of the anti diester diacid chloride after recrystallization.

In figure 3.2, it is quite evident that the only isomer remaining after recrystallization is the anti isomer. This is an improvement in the
synthesis of anti diester-diacid chlorides in terms of simplicity and time required. When other analogs are used, such as the ethyl ester, a series of as many as 8-10 triturations with ethyl acetate are required to separate the syn and anti isomers of the diester diacid.\(^8\) The corresponding anti diester diacid chloride is then prepared from the separated diester diacid and recrystallized from the resultant reaction mixture.

The diamine component, 4-aminophenyl ether, was purified by recrystallization in either ethanol or isopropyl alcohol and then sublimed under vacuum. The sublimation step is absolutely necessary as the diamine as received was a purple gray amorphous power. The first crystallization produces off white crystals after decolorization with charcoal. The diamine crystals first melt into a purple liquid whose vapor deposits in the form of white needles. In all polymerizations, the white needles of the highly purified diamine was employed.

3.3 Synthesis of the Copolymer Systems.

The synthesis of the polymer systems is illustrated in reaction 3.1. The compositions, yields, and intrinsic viscosities of the products are summarized in table 3.1. Requisite amounts of acid chloride monomers dissolved in THF were added to a solution of the diamine in NMP in a dry box and stirred overnight. After precipitation in water and redissolution in NMP, the intrinsic viscosities were determined. The largest intrinsic
viscosity, 1.44 dl/g, was obtained for the pyromellitic acid derived homopolymer. This is attributable to the inherent rigidity of this polymer system. The intrinsic viscosity drops monotonically with the addition of the anthracene derived monomer until its concentration reaches approximately 50%. From 50% anthracene monomer to the anthracene homopolymer, the intrinsic viscosity remains fairly constant at about 0.22 dl/g.

Figure 3.3 is the NMR spectrum of the 30% anthracene copolymer and its corresponding proton assignments. The anthracenic amide protons “a” resonate further downfield than those of the benzene derived unit at “b” which is attributable to the anthracene ring’s greater tendency to withdraw electrons. Proton signals “c” correspond to the protons in the 9,10 positions of the anthracene nucleus and show that the syn to anti
diester distribution of anthracene units in the polymer are approximately 50:50. The central peak of signals “c” corresponds to the equivalent 9,10 protons of the anti ester. The surrounding two peaks are due to the unequivalent protons of the syn ester. An approximate 1:2:1 ratio of the peaks indicates an approximate 50:50 syn to anti ratio. By comparing the integrals of the signals “i” and “j” corresponding to protons on the carbon adjacent to the oxygen in the esters, one may obtain the ratio of anthracene derived units to benzene derived units. This method allowed us to verify the composition of the copolymers. Table 3.1 includes the NMR data for the verification of the compositions.

Figure 3.3 \(^1\)H NMR spectrum of 30% copolymer.

As expected, all homo and copolyamic esters in this series imidize thermally. The starting polyamic esters are colorless to lemon yellow in
color depending upon anthracene derived monomer content while the resultant polyimides are red-brown in color and take a darker brown color with increasing anthracene derived monomer content. A very thin film of 30% anthracene derived polymer was cast on a NaCl plate and its IR spectrum is figure 3.4. Evident in this spectrum are the N-H stretching band at 3298 cm\(^{-1}\), the C-H stretching bands at 2945 and 2859 cm\(^{-1}\), and the amide and ester carbonyl stretching bands between 1676 and 1728 cm\(^{-1}\). The sample was then baked at 320°C for four hours under nitrogen to give an imidized film whose IR spectrum is figure 3.5.

Figure 3.4 IR spectrum of the 30% copolyamic ester.
The transition to the imidized polymer is quite pronounced. In addition to a shifting of the carbonyl stretching frequencies, the bands corresponding to N-H stretching of the amide functions as well as the C-H stretching bands corresponding to the aliphatic ester groups have vanished. Furthermore, the heat treated film shows the four bands characteristic of imide structures.\textsuperscript{90} The symmetric and asymmetric carbonyl stretches occur at 1781 and 1730 cm\(^{-1}\) respectively. The other associated bands are the C-N stretch at 1376 cm\(^{-1}\), and the band at 737 cm\(^{-1}\) which is deformation of the imide ring or to imide carbonyls. The IR spectrum of all the copolymers was nearly identical.

![Figure 3.5 IR spectrum of 30% copolyimide.](image-url)
3.4 Thermal Analysis.

A representative TG/DTG analysis of the 30% anthracene copolymer is shown in figure 3.6. The thermogram shows two major features. The first, between 235 and 291°C, is due to the imidization of the polyamic ester with concomitant loss of n-butyl and cyclohexyl alcohols. The 27.7% loss of mass corresponds almost exactly to the calculated value of 27.5% for the requisite elimination of alcohols. After the loss of the alcohols and concomitant formation of the polyimide, the polymer remains stable up to about 600°C at which point is the maximum rate of thermal decomposition.

Figure 3.6 TG/DTG thermogram for 30% copolymer.
Table 3.1 also includes TG/DTA data for the copolymer series. In general, the onset of imidization takes place at between 200°C and 250°C. Imidization requires progressively higher temperatures as the copolymers become richer in anthracene derived units. This is not surprising since a study of the thermal imidization of methyl, ethyl, n-propyl, and n-butyl polyamic esters showed that the rate of imidization for the butyl ester was as much as 60 times slower than that for the other esters. After imidization, the trend is toward an incremental increase in thermal stability of the polyimides with increasing concentrations of anthracene containing monomer in the polymer. This increase in thermal stability for this series of polymers appears to be linear, but the data are slightly scattered due to a statistically insufficient number of samples from different synthetic runs.

3.5 Differential Scanning Calorimetry in the “Oscillation” or “Modulated” Mode.

Calorimetric studies on the 30% anthracene copolyamic ester were performed by DSC in the “modulated” or “oscillation” mode. To explain the concept, let us consider the heat flow, \( \frac{dQ}{dT} \), which is directly proportional to the DSC signal, to be the superposition of two components

\[
\frac{dQ}{dT} = -C_p \frac{dT}{dt} + K(T,t) \quad \text{Equation 3.1}
\]
where $C_p$ is the sample heat capacity, $dT/dt$ is the time rate of change of temperature, and $K(T,t)$ is the kinetic DSC response. If we reverse the sign of time and consider the kinetic term to be independent of time then we may rearrange to get:

$$\frac{dQ}{dT} = C_p \frac{dT}{dt} - K(T) \text{ Equation 3.2}$$

Comparison of equation 3.1 with equation 3.2 reveals that the thermal component, $C_p(dT/dt)$ is reversible while the kinetic component is not. If the temperature program is then fashioned to be the superposition of a linear heating rate plus a sinusoidal oscillation, the resulting DSC signal can be deconvoluted via a Fourier transform approach into 3 separate signals. The three signals are the deconvoluted curve (DSC-D), in which the sinusoidal variation of the components has been removed. The plotted data resemble the usual DSC thermograms and is virtually identical. Separation of the convoluted scan also yields a "thermal" or "reversible" component (DSC-Cp), and a "kinetic" or "irreversible" component (DSC-K). The thermal component of the first heating is indicated in figure 3.7. The endotherm between 215 and 280°C corresponds to imidization. An integration of the signal within this endothermic peak gives the heat of imidization for this copolymer of approximately 50.7 J/g.
<table>
<thead>
<tr>
<th>Copolymer Composition Calculated (% Anthracene)</th>
<th>Yield (%)</th>
<th>Copolymer Composition by NMR (% Anthracene)</th>
<th>Intrinsic Viscosity</th>
<th>Temp. (°C) at Max. Rate of Imidization</th>
<th>Temp. (°C) at Max. Rate of Decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>98</td>
<td>0.00</td>
<td>1.44</td>
<td>274</td>
<td>597</td>
</tr>
<tr>
<td>10.00</td>
<td>98</td>
<td>14.00</td>
<td>0.94</td>
<td>274</td>
<td>598</td>
</tr>
<tr>
<td>20.00</td>
<td>97</td>
<td>19.50</td>
<td>0.74</td>
<td>272</td>
<td>603</td>
</tr>
<tr>
<td>30.00</td>
<td>97</td>
<td>29.50</td>
<td>0.60</td>
<td>269</td>
<td>593</td>
</tr>
<tr>
<td>40.00</td>
<td>96</td>
<td>37.70</td>
<td>0.30</td>
<td>271</td>
<td>603</td>
</tr>
<tr>
<td>50.00</td>
<td>96</td>
<td>47.80</td>
<td>0.24</td>
<td>264</td>
<td>596</td>
</tr>
<tr>
<td>60.00</td>
<td>96</td>
<td>56.10</td>
<td>0.20</td>
<td>277</td>
<td>603</td>
</tr>
<tr>
<td>70.00</td>
<td>97</td>
<td>64.30</td>
<td>0.20</td>
<td>277</td>
<td>609</td>
</tr>
<tr>
<td>80.00</td>
<td>97</td>
<td>77.80</td>
<td>0.18</td>
<td>279</td>
<td>610</td>
</tr>
<tr>
<td>90.00</td>
<td>98</td>
<td>84.50</td>
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<td>612</td>
</tr>
<tr>
<td>100.00</td>
<td>96</td>
<td>100.00</td>
<td>0.20</td>
<td>304</td>
<td>619</td>
</tr>
</tbody>
</table>
After cooling the sample below the imidization temperature the sample was subjected to a second heating. The kinetic component of this signal is shown in figure 3.8. This analysis shows a weak glass transition temperature, $T_g$, at 373.0°C and the absence of any other significant thermal transition in this temperature range.

Both the imidization and the glass transitions of these materials are well illustrated in the dynamic mechanical analysis of the 30% copolyamic ester film, figure 3.9. We may think of Young's modulus of elasticity, $E$, as being the sum of two components, $E'$, and $iE''$ relating to the elastic and viscous properties of a given material, respectively. A dynamic mechanical glass transition occurs when the imaginary component, $E''$, known as the loss modulus, reaches a maximum while the real component, or storage modulus, $E'$, reaches a minimum.
In region 1 of figure 3.9, a dynamic mechanical glass transition of the polyamic ester occurs at approximately 230°C. This transition was not observed in the modulated DSC experiment. In region 2, a peak corresponding to the imidization reaction occurs at about 240°C. The expected increase in stiffness of the polyimide structure is confirmed by a sharp increase in $E'$. In region 3 the dynamic mechanical glass transition temperature of the polyimide is shown to occur at approximately 414°C. The dynamic mechanical measurement corresponds within 40°C to the

---

**Figure 3.8** Oscillation mode DSC of 30% copolyimide (kinetic component).
modulated DSC measurement for the glass transition temperature of the polyimide. The results of this mechanical test will not give correct values for the Young's moduli as the cross section of the film shrunk considerably during the test. This test was only meant to illustrate thermal changes and was not to determine mechanical properties.

Figure 3.9 Dynamic mechanical spectrum of 30% copolymer.

3.6 Fluorescence of Copolymer Systems.

In addition to being more thermally stable than their pyromellitic acid based counterparts, the anthracene moiety imparts to these polymers a tendency to fluoresce both in the solid state and in solution. We have
investigated the fluorescence of these materials in solution. Figure 3.10 is the fluorescence spectrum of the 30% copolyamic ester in DMSO at a concentration of 0.00433 g/dL (2.20 x 10^{-5} M in chromophore). The excitation spectrum consisted of a broad featureless hump with a maximum at about 386 nm. We chose 380 nm as the excitation wavelength.

Care must be taken in such measurements as it is known that anthracene containing polymers may form interchain photodimers when exposed to ultraviolet radiation. At least 5 fluorescence scans were taken per sample and no decrease in fluorescence intensity was observed. Since formation of the 4+4 photodimer entails loss of the fluorophore and concomitant loss of fluorescence intensity, this possibility was discounted.

The first band associated with anthracene occurs at approximately 425 nm. This is significantly red shifted from that of pure anthracene, which occurs at 380 nm. This can be attributed to the lowering of energy of the S^0 to S^1 transition due to the increase in conjugation associated with the carbonyl groups on the anthracene nucleus. UV absorption spectra were taken in DMSO and showed that the homopolymer containing no anthracene moieties started absorbing at around 380 NM and the absorbance increased exponentially going towards lower wavelengths. Therefore, the pyromellitic acid derived repeat units could not absorb fluorescence light from the anthracene fluorophore. This implies that
there will be no energy transfer from anthracene based units to non anthracene based units in the chain.

![Fluorescence spectrum of 30% copolymer](image)

Figure 3.10 Fluorescence spectrum of 30% copolymer.

A series of solutions of our copolyamic esters were prepared such that the chromophore concentration remained constant at $2.20 \times 10^5$ M. The fluorescence intensity, as well as the spectral shape, remained the same regardless of the percentage of anthracene monomer in the copolymer. These spectra differ substantially from that of poly(2-(9-anthryl)ethyl methacrylate). None of our polyamic esters show the broad band between 430 and 670 nm characteristic of exiplex formation, the intensity of which is
an indicator of chromophoric interaction during the excited state lifetime. Poly(2-(9-anthryl)ethyl methacrylate) is a flexible backbone polymer with pendant anthryl units. The mobility of the chain as well as the mobility of the pendant chromophores allows efficient interaction among chromophores. Since the chromophores in our polymers are incorporated along their long axis in the backbone of the polymer, their mobility is diminished compared to poly(2-(9-anthryl)ethyl methacrylate). The geometry of the anthracene tetracarboxyl site is also deleterious to the formation of an exiplex. To understand the local environment of the anthracene moiety, the compound 2,6-di-n-butyloxycarbonyl-3,7-anthracenedicarboxylic-di-(4-oxyphenyl)phenyl diamide was modeled using SYBYL on a VaxStation 2300. The minimization was conducted using Hückel parameters for the calculation of electrostatics. The result of the calculation in the form of a space filling model is presented in figure 3.11. Two major factors influence the steric environment around the anthracene moiety. The first is the bending of the ester carbonyl away from the plane of the anthracene ring. The second and more influential steric effect is that of the amide’s phenyl ring being rotated out of the plane of the anthracene ring. In order for the formation of an exiplex to occur, molecules must have proper alignment as well as exist in close enough proximity. 2,3,6,7-Anthracenetetracarboxyl containing polyamic esters are not able to form exiplexes due to unfavorable steric interference of the ester and amide groups.
3.7 Experimental.

3.7.1 Materials and Methods.

Dichloromethane, triethylamine, and ethyl acetate were dried by distillation from calcium hydride. N-Methyl-2-pyrollidinone (NMP) was distilled from phosphorous pentaoxide. 4-Aminophenyl ether and pyromellitic anhydride were sublimed in-vacuo. DMSO was Mallinkrodt spectral grade. All other solvents and reagents were purchased from Aldrich Chemical Co. and were used without further purification. NMR spectra were taken with Bruker AC series instruments of the specified field. FAB mass spectra were taken with a Finnigan TSQ-70 mass spectrometer. FT/IR spectra were taken on a Perkin Elmer 1760 X spectrometer. Steady state fluorescence measurements were acquired with a Perkin-Elmer LS50 spectrofluorometer. The solutions were excited at 380 nm and excitation and emission slit widths of 15 and 5 nm respectively. Thermogravimetric
measurements were carried out using a Seiko TG/DTA 220 instrument at a heating rate of 10°C/min. Dynamic mechanical tests were conducted using a Seiko DMS 200 spectrometer using a film measuring 20 x 5.0 x .022 mm at a frequency of 1 Hz and a heating rate of 2°C/min. A Seiko DSC 220C instrument in the oscillating mode was used for calorimetric determinations. The experiment was carried out under the following conditions: time temperature wave frequency 0.01 Hz, temperature wave amplitude 4°C, heating rate 2°C/min and data collection rate 2/sec.

### 3.7.2 Synthesis of 1,4-Dichlorocarbonyl-2,5-dicyclohexyloxycarbonyl-benzene (3.1).

Pyromellitic dianhydride, 10 g (0.046 mol) was dissolved in 50 mL of dry cyclohexanol by heating the mixture to 90°C until dissolved (=1.5 hr). The residual alcohol was evaporated in-vacuo and the remaining viscous liquor triturated with hexane. A white amorphous solid was recovered; chromatography of 2.00g of the material on silica gel (methyl acetate) afforded 1.42 g of the syn and anti diester diacid mixture, $^1$H NMR (200 MHz, acetone-d6) δ 8.24 (s, 1H), 8.08 (s, 2H), 7.95 (s, 1H), 5.00 (m, 2H), 1.98-1.33 (m, 20H). The diester diacid was converted to the diacid chloride by suspending 1.00 g (0.00239 mol) in 25 mL of ethyl acetate and adding 0.500 mL (0.740g, 0.00583 mol) of oxalyl chloride and one drop of NMP. The mixture was stirred at room temperature until the suspension was totally dissolved and gas evolution had ceased. After evaporation of the solvent,
the residue was recrystallized three times from dry hexane; 0.390 g of pure anti-isomer was obtained; $^1$H NMR (ppm) (200 MHz, CDCl$_3$) $\delta$ 8.13 (s, 2H), 5.07 (m, 2H), 2.02-1.27 (m, 20H).

3.7.3 Purification of 4-Aminophenyl Ether (3.1)

4-Aminophenyl ether was first recrystallized from ethyl or isopropyl alcohol. After drying under vacuum, 1g of the purplish brown crystals and silica gel, (6-16mesh), were placed in a sublimator 5cm in diameter and 8cm tall. After reducing the pressure to about 0.5 torr, the sublimator was gently heated with a bunsen burner. Care was taken not to heat any one part of the sublimator unevenly as melting and boiling would occur that added impurities to the sublimate. White crystals were scraped from the sublimator and stored in a dry box under argon until used in the synthesis.

3.7.4 Polymer Synthesis.

Polyamic esters were prepared according to the general method of Volksen et al.$^{96}$ The monomer stoichiometry was based upon a constant concentration of 4-aminophenyl ether, 0.300 g (0.0165 mol); the requisite molar ratio of diester diacid chlorides totaled 0.0165 mol. The diester acid chlorides were dissolved in 2 mL of THF and added to a stirred solution of the diamine in 2 mL of NMP. All operations were conducted in an inert
atmosphere. The polymerization was allowed to proceed for 16 hr before the polymer was isolated by pouring the reaction mixture into 250 mL of deoxygenated water. The copolymers were dried at 120°C overnight.
CHAPTER FOUR.
Diels-Alder Reaction and Crosslinking of Polymers Containing the 2,3,6,7-Anthracenetetracarboxylic Acid Unit.

4.1 Introduction.

One of the goals of this project was to show the Diels-Alder reactivity of the anthracene moiety in the polymer backbone. It is well known that molecules with variously substituted anthracene nuclei react as Diels-Alder dienes. The 4+2 cycloaddition of tetracyanoethylene to an anthracene-containing polysulfone by Percec and Tingerthall was presented in chapter one, 1.XIV.

Müllen later reported the Diels-Alder reaction of polyanthralenevinylene with 4-phenyl-1,2,4-triazoline-3,5-dione to produce adduct 4.I. There have been no reports to date on a Diels-Alder crosslinking reaction that takes place on the backbone of polymer chains. In this section will be presented evidence of the reaction of N-phenylmaleimide with the anthracene moiety in our polymer’s backbone.
Later is presented the evidence for the successful Diels-Alder crosslinking of our polymer system. These or similar crosslinked materials may provide a unique ability to provide high temperature materials suitable for use in load bearing structures.

4.2 Diels-Alder Reaction with N-Phenylmaleimide: a Model Reaction.

We first attempted the Diels-Alder reaction of 4-phenyl-1,2,4-triazoline-3,5-dione with our polymer in a sealed tube at elevated temperature. 4-Phenyl-1,2,4-triazoline-3,5-dione does not appear to be stable at elevated temperatures and the reaction failed. Another powerful and far less expensive dienophile is N-phenyl maleimide.

The reaction of the 20% copolymer with N-phenylmaleimide at 175°C produced the desired cycloaddition of the anthracene moiety 4.II.
Dramatic evidence for this transformation is found in the proton NMR. Figure 4.1 shows the $^1$H NMR spectrum of the unreacted and then reacted polymers between 5.5 and 12 ppm. The three absorbances at about 9.1 ppm are due to the protons on the 9,10 positions of the anthracene ring while the ones at 8.75 and 8.45 are due to the 1,4,5,8 positions. After the reaction, we see the loss of all absorbances due to the anthracene ring and many absorbances are pushed back into the 7-8 ppm range. In addition, we are able to see the emergence of two bands at 7.6 and 6.4 ppm which are attributable to the bridgehead protons at the 9,10 position of the anthracene ring and 3',4' position of the maleimide ring.

Before the reaction, the polymer was a canary yellow color. After the reaction the color changed to a tan or buff color. As demonstrated earlier, the imidization of the polymers produced a material that was dark red-brown so that the change in color was not the result of imidation.
Proton NMR in the region of 0 to 5.5 ppm shows that the ester portions of the molecule remain unaffected by the solution treatment at elevated temperatures. The same reaction was also carried out on a 50% anthracene containing copolymer with identical results. In the $^{13}$C spectrum of the 50% anthracene polymer, figure 4.2, the carbonyl carbons of the maleimide are plainly evident at 175 ppm while additional peaks occurring at about 45 ppm are attributable to the bridgehead protons at the 9,10 position of the anthracene ring and 3',4' position of the maleimide ring.
4.3 Diels-Alder Crosslinking Studies with a Phenyl Maleimide Analog.

Having sufficiently established the Diels-Alder reaction of N-phenyl maleimide with the anthracene moiety in the polymer’s backbone, we extended the methodology in an attempt to crosslink the polymer. Since N-phenyl maleimide worked well as our model system, 1,1’-(methylene-di-4,1-phenylene)bismaleimide, 4.III, was used because of its similarity to the former.

In a manner exactly analogous to the reaction with the monofunctional maleimide, intra or inter- molecular crosslinks can take place, 4.IV. In the case of a 10% w/w solution of the 20% copolymer, the crosslinker concentration was adjusted such that there were 2 moles of
anthracene centers for every mole of crosslinker. The solution was heated in a sand bath to approximately 180°C for about 5 minutes. The result was a yellowish tan, rubbery, solvent swollen mass. The resulting crumby mass was triturated with methanol and dried. The mass became reddish in color and collapsed into a hard solid.

4.4 Monitoring the Crosslinking Reaction by Dynamic Light Scattering.

In a further crosslinking experiment, a 2.5% w/w solution of a 40% copolymer was prepared with 1,1’-(methylene-di-4,1-phenylene)bis-maleimide in DMAc. The crosslinker to anthracene moiety ratio was 2:1.
The solution was filtered through a 0.2 micron filter into a dust-free ampoule. The solution was then frozen, evacuated and flame sealed.

The sample was then placed into a home made dynamic light scattering apparatus using the photon correlation or "time-domain" technique. A helium-neon laser was used as the light source. The sample holder was heated electrically with a temperature controller. The first run was conducted at 30°C. The Stokes radius was calculated to be approximately 90 Å. The temperature was elevated first to 70°C. The effect of the rise in temperature could be seen in the modest but discernable rise in the scattering intensity. Diffusion decreased notably during this time despite the decrease in solvent viscosity at elevated temperatures. At 165.3°C, the scattering intensity was on the order of 1.4 Mhz compared to the initial value at 30°C of 24 Khz. Furthermore, the intensity vs. time data showed very slow fluctuations in the scattering intensity. Such fluctuations are caused by large particles moving slowly through the beam. This behavior is an indicator of the change from ergodic systems, whose systems can occupy all spatial configurations given enough time, to nonergodic, whose systems are frozen into limited configurations due to a loss of mobility. A plot of diffusion versus time for two experiments is shown in figure 4.3.

As particles become larger, their movement or diffusion is hindered by the corresponding larger drag. If a particle's size in solution remains the
same, its diffusion will remain the same given no change in configuration of the particle or solvent viscosity.

![Figure 4.3 Diffusion vs. time for two crosslinking experiments.](image)

Since the data indicate that the diffusion decreases with time, the size of the particles in solution must be getting bigger. As conformational changes leading to expansion are not expected, the polymers must be crosslinking to form larger particles. The difference in slopes in the linear fits to the above data indicate that the reaction is faster during the initial phase of the reaction, growth occurs faster than at later phases. These data serve only to illustrate the trend towards crosslinking of the system. The scattering experiment was performed at a temperature close to the solvent's boiling point at atmospheric pressure. Therefore, neither the solvent's viscosity
nor its refractive index were known with certainty. Accurate measurements would require that these quantities be determined - a difficult task.

4.5 Experimental.

4.5.1 Materials and Methods.

All reagents were purchased from the Aldrich Chemical Company and used without further purification. N,N-Dimethylacetamide (DMAc) was purchased as anhydrous grade. NMR Spectra were recorded with a Bruker AC-200 or AC-400 MHz instrument as specified.

4.5.2 Reaction with N-Phenylmaleimide.

N-Phenylmaleimide (.05g) and a 20% anthracene copolymer (.12g) were dissolved in dry N,N-dimethylacetamide (2 mL) in an ampoule. The solution was frozen in dry ice/isopropyl alcohol and evacuated. The ampoule was subsequently flame sealed. The ampoule was then placed in a sand bath and the temperature raised to 190°C for 6 hours. The resulting polymer was precipitated in water and then reprecipitated from DMSO into methanol 4 times. Obtained was 0.10g of a tan polymer.
4.5.3 Crosslinking with 1,1′-(Methylenedi-4,1-phenylene)bis-maleimide.

4.5.3.1 Crosslinking of 20% Polymer.

For the purpose of qualifying the gelation of our polymer, a 10% w/w solution of polymer was required. The 20% polymer 0.200g and 1.20mg of 1,1′-(methylenedi-4,1-phenylene)bismaleimide were dissolved in enough dry DMAc to make two grams of solution. The solution was frozen in an isopropanol/dry ice bath and evacuated. The ampoule was and flame sealed. The sample was then heated to about 185°C for about 8 minutes. The solution set into a rubbery yellow gel.

4.5.3.2 Crosslinking of 40% Polymer.

A 2.5% w/w solution of a 40% polymer was prepared. 0.066g of 1,1′-(methylenedi-4,1-phenylene)bismaleimide was dissolved in dry DMAc to make 5g of solution. One gram of this solution was added to 0.1107g of polymer and DMAc was added to make the mass of the solution 4.4g. This polymer solution was filtered into a dust free ampoule. The sample was then frozen, evacuated, then flame sealed. The reaction then took place on a heated sample holder for a light scattering device. The following constants were assumed for the sample: refractive index of solvent - 1.41, in-vacuo wavelength of light - 6328Å, and viscosity of solvent - 0.007 Poise.
These values were assumed constant throughout the investigation. The angle used for the light scattering experiment was 60°.
CHAPTER FIVE.

Conclusions and Recommendation for Further Work.

5.1 Monomer Synthesis.

Perhaps the greatest contribution of this work is the improved technique for the synthesis of 2,3,6,7-anthracenetetracarboxylic acid. Previous methods were low yielding and required many step syntheses. From this acid, we were able to derive purified diester diacid chloride monomers. One deficiency of this current system is that we work with a mixture of syn and anti isomers. A way to solve this problem would be to experiment with different ester combinations to determine a system suitable for separation and purification by any number of methods to include simple recrystallization, chromatography, or perhaps even distillation or sublimation.

5.2 Polymer Synthesis.

The procedure for the formation of polyamic esters from diester diacid chlorides is well known. In this work, we only synthesized one series of polymers containing 4-aminophenyl ether, pyromellitic acid, and 2,3,6,7-anthracenetetracarboxylic acid. We determined that an increase in the amount of anthracene in the polymer causes an increase in the thermal
stability of the polymer system. Also, these materials are fluorescent in both the solution and solid state.

To better quantify the effect of extended aromatic structures in the backbone of polymer systems, a series of three homopolymers could be synthesized that contain 1,2,4,5-benzenetetracarboxy, 2,3,6,7-naphthalenetetracarboxyl, and 2,3,6,7-anthracenetetracarboxyl units in them. This comparison may open new areas of research.

5.3 Diels-Alder Crosslinking.

The second most significant aspect of this work is that we are the first to crosslink a polymer in a Diels-Alder fashion directly to the backbone of a polymer chain. Specifically designing the polymer to be liquid crystalline and crosslinking the material in the liquid crystalline phase could be interesting from the standpoint of future high strength materials.

The long sought after "molecular composite" material might be possible by crosslinking a random coil polymer with pendant maleimide units to rodlike polymers containing the 2,3,6,7-anthracenetetracarboxyl group. Polymer coatings might also be applied that take advantage of the thermal 4+2 cycloaddition chemistry of the anthracene nucleus. Also, the anthracene nucleus is able to undergo 4+4 cycloaddition reaction in the presence of UV light. This possibility should be explored.
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VITA

James Larry Morris was born on November 16, 1964, the son of James Curtis and Mary Elizabeth Moore Morris. Through the third grade, he attended Southside Elementary School, of Tuscumbia, Alabama. From the fourth grade through the seventh grade, he attended Northside Elementary School, also in Tuscumbia, Al. The term of the ninth grade through the twelfth grade was spent at Deshler High School where he graduated in 1983. From September of 1983 to May of 1988 he attended the University of North Alabama, graduating with a B. A. in Industrial Chemistry with minors in math and physics.

After teaching at the United States Space Camp and Academy in the summer of 1988, he entered graduate school at the Louisiana State University majoring in Macromolecular Chemistry and minoring in Mechanical Engineering. He is currently a candidate for the Ph. D. degree.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: James Larry Morris

Major Field: Chemistry

Title of Dissertation: Synthesis, Characterization, and Diels-Alder Reactivity of Polymers Containing the 2,3,6,7-Anthracenetetracarboxyl Unit

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

12/21/94