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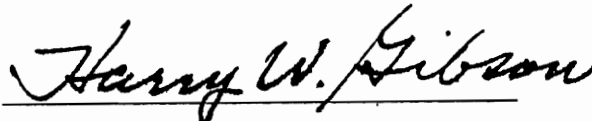
**SYNTHESIS OF NOVEL HETEROCYCLIC POLYMERS
VIA THE CHEMISTRY OF REISSERT COMPOUNDS**

by

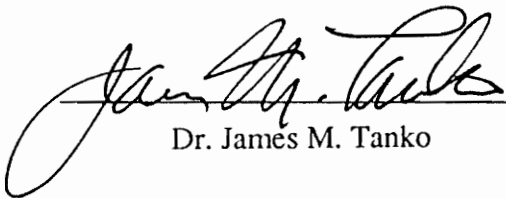
Bardia Guilani

Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE
in
Chemistry

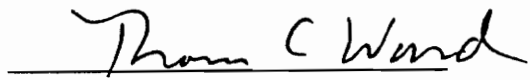
APPROVED:



Dr. Harry W. Gibson, Chairman



Dr. James M. Tanko



Dr. Thomas C. Ward

January, 1990

Blacksburg, Virginia

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**SYNTHESIS OF NOVEL HETEROCYCLIC POLYMERS
VIA THE CHEMISTRY OF REISSERT COMPOUNDS**

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Committee Chairman: Dr. Harry W. Gibson
Chemistry

(ABSTRACT)

The chemistry of a well established class of compounds, known as Reissert compounds, was used to prepare several novel N-heterocyclic polymers. Initially, alkylation of quinoline Reissert compounds was closely examined to test the feasibility of the use of such compounds as difunctional monomers. An A-B and an A-A monomer were then prepared by the reaction of quinoline with p-formylbenzoyl chloride and isophthaloyl chloride, respectively. The former monomer could be polymerized interfacially to afford a low molecular weight polyester exhibiting Tg of 190 °C.

Several novel bis-isoquinolines were prepared using an enamine reaction reported by Minter and Re.⁵² One of these bis-isoquinolines was used to prepare two novel bis-Reissert compounds which could be polymerized with several dialdehydes to obtain high molecular weight N-heterocyclic polyesters. Cleavage of the ester groups afforded a novel N-heterocyclic polyalcohol. It was observed that circumvention of a rearrangement reaction particular to Reissert compounds by molecular design led to the synthesis of

N-heterocyclic polyesters that had the highest molecular weights and intrinsic viscosities.

A novel N-heterocyclic difluorodiketone was prepared in four steps using the enamine reaction of Minter and Re⁵² and Reissert compound chemistry. The diketone was polymerized via standard techniques⁷² to afford several novel poly(N-heteroaryl-ether-ketones) with high glass transition temperatures and thermal stabilities. Thus, polymerization of 1,4-bis(4-fluorobenzoyl)isoquinoline with biphenol yielded a poly(ether-ketone) with an intrinsic viscosity of 0.34 dl/g. This polymer showed T_g at 209 °C and was stable up to 500 °C in air.

ACKNOWLEDGMENTS:

The completion of this thesis would not have been possible without the guidance and encouragement of a great number of people, beginning with Dr. James F. Wolfe who allowed me and others members of my group to share his lab space with other members of his group. The time that I spent in Dr. Wolfe's lab was extremely productive mainly because of the helpful suggestions of Drs. Thomas D. Greenwood, James A. Campbell, and Godson Nwokogu.

I would like to thank the members of Dr. Gibson's group: Pierre, Paul, Mike, Ashish, Mel, Jois, Mukesh, Yadi, Jenny, Chao, Yadi, and Jean. I wish the best for the new members of the group: Roger and Kim.

I would also like to thank the graduate students and post-doctoral associates who have in some way helped me during my stay at Virginia Tech. In particular, I should mention Guru, Joe L., Joe D., Rob, Carl, Gustavo, Dave, and Maria Spinu.

I would like to thank Drs. James M. Tanko and Thomas C. Ward, not only as members of my committee, but also as two distinguished professors. I would like to acknowledge and thank Dr. Ward's group who performed characterizations of the polymers (and oligomers) that I was able to synthesize.

Most of all, I would like to thank Dr. Harry W. Gibson whose example, patience, support, and enthusiasm was invaluable in helping me reach my goal.

To My Mother

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I. INTRODUCTION:

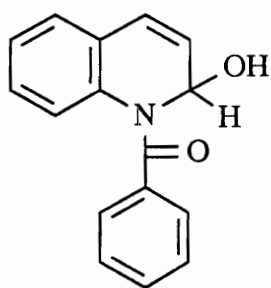
Synthetic heterocyclic polymers are an important class of polymers exhibiting highly desirable properties. Applications for heterocyclic polymers such as polyquinolines, polyimidazoles, and polypyrroles range from high temperature structural and adhesive materials to water soluble and conducting polymers. The usual method of incorporating heterocyclic units into a polymer backbone is via a high temperature two-step process such that the heterocyclic ring formation occurs in the propagation step. The materials prepared this way show high thermal stability but are typically intractable.

Another route to the incorporation of heterocyclic rings into a polymer backbone is via the chemistry of Reissert compounds. Several synthetic schemes in this thesis describe the synthesis of novel A-A and A-B monomers containing quinoline and isoquinoline rings. The novel polymers prepared range from a tough poly(N-heterocyclic ester) to a poly(N-heteroaryl ether ketone) exhibiting high transition temperatures and thermal stability.

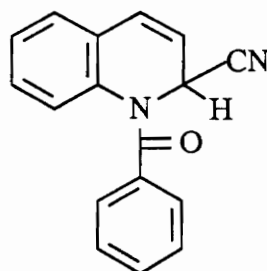
II. HISTORICAL SECTION:

1. REISSERT COMPOUNDS:

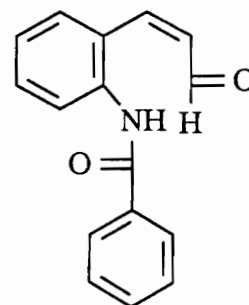
The first Reissert compound was reported in 1905 by its creator Arnold Reissert,¹ who observed that the reaction of quinoline and benzoyl chloride in aqueous sodium hydroxide yielded a crystalline solid with an empirical formula of $C_{16}H_{13}NO_2$. It was also observed that use of an aqueous solution of potassium cyanide yielded a crystalline solid, $C_{17}H_{12}N_2O$.¹ The structures assigned were **1** and **2**, respectively:



1



2

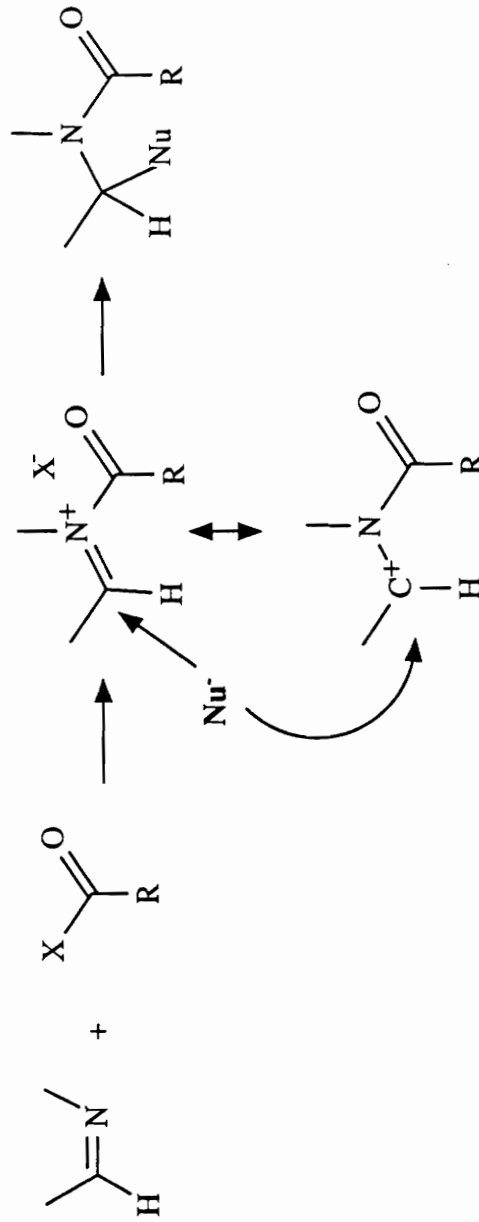


1a

Structure **1a** is the tautomer of **1** and was confirmed by Elliott in 1964.²

As illustrated, Reissert compounds are the result of the addition of the elements of benzoyl cyanide across a carbon-nitrogen double bond, i.e., an imine bond. The addition is believed to occur in two steps,³⁸ shown in Scheme 1. Initially, the nitrogen of the imine is acylated, forming an acyliminium ion. In the second step, the nucleophile, i.e., cyanide, attacks the carbon of the imine.

Typically, acyl chlorides and bromides are used in the synthesis of Reissert compounds. However, considerable work has been done using chloroformates, sulfonyl



Scheme 1: Mechanism of Reissert Compound Formation

chlorides, thiocarbonyl chlorides, and dialkyl chlorophosphates. Generally, these Reissert analogs are less stable than the amide and exhibit unusual reactivities. The reader is referred to several excellent reviews by Frank D. Popp.³ The nucleophile is almost exclusively cyanide ion. The first Reissert compound, however, incorporated hydroxide as the nucleophile as shown in structure 1. These analogs have been termed pseudobases and are converted to ethers in refluxing alcohol. A review is available on this subject as well.⁴

The imine bond may be part of any number of heterocycles, the most common of which are shown in Scheme 2. The imine bond may also be part of an acyclic compound, leading to the formation of the corresponding open-chain Reissert compound.⁵ The most studied heterocyclic cases, however, are those of quinoline and isoquinoline, i.e., 1-acyl-1,2-dihydroquinaldonitriles, 3, and 2-acyl-1,2-dihydroisoquinaldonitriles, 4, respectively. The major portion of the historical section will concentrate on these.

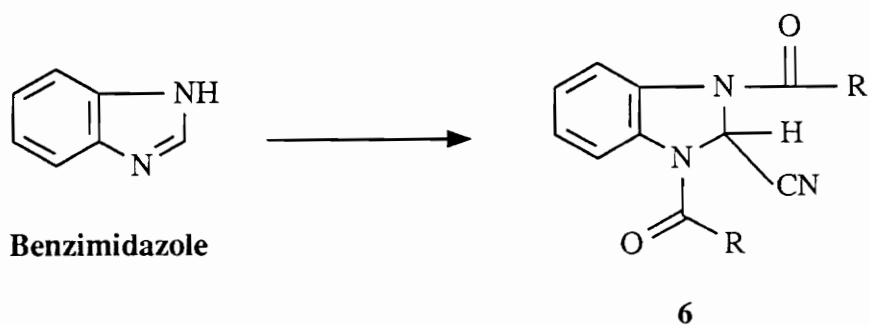
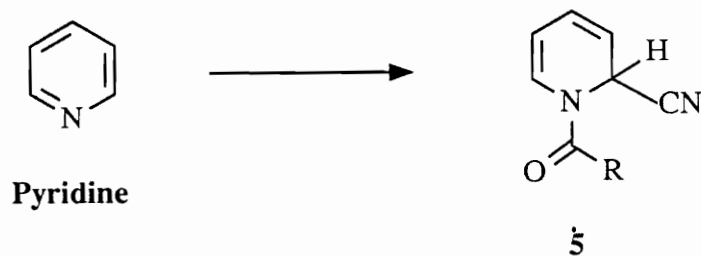
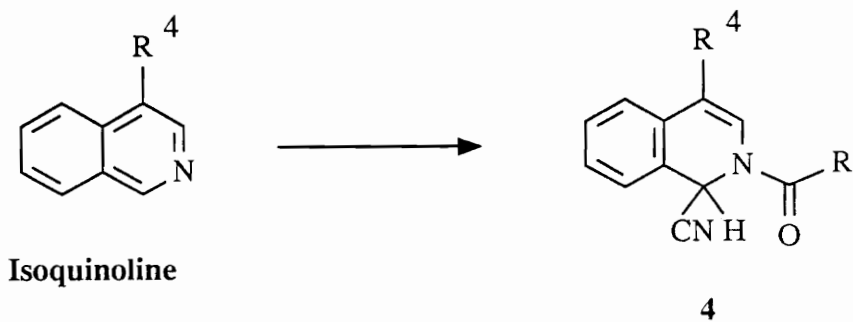
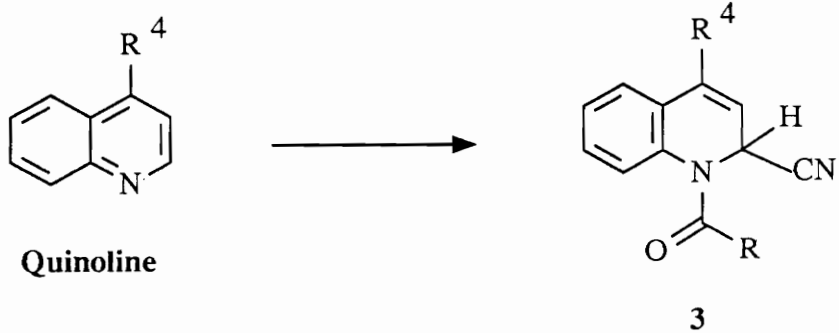
1.1. Preparation of Reissert Compounds:

There are 3 standard methods for preparation of Reissert compounds:

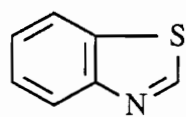
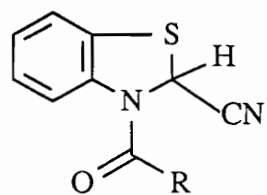
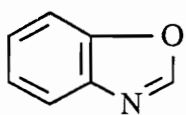
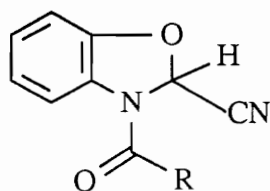
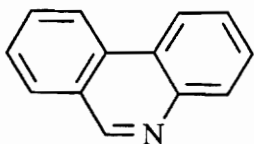
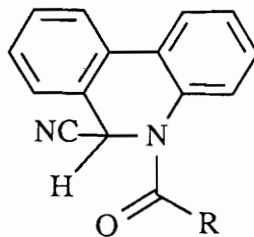
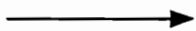
- a. preparation in aqueous media,
- b. preparation in non-aqueous media (or single phase method),
- c. preparation in methylene chloride-water (or 2-phase method).

a. Preparation in aqueous media:

Similar to the Schotten-Baumann reaction, the aqueous method was developed by Arnold Reissert.¹ The yields in some cases can be improved with efficient mechanical



Scheme 2: Common Heterocyclic Bases and Their Reissert Derivatives

**Benzothiazole****7****Benzoxazole****8****Phenanthridine****9****Scheme 2:** (continued)

stirring.⁶ Although this is the most simple and economical method, many acyl chlorides are hydrolyzed before reacting with the heterocycle. In addition, the majority of starting materials are insoluble in water, making this method even more disadvantageous.

b. Preparation in non-aqueous media:

The preparation of Reissert compounds in anhydrous media has proven useful in that the hydrolysis of even highly reactive acid chlorides can be avoided. Elimination of water from the reaction also prevents the formation of pseudobase, e.g., where OH^- adds instead of CN^- . An example of this method used anhydrous benzene as the solvent and liquid hydrogen cyanide as the cyanide source.⁷ It has been noted, however, that half of the quinoline is tied-up as the quinolinium.HCN salt.⁷ Even though liquid hydrogen cyanide was involved, this method found widespread use prior to 1961.

A more recent non-aqueous procedure uses dichloromethane as solvent and trimethylsilyl cyanide (TMSCN) as the cyanide source.⁸ Addition of a catalytic amount of aluminum chloride has been shown to improve the yields.^{9,10} The reported yields using this method are nearly quantitative, making it the method of choice for highly reactive and/or expensive reagents. The disadvantages include the high cost and toxicity of TMSCN. Yet another reported non-aqueous method used silver cyanide in chloroform.¹¹

c. Preparation via the methylene chloride-water (2 phase) method:

By far, this is the most convenient method for preparation of Reissert compounds, initially reported by F.D. Popp and coworkers in 1961.^{12,13} The water which serves to dissolve the cyanide source, KCN, only slowly hydrolyzes the acid chloride. Typically, the heterocycle is dissolved in dichloromethane and a saturated solution of 3-fold excess KCN is added. A 2-fold quantity of the acid chloride is then added dropwise over 2-4 hours to the vigorously stirring mixture. The use of a phase transfer catalyst such as benzyltrialkylammonium chloride improves the yield of the Reissert compound in some cases.⁹ Even though the yields are not as high as the TMSCN method, the methylene chloride-water method is more practical with respect to the cost and availability of starting materials. Highly reactive acid chlorides and diacid chlorides generally give poor yields by this method.

Table 1 shows a brief comparison of the three preparative methods outlined. As evident, heterocycles with electron withdrawing groups generally give lower yields of Reissert compounds by virtue of the destabilizing effect of such groups on the acyliminium intermediate. Electron withdrawing groups also render the nitrogen of the heterocycle less reactive toward acylation. Electron donating groups have the opposite effects and therefore lead to higher yields of the Reissert derivative.¹³ In addition, quinolines with substituents at the 2- and 8-positions fail to yield the Reissert compound presumably due to the steric effects resulting from such substituents.¹³ The same reasoning explains the lack of reactivity of 1-substituted isoquinolines.¹⁷

On the other hand, electron donating groups on the acid chloride lead to lower yields

Table 1: A Brief Comparison of Preparative Methods of Reissert Compounds:

<u>Reissert</u> <u>Compound</u>	<u>R</u>	<u>% Yield</u> ^{ref.}		
		<u>a</u>	<u>b</u>	<u>c</u>
3, R ⁴ = H	C ₆ H ₅	94 ¹	96(1) ⁷ 89(2) ⁸	70 ¹⁴
3, R ⁴ = H	4-NO ₂ C ₆ H ₄	--	--	3 ¹⁴
3, R ⁴ = H	4-ClC ₆ H ₄	26 ⁴⁶	77(1) ⁶⁷	20 ¹⁴
3, R ⁴ = H	2-OCH ₃ -C ₆ H ₄	51 ⁶⁸	88(1) ⁷	80 ¹⁴
3, R ⁴ = H	CH ₃ (CH ₂) ₂	--	10(1) ⁷	12 ¹⁴
3, R ⁴ = H	-(CH ₂) ₆ -*	--	--	trace ¹⁴
3, R ⁴ = OH	C ₆ H ₅	--	--	98 ¹⁴
3, R ⁴ = CH ₃	C ₆ H ₅	32 ¹⁵	--	71 ¹³
4, R ⁴ = H	C ₆ H ₅	58 ³⁷	84(2) ⁸	69 ¹⁴
4, R ⁴ = H	CH ₃	--	85(1) ²⁶ 84(2) ⁸	87 ¹⁴
4, R ⁴ = H	4-ClC ₆ H ₄	11 ¹⁴	--	30 ¹⁴
4, R ⁴ = H	-(CH ₂) ₆ -*	--	--	6 ⁴²
4, R ⁴ = H	-C ₆ H ₄ -O-C ₆ H ₄ -*	--	22(3) ¹⁶	8 ¹⁶
4, R ⁴ = H	OCH ₂ CH ₃	--	88(2) ⁸	57 ¹⁸

Table 1: (cont.)

<u>Compound</u>	<u>R</u>	<u>% Yield</u> ^{ref.}		
		<u>a</u>	<u>b</u>	<u>c</u>
4, R ⁴ = NH ₂	C ₆ H ₅	--	--	20 ¹⁶
6	OC ₆ H ₅	--	90(2) ⁶⁹	--
6	OCH ₂ CH ₃	--	90(2) ⁶⁹	--
7	C ₆ H ₅	--	44(2) ¹⁹	0 ¹⁹
7	2-CH ₃ C ₆ H ₄	--	86(2) ¹⁹	--
8	C ₆ H ₅	--	50(2) ¹⁹	--
8	OCH ₂ CH ₃	--	52(2) ¹⁹	--
5	OCH ₂ CH ₃	--	92(2) ⁴⁰	25 ⁴¹
9	C ₆ H ₅	--	94(1) ¹⁴	71 ¹⁴
9	4-OCH ₃ C ₆ H ₄	--	--	60 ¹⁴

a: aqueous method.

b: non-aqueous method, (1) HCN/benzene, (2) TMSCN/CH₂Cl₂, (3) AgCN/CHCl₃.

c: 2-phase, CH₂Cl₂/water.

A dash indicates that no reported yield was found.

* Diacid chloride, yields dimeric Reissert compound.

of the Reissert compound. Such groups decrease the electrophilicity of the acyl chloride carbonyl toward the nitrogen of the heterocycle. Acid chlorides with electron withdrawing groups give lower than expected yields of the Reissert derivatives. In this case, hydrolysis of the acid chloride competes with acylation of the imine.¹⁴

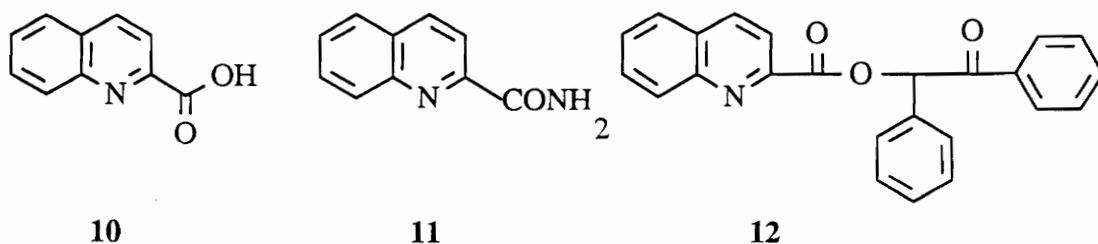
1.2. Reactions of Reissert compounds:

In the present context, the reactions of interest pertaining to Reissert compounds are:

- a. acid hydrolysis
- b. alkylation
- c. base hydrolysis
- d. condensation with aldehydes
- e. rearrangement

a. Acid hydrolysis:

Early research on Reissert compounds focused on their use as intermediates in conversion of acid chlorides to aldehydes. The original acid-catalyzed hydrolysis of **2** afforded benzaldehyde in quantitative yield.¹ Other products obtained were quinaldic acid,



10, quinaldamide, **11**, and benzoin quinaldate, **12**. The mechanism of the reaction,²⁰ which

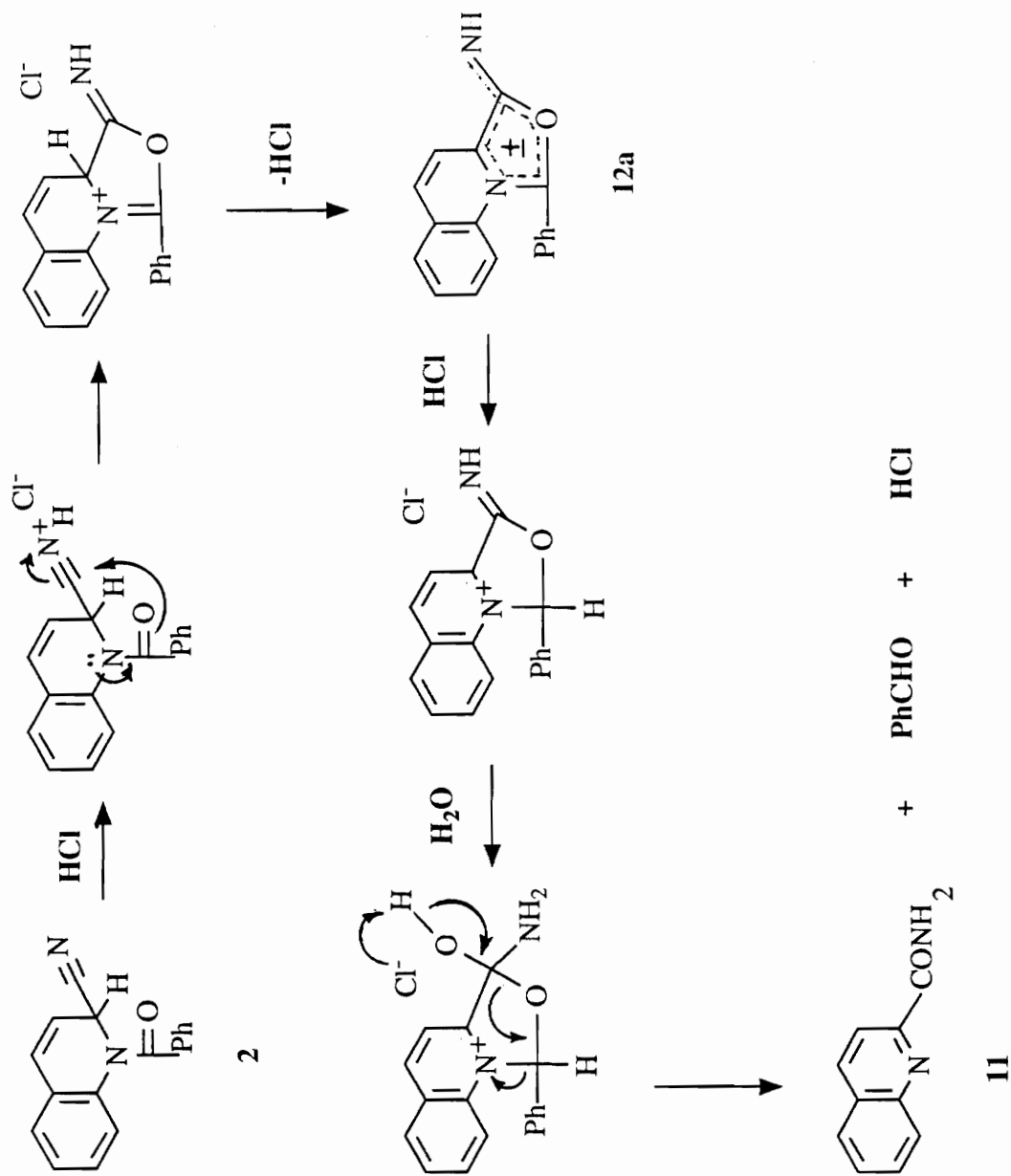
generally proceeds in good to excellent yields, is outlined in Scheme 3. Hydrolysis of quinaldamide, **11**, yields quinaldic acid. The benzoin product, **12**, results from the addition of the conjugate acid of the aldehyde to the intermediate, **12a**, followed by rearrangement and hydrolysis.²⁰ The reaction works equally well using isoquinoline Reissert compounds. Table 2 lists several examples of the acid hydrolysis of Reissert compounds.

Acid hydrolysis of Reissert compounds thus offers an attractive alternative for the reduction of acid chlorides to aldehydes. Such reductions are commonly done with varying efficiencies using the Rosenmund technique, which uses hydrogen gas at high temperatures and pressures and a poisoned palladium catalyst.⁵⁸ As evident, the aldehyde obtained contains the acyl moiety that originated from the acid chloride. One value of this reaction lies in the preparation of deuterio-labelled benzaldehyde using deuterated acid and deuterium oxide.²¹ In addition, the reaction has been useful in the synthesis of heterocyclic derivatives, particularly those of quinaldic acid.²²

b. Alkylation of Reissert compounds:

As evident from the structure of **2**, the α -proton is acidic and can be abstracted with a variety of base/solvent combinations. The major combinations are: sodium hydride/dimethylformamide,²³ phenyllithium/ether-dioxane,²⁴ and 50% sodium hydroxide/acetonitrile catalyzed by trialkylbenzylammonium chloride.²⁵ The resulting anion may be localized, as in isoquinoline Reissert compound, **14**, or ambident as in quinoline Reissert compound, **15a-b**, shown in Scheme 4.

Alkylation of **14** occurs exclusively at the 1-position in generally high to



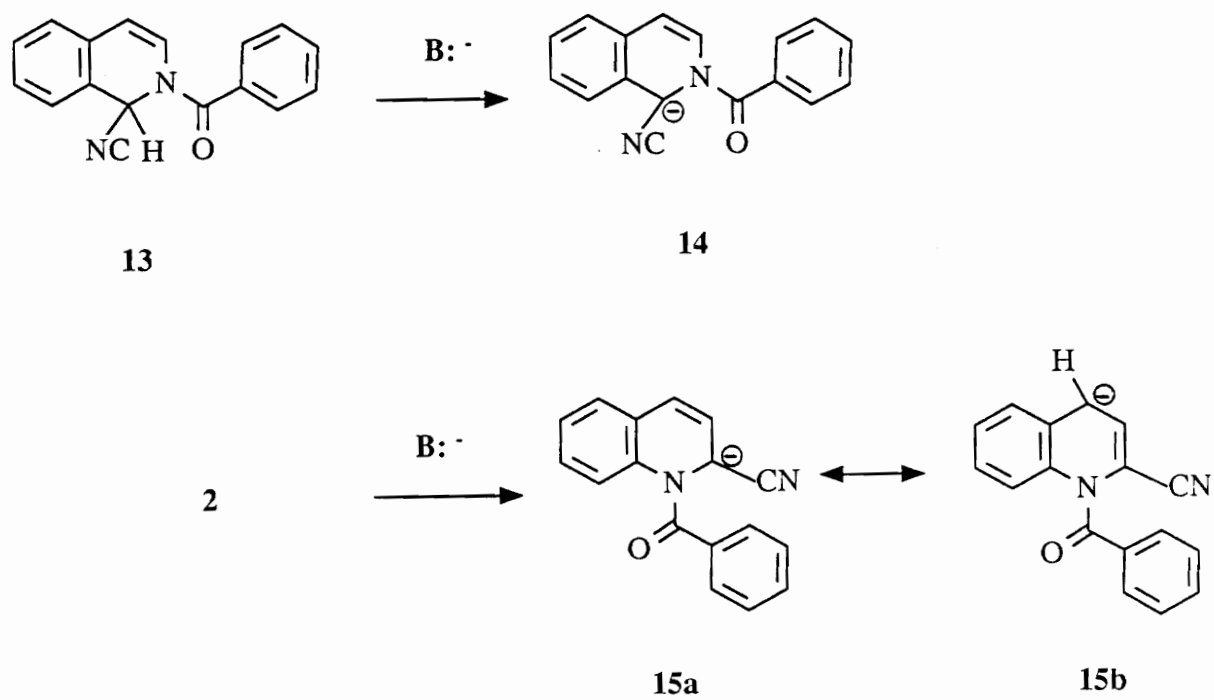
Scheme 3: Mechanism of Acid Hydrolysis of Quinoline Reissert Compounds.

Table 2: Examples of the Acid Hydrolysis of Reissert Compounds to Yield Aldehydes:*

<u>Heterocycle</u>	<u>Acyl group</u>	<u>% Yield aldehyde</u>	<u>Ref.</u>
Quinoline	Benzoyl	98**	7
Quinoline	p-Chlorobenzoyl	92	7
Quinoline	o-Methoxybenzoyl	97	7
Quinoline	Acetyl	99	7
Quinoline	Propionyl	96	7
Quinoline	Isobutyryl	98	7
Isoquinoline	Benzoyl	95**	17
6-Methylquinoline	Benzoyl	91**	42
Isoquinoline	p-Chlorobenzoyl	50	43
Isoquinoline	Butyryl	57**	14
Isoquinoline	Propionyl	75	14
3-Methyliso- quinoline	Benzoyl	95**	42
Phenanthridine	Benzoyl	97	44
Phenanthridine	Cinnamoyl	97	44

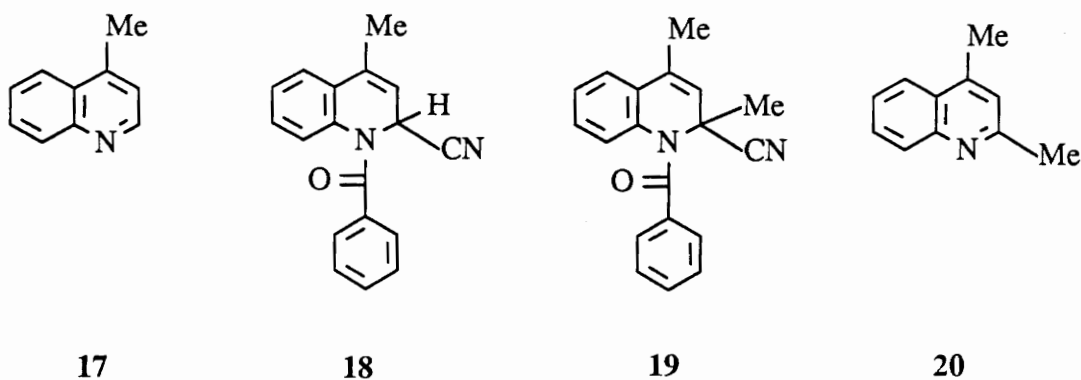
* No references to benzimidazoles, benzoxazoles, and benzothiazoles were found.

** The yield is that of the substituted hydrazone or similar derivative.



Scheme 4: Generation of Reissert Compound Anions

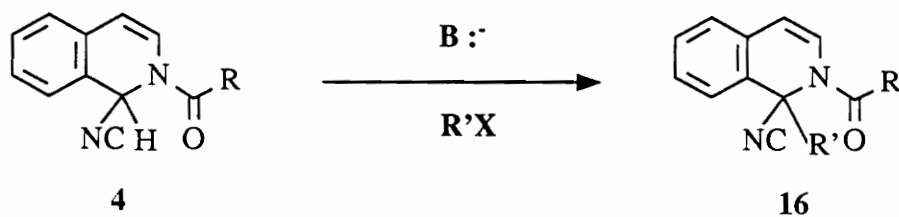
quantitative yields, exemplified in Table 3. Alkylation of quinoline Reissert compounds, however, is more complicated. It has been reported²⁶ that methylation of the anion **15a-b**, generated by phenyllithium in ether-dioxane afforded **18** in 29% yield. The melting point



of **18** prepared in this way was 10° lower than the previously reported melting point.¹³ Lepidine, **17**, was obtained in low yield via base hydrolysis of **18** and identified by its picrate. The second methylation was then found to occur exclusively at the 2-position to yield 47% of the dimethylated product, **19**. Subsequent hydrolysis afforded 2,4-dimethylquinoline, **20**, which was reported in unspecified yield and identified by its picrate.²⁶ Popp and Wefer reported on the use of NaH/DMF system for methylation of **2**, but obtained a "dark messy reaction mixture."²³ The reported regioselectivity was supported by Uff and co-workers,²⁷ who obtained 40% of the 4-methylated product, **21**, from N-benzoyl-6-methyl-1,2-dihydroquinaldonitrile using the NaH/DMF method.

c. Basic hydrolysis of Reissert compounds and alkylated derivatives:

Hydrolysis, e.g., with NaOH or KOH, of Reissert compounds and alkylated derivatives results in loss of the elements of benzoyl cyanide, yielding the heterocycle²⁶ via

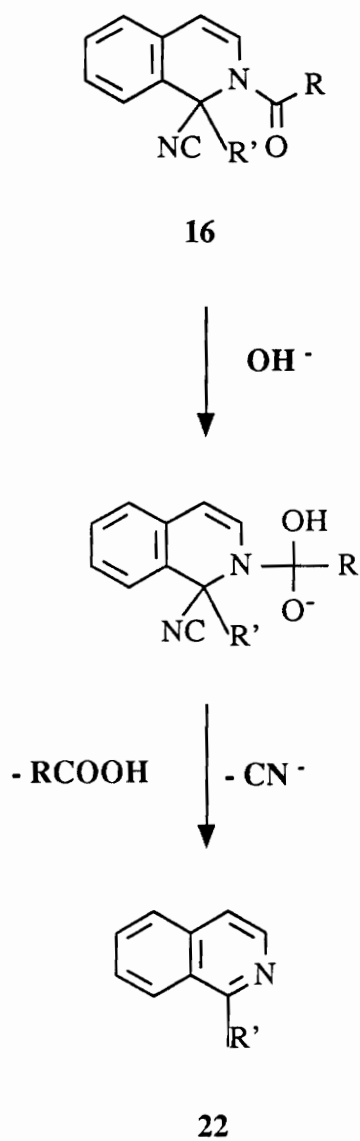
Table 3: Selected Alkylations of Isoquinoline Reissert Compounds:

<u>R</u>	<u>R'X</u> ^a	<u>Conditions</u>	<u>% Yield 15</u>	<u>Ref.</u>
C ₆ H ₅	CH ₃ I	PhLi/dioxane- ether, -10 °C	72	26
C ₆ H ₅	CH ₃ I	NaH/DMF	98	23
C ₆ H ₅	n-C ₃ H ₇ I	NaH/DMF	99	34
C ₆ H ₅	C ₆ H ₅ CH ₂ Cl	50% NaOH/aceto- nitrile, PTC ^b	91	28
C ₆ H ₅	2-NO ₂ - C ₆ H ₄ CH ₂ Cl	50% NaOH/aceto- nitrile, PTC ^b	83	28
C ₆ H ₅	C ₆ H ₅ CH ₂ Cl	NaH/DMF	84 ^c	29
p-C ₆ H ₄ Cl	i-C ₃ H ₇ I	NaH/DMF	78	30
o-C ₆ H ₄ Cl	i-C ₃ H ₇ I	NaH/DMF	95	30
C ₆ H ₅	i-C ₃ H ₇ I	NaH/DMF	95	30
CH ₃	CH ₃ I	NaH/DMF	19	30

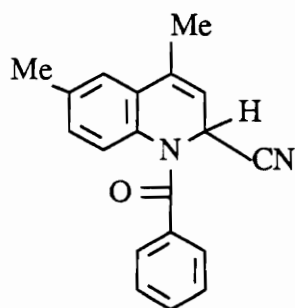
Table 3: (cont.)

<u>R</u>	<u>R'X</u>	<u>Conditions</u>	<u>% Yield 16</u>	<u>Ref.</u>
CH ₃	i-C ₃ H ₇ I	NaH/DMF	81	30
C ₆ H ₅	Br-(CH ₂) ₆ -Br	NaH/DMF	100 ^d	23
C ₆ H ₅	Br-(CH ₂) ₃ -Br	NaH/DMF	95 ^d	39
C ₆ H ₅	o-C ₆ H ₄ (CH ₂ Br) ₂	NaH/DMF	70 ^d	39

(a). all alkyl halides were used in 1 to 3-fold excess, except dihalides which were used in stoichiometric quantities, (b). phase transfer catalyst used was cetrimonium bromide, (c). the yield is that of the hydrolysis product, (d). the yield is that of the dimeric product.



Scheme 5: Mechanism of Hydrolysis of Isoquinoline Reissert Compounds and Alkylated Derivatives

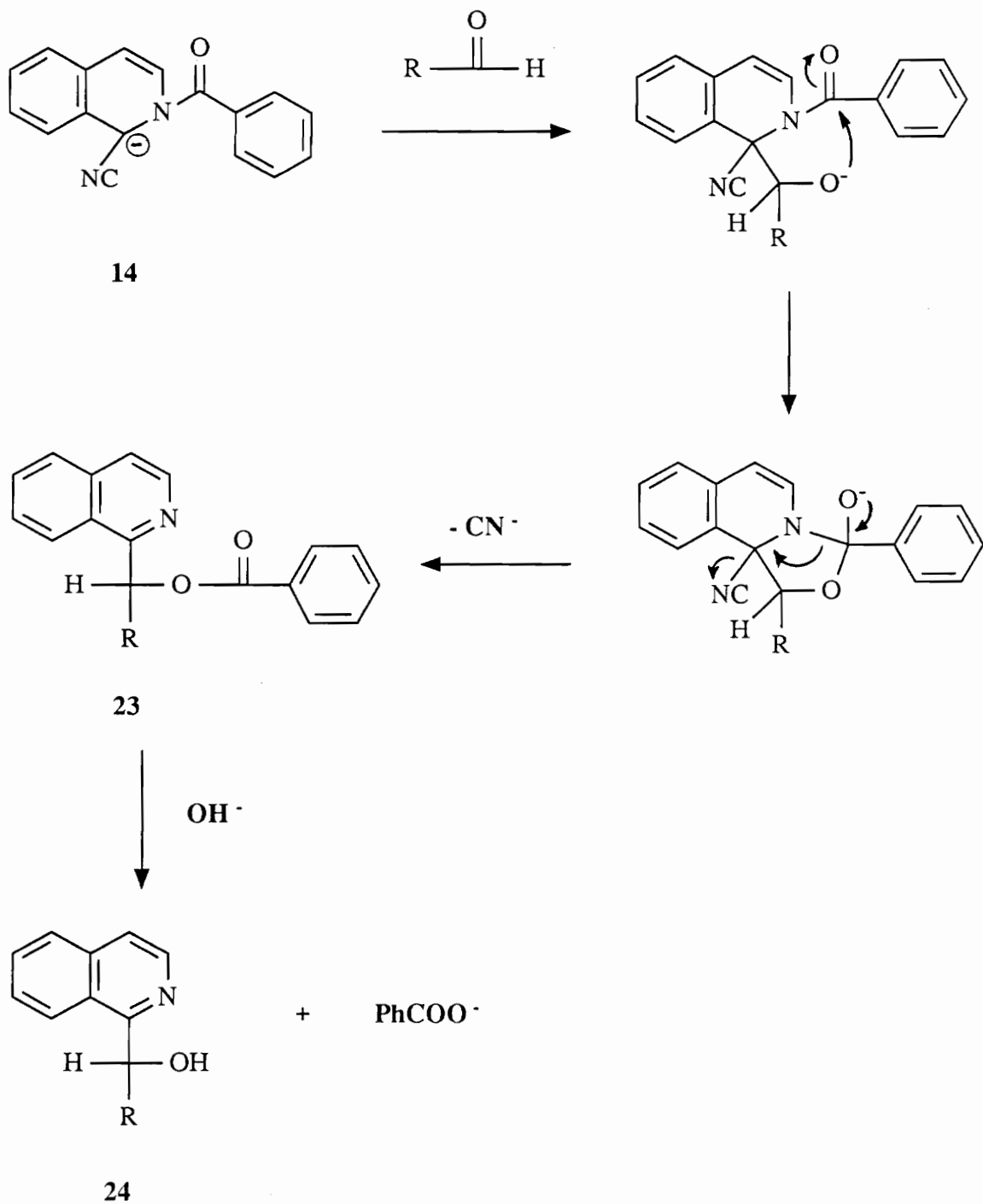


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the mechanism shown in Scheme 5. The driving force for the reaction is the rearomatization of the heterocyclic ring. Generally, the yields are high to quantitative. The synthetic utility of this reaction lies in the area of alkaloid synthesis.³³ Alkylation of the Reissert compound, followed by hydrolysis is one of the preferred methods of preparing alkyl or benzyl substituted isoquinolines and quinolines.³³

e. Condensation with aldehydes:

The reaction of a Reissert compound anion with an aldehyde produces an ester in good to excellent yields according to the mechanism depicted in Scheme 6.³¹ The driving force for the reaction, again, is rearomatization of the heterocyclic ring. The choice of reaction conditions determines the relative yield of ester and alcohol. If the sodium hydride/DMF technique is employed, the ester will be the only product obtained provided that the reaction is carried out at room temperature or colder.³⁴ On the other hand, if the 50% NaOH/acetonitrile method is used, both ester and alcohol are obtained.³⁵ Shorter reactions times favor the yield of the ester, as expected.^{32,35} The alcohol obtained via the

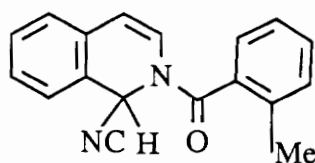


Scheme 6: Mechanism of Condensation of Isoquinoline Reissert Compounds with Aldehydes.

hydrolysis of the ester is a key intermediate in numerous alkaloid syntheses.³³ Selected literature examples can be found in Table 4.

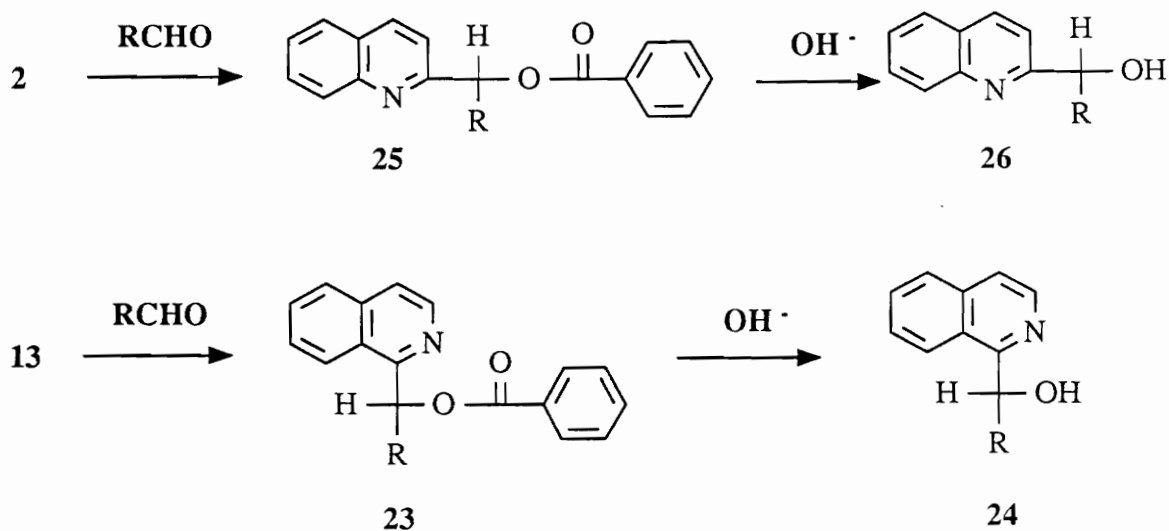
e. Rearrangement of Reissert compound anions:

In the absence of an electrophile, anions **14** and **15** rearrange to ketones via the intramolecular mechanism³⁶ exemplified by quinoline Reissert compound in Scheme 7. Using NaH and refluxing xylene, Boekelheide and Weinstock prepared ketones from quinoline and isoquinoline benzoyl Reissert compounds.²⁶ The reported yields were 54% and 70%, respectively. The reaction has been found to proceed equally well by treatment with sodium hydride in DMF.³⁴ In the case of isoquinoline Reissert compounds, Gibson found that the rearrangement can be promoted by the presence of a methyl group at the 3-position of the heterocycle and by the presence of electron withdrawing groups on the acyl group.³⁰ Obviously, the above rearrangement is of value in the synthesis of α -acyl heterocyclic compounds. In other reactions such as alkylations, rearrangement decreases the yield of the desired product. The best way of decreasing rearrangement is to lower the



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reaction temperature to 0 °C.³⁸ Another way of reducing rearrangement is by ortho-substitution of the aroyl moiety of the Reissert. Gibson found that o-toluoyl

Table 4: Selected Condensations of Reissert Compounds with Aldehydes:Reissert

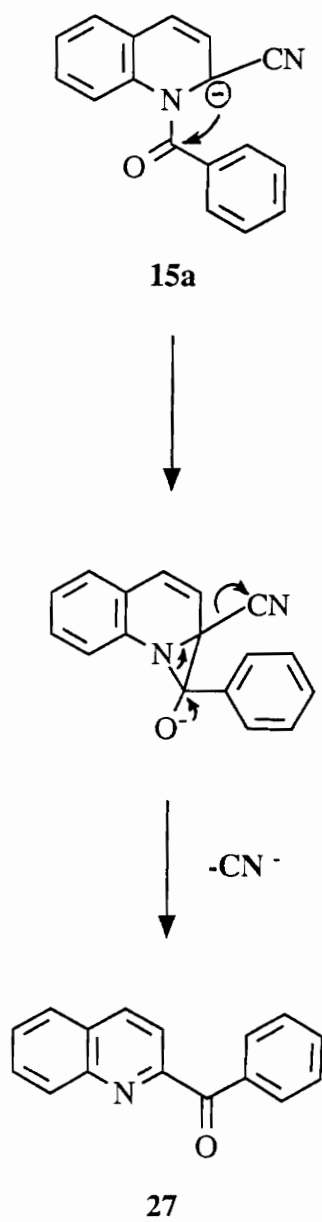
<u>compound</u>	<u>R</u>	<u>Conditions</u>	<u>% Ester</u>	<u>% Alcohol</u>	<u>Ref.</u>
2	C ₆ H ₅	a	97	--	31
2	(CH ₃) ₂ CH	a	*	55	31
2	2,6-Cl ₂ C ₆ H ₃	a	82	--	31
2	CH ₃ (CH ₂) ₂	a	*	89	31
13	C ₆ H ₅	a	88	--	31
13	C ₆ H ₅	b	65	--	34
13	o-C ₆ H ₄ (CHO) ₂	b	45**	--	39
13	2,6-Cl ₂ C ₆ H ₃	a	--	54	31

Table 4: (cont.)Reissert

<u>compound</u>	<u>R</u>	<u>Conditions</u>	<u>% Ester</u>	<u>% Alcohol</u>	<u>Ref.</u>
13	4-OCH ₃ C ₆ H ₄	a	--	62	31
13	(CH ₃) ₂ CH	c	83	85***	35
13	C ₆ H ₅	c	89	93***	35
13	2-CH ₃ C ₆ H ₄	c	85	82***	35

* isolated as picrate; ** yield is of the dimeric product; *** obtained via hydrolysis of ester.

a: phenyllithium in ether-dioxane, b: NaH/DMF, room temperature, c: 50% NaOH, acetonitrile, phase transfer catalyst.



Scheme 7: Mechanism of Rearrangement of Quinoline Reissert Compound

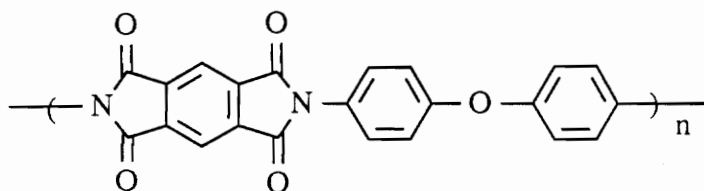
isoquinoline Reissert, **28**, does not rearrange at room temperature whereas the benzoyl analog, **13**, does.³⁰

2. HETEROCYCLIC POLYMERS:

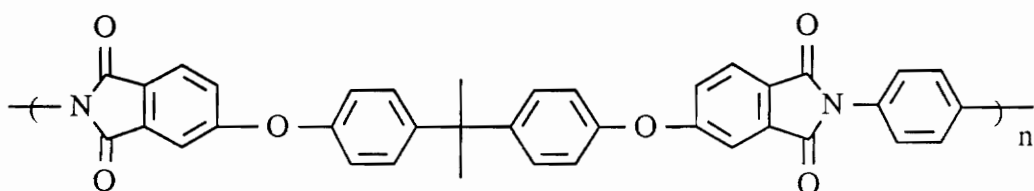
In the recent years, synthetic heterocyclic polymers have received considerable attention because of their highly desirable properties. More specifically, aromatic nitrogen-containing polymers are considered as they relate to the work presented in this thesis. Applications for N-heterocyclic polymers range from high temperature structural and adhesive materials to conducting polymers and water soluble catalysts. Several important N-heterocyclic polymers have been classified according to their physical properties and will be discussed in more detail.

2.1. Heat-Resistant N-Heterocyclic Polymers:

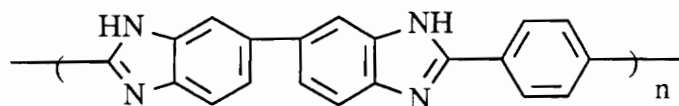
Nitrogen-containing heterocyclic rings are widely used to impart thermal stability to polymers because of the high dissociation energy and large dipole-dipole interactions of carbon-nitrogen single and double bonds. Scheme 8 lists several examples of heterocyclic polymers along with their thermal characteristics. Polyimides are a well known class of heterocyclic polymers. For example, Kapton (Scheme 8) is used for high temperature structural and adhesive applications, as well as electronic insulator and packaging material applications.⁴⁵ Typical of other heterocyclic polymer syntheses, Kapton is made via a two step reaction requiring temperatures near 300 °C for imide formation. Lower reaction temperatures favor the formation of the intermediate polyamic acid, which is hydrolytically



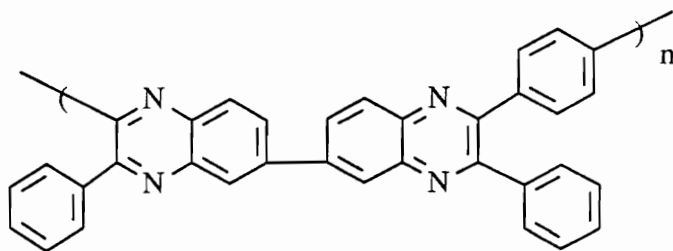
Kapton, polyimide, Tg= 327 °C (ref. 61)



Ultem 1000, polyetherimide, Tg= 220 °C (ref. 45)



. polybenzimidazole (PBI), Tg= 430 (ref. 45)



polyquinoxaline (+2 isomers), Tg= 370 (ref. 45)

Scheme 8: Examples of Heat-resistant N-Heterocyclic Polymers

unstable. Other polyimides prepared in this way exhibit severe processing problems, which include evolution of solvent and condensation volatiles, as well as low melt viscosities.⁴⁵

An improved synthesis of polyimides has been reported to proceed by aromatic displacement polymerization of activated nitro, fluoro, or chloro groups on bisimides by the dianion of bisphenols. Compared to the 2-step process, the imide rings are pre-formed prior to polymerization, leading to a more stable polymer with a more predictable repeat unit structure.⁵⁹ The polyetherimide Ultem 1000 (Scheme 8) is commercially made this way and has its glass transition temperature near 220 °C.⁶⁰

Another example of thermally stable heterocyclic polymers is polybenzimidazole (PBI), also shown in Scheme 8, generally prepared by melt condensation of aromatic bis(o-diamines) with diphenyl esters of aromatic dicarboxylic acids.⁴⁵ Unless reaction parameters are carefully controlled, PBI's made by this route are intractable and therefore require high temperatures and pressures for melt processing. Another approach has been explored by Connell and Hergenrother at NASA, who were able to synthesize polybenzimidazoles⁴⁷ via aromatic nucleophilic displacement of diphenols containing the heterocyclic units with activated aromatic dihalides in the presence of potassium carbonate. Similar to the above mentioned polyetherimide synthesis, this approach has several advantages over the conventional high temperature process. Most importantly, the polymer obtained has a more predictable repeat unit structure and is considerably more processable with little sacrifice of thermal stability.⁴⁷ PBI's have found use as films, fibers, and low to medium density foams possessing very high thermal stabilities.⁴⁵

Other examples of heat-resistant polymers include polyquinolines and

polybenzothiazoles (not shown). The former are synthesized via the reaction of a bis(o-aminoketone) with aromatic diacetyl or di(phenylacetyl) monomers at 130 °C in a 3:1 mixture of m-cresol and polyphosphoric acid.⁴⁵ The degree of crystallinity of the resulting polyquinoline depends on the chemical structure and thermal history. Bulky substituents on the aromatic rings inhibit molecular motion leading to higher glass transition temperatures.⁴⁵

Polybenzothiazole belongs to a unique class of polymers which also includes polybenzoxazole and poly(4-hydroxybenzoic acid). Classified as rigid rodlike polymers, these polymers possess a high degree of molecular orientation along the main chain, as well as a well-developed two-dimensional order.⁴⁵ Polybenzothiazole is prepared by the reaction of 1,4-dimercapto-2,5-diaminobenzene with terephthalic acid in polyphosphoric acid at 190-200 °C. Solutions of polybenzothiazole are lyotropic and have intrinsic viscosities near 30 dl/gram. Fibers of polybenzothiazole can be spun from anisotropic acid solutions and have very high moduli and strengths along the fiber axis. Polybenzothiazole and other rigid rodlike polymers are being developed primarily as high temperature reinforcements, such as fibers and ribbons.⁴⁵

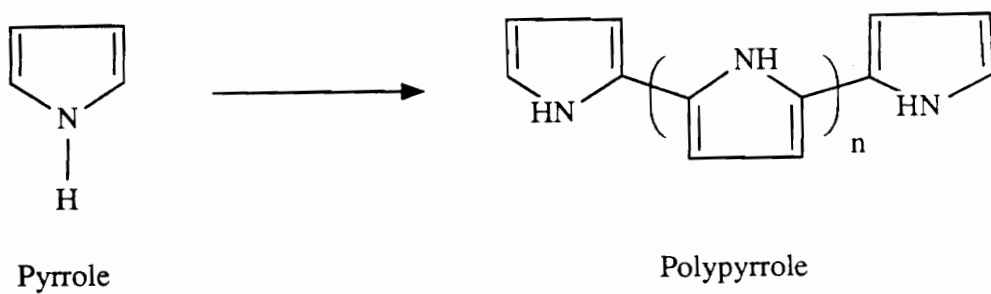
2.2. Conductive N-Heterocyclic Polymers:

Another area of active research is the synthesis of conducting polymers. In addition to the well known polyacetylenes, a novel series of conducting polymers have been reported which contain heterocyclic rings in the main chain. Compared to classical conducting polyacetylenes, heterocyclic polymers such as polythiophenes and polypyrroles offer better

oxidative stability and processability. The focus here will be on the N-heterocyclic polymers, e.g., polypyrroles.

There has been renewed interest in polypyrroles in the past decade because, when doped, such polymers become intrinsically electrically conductive.⁶² The general structure of pyrrole and undoped polypyrrole is shown in Scheme 9. Electrically conductive polymers of pyrrole are best prepared electrochemically, using constant voltage (potentiostatically) or constant current (galvanostatically).⁶² The conductive form of the doped polymer precipitates onto the anode as a brown-black film and continues to deposit because of the conductive nature of the film. The observed conductivity is strongly dependent on the counterion employed, the largest values observed with perchlorate (ClO_4^-) as the counterion. Conductive films of polypyrrole are insoluble in all common organic solvents, as well as most inorganic acid and base solutions.⁶²

Improved solubility and processability are achieved when pyrrole is electrochemically polymerized in the presence of latex particles that have anionic surface characteristics. The resulting polymer compositions, which also precipitate onto the anode, can be dissolved in a variety of common solvents. Films cast from such solutions are free-standing and conductive.⁶³ The magnitude of the conductivity depends on the type of latex employed as the counterion. Overall, polypyrroles have been in the forefront of research because of their overall stability in the doped state. The proposed uses for doped polypyrroles range from lightweight secondary batteries to information storage in the form of surface relief patterns.⁶²



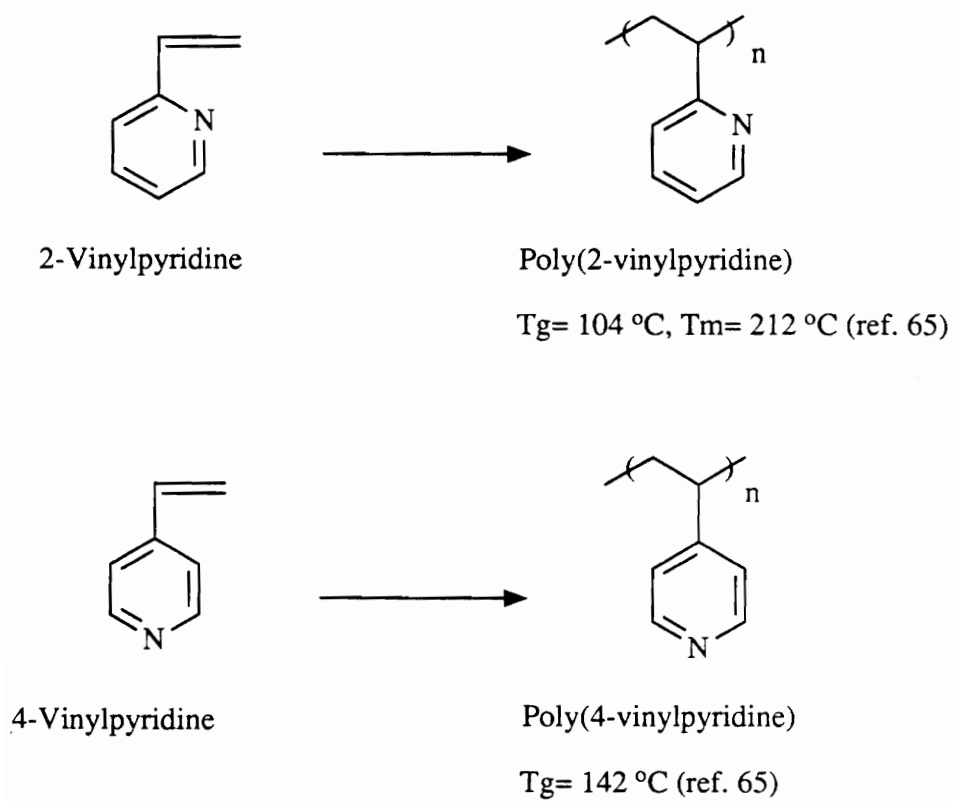
Scheme 9: Structures of Pyrrole and Polypyrrole

2.3. N-Heterocyclic Polymers as Catalysts and Reagents:

Another active area of research in polymer science is the synthesis of polymeric reagents and catalysts. Recently, polyvinylpyridines have received considerable attention because of their interesting properties which arise from the weakly basic nitrogen of the pyridine ring. Scheme 10 shows the two most common monomers as well as the polymers derived from them. Since the electronic structure of vinylpyridine is similar to styrene, polyvinylpyridines are easily synthesized via radical techniques, yielding the atactic forms of the polymers.⁶⁴ A number of copolymers have been reported using acrylic and styrenic co-monomers. Polyvinylpyridines can also be prepared anionically. Compared to styryl anion, the living vinylpyridyl anion is more stable because of the extra delocalization made possible by the pyridyl nitrogen. Poly(2-vinylpyridine) prepared anionically is isotactic, whereas poly(4-vinylpyridine) is atactic, the difference attributed to the intramolecular coordination possible with the 2-vinyl isomer.⁶⁴

A number of copolymers have been reported using acrylic and styrenic comonomers via radical and anionic techniques. Uses of vinylpyridine copolymers include emulsifying agents, thermoplastics, adhesives, and membranes. Quaternization of the vinylpyridyl segments results in an increase in the T_g of the material. The tensile strength then becomes similar to a highly crosslinked elastomer. It is believed that the quaternized vinylpyridine domains function like crosslink junctures. Quaternization also decreases the solubility in organic solvents, but increases water solubility.⁶⁴

An important use of vinylpyridine polymers is in the area of flocculation and adsorption of metals. Cross-linked networks of 4-vinylpyridine and divinylbenzene are



Scheme 10: Structures of Vinylpyridines and Poly(vinylpyridines)

used for the removal of heavy metals from waste water.⁶⁴ Vinylpyridine polymers are also used as polymer supports in reaction catalysis. Polymerization of 2,6-disubstituted phenols can be carried out by complexes of vinylpyridine polymers to yield high molecular weight poly(phenylene ethers).⁶⁴ Doping of poly(2-vinylpyridine) yields semiconductors with conductivities of 10^{-4} to 10^{-2} S/cm ($\text{ohm}^{-1}\text{cm}^{-1}$).⁶⁴ The technologically important uses of vinylpyridine polymers are a consequence of the basic nitrogens on the pyridyl rings.

III. OBJECTIVE:

The present work seeks to develop routes to novel N-heterocyclic polymers via the chemistry of Reissert compounds. The success of this work will depend on the careful selection of substrates and reaction conditions that will result in high extents of reaction and, therefore, high molecular weight polymers. The polymerization reactions are, technically speaking, linear step-growth condensation polymerizations and hence require difunctional monomers which can be of the A-A or A-B types. The heterocyclic units are introduced into the polymer backbone by the way of the monomer(s), i.e., the heterocyclic units are pre-formed prior to polymerization. This approach has been explored by Connell and Hergenrother at NASA, who were able to synthesize polyphenylquinoxalines and polybenzimidazoles as mentioned in the Historical Section. The advantage of this approach is that the polymer structure can be easily controlled by variations in the functional groups, heterocycles, and linking units, allowing tailoring of the polymer structure to attain desirable properties.

IV. RESULTS AND DISCUSSION:

1. Introduction:

Successful incorporation of the chemistry of Reissert compounds into step-growth or condensation polymerization is governed by seven factors of equal importance:

1. Purity of starting materials: the starting materials must be as pure as can possibly be achieved, often 99.9% and better. Impurities that can hinder polymerization include monomer residues, water, and other solvents.

2. Functionality of starting materials: for linear step-growth polymerizations, the monomer(s) must be difunctional. Two ways of achieving this are with "AA, BB" monomers and with "AB" monomers, where "A" and "B" represent different functional groups which condense in the polymerization step.

3. Stoichiometry, which must be carefully controlled. In an A-A, B-B system, the number average degree of polymerization, X_n , is related to the stoichiometric imbalance ratio, r , via the equation:⁶⁶

$$X_n = (1+r)/(1+r-2rp),$$

where p denotes extent of reaction. It is essential that the molar ratio of the two monomers be 1.000 to 1.000 if high molecular weight is desired. The slightest excess of either monomer can drastically reduce the degree of polymerization, X_n .

4. Reactions that proceed to quantitative yields: the above equation also shows the relationship between X_n and p . When the monomers in the above system are present in

stoichiometric quantities ($r = 1.000$), the equation simplifies to:

$$X_n = 1/(1-p),$$

Naturally, the extent of reaction between the monomers should be nearly quantitative.

5. Solvent: a solvent must be chosen that will dissolve the polymer as it is formed. If the polymer precipitates, low molecular weights will certainly result.

6. Catalyst: inclusion of a catalyst is often necessary in that it promotes the reaction between monomers.

7. Temperature, which can play a significant role in polymerizations. Higher temperatures usually lead to higher reaction rates, but also to undesirable side reactions.

The discussion is subdivided into two parts. The first part will describe the use of quinoline as the heterocyclic base in the preparation of novel monomers and polymers. The second part of the discussion will be devoted to the use of isoquinoline as the heterocyclic base.

2. Use of Quinoline as Heterocyclic Base:

The initial thrust was to use quinoline as the heterocyclic base due to its low cost. Moreover, reactions involving quinoline Reissert compounds proceed to high yields, as evident from the literature. Compared to isoquinoline Reissert compounds, however, there are fewer references to quinoline Reissert compounds, partly because fewer natural products contain substituted and unsubstituted quinoline rings.

Because of the ambident character of their anions (see **15a-b**), quinoline Reissert compounds are inherently partially difunctional in alkylation reactions, i.e., they may

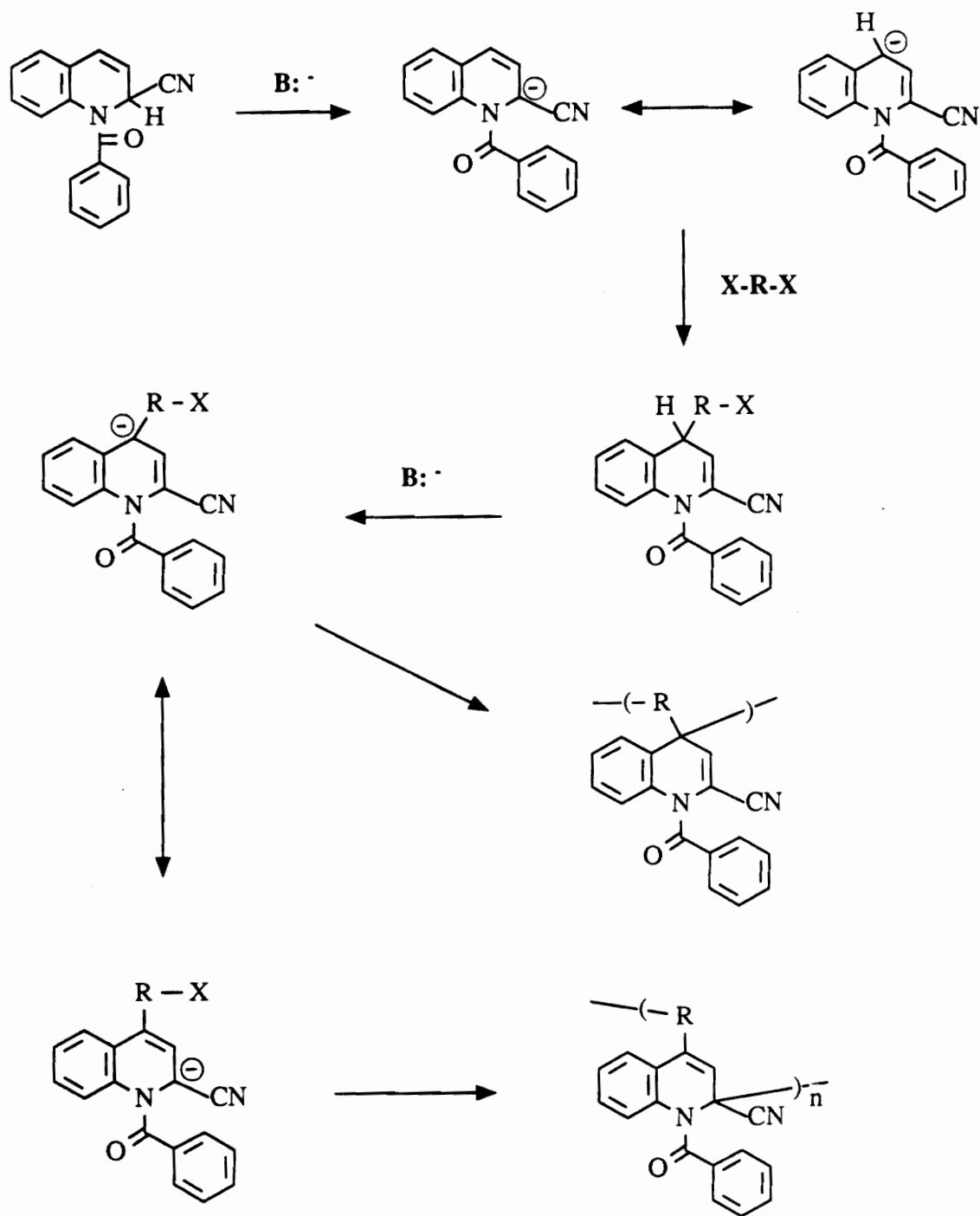
behave as "AA" monomers. Alkylation of quinoline Reissert compounds was carefully examined to test the feasibility of such compounds as A-A monomers. Other approaches to difunctionality include the synthesis of an A-B monomer, and an A-A monomer derived from a diacid chloride.

2.1. Alkylation Reactions of Quinoline Reissert Compounds:

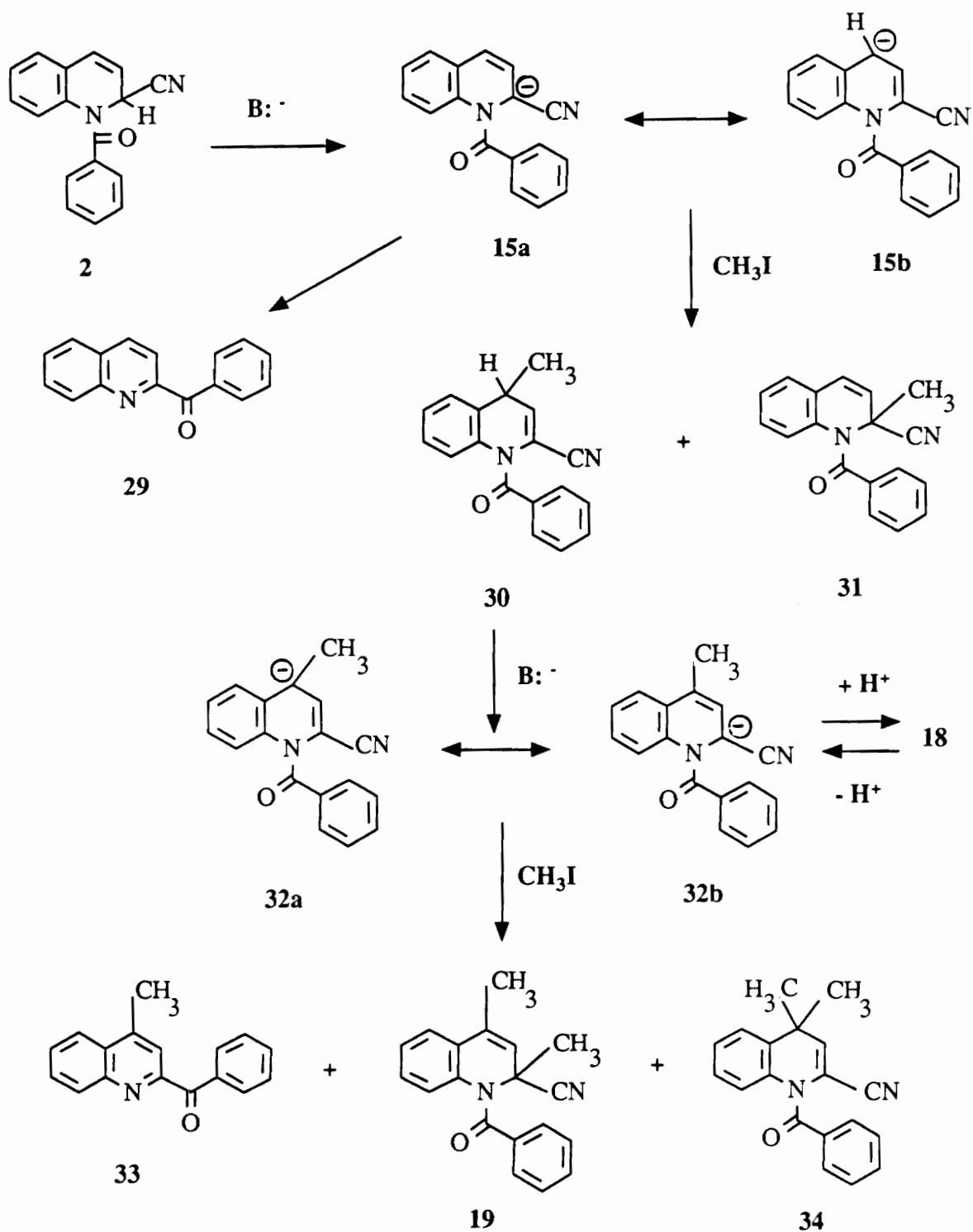
As the literature would suggest, certain quinoline Reissert compounds are difunctional to some extent in alkylation reactions. The first alkylation reportedly occurs at the 4-position, while the second alkylation occurs at the 2-position.²⁶ If this regioselectivity was in fact true, the reaction of quinoline Reissert compound, **2**, with dihaloalkanes should produce a novel series of polyamides via the mechanism depicted in Scheme 11. Naturally, rearrangement or initial alkylation at the 2-position would terminate polymerization.

To evaluate the feasibility of such polymerizations, a model regioselectivity study was performed. The alkyl halide used was methyl iodide; the base/solvent system chosen was NaH/DMF. Scheme 12 lists all of the possible products that could be obtained. The approach to this rather complex study was to synthesize and obtain NMR spectra of as many of the products as possible, so that in subsequent reactions, NMR could be used to determine the percent composition of the crude product.

The first compound prepared was the lepidine Reissert compound, **18**, via the 2-phase method.¹³ After work-up, the Reissert compound was obtained in 57% isolated yield, melting at 169-170 °C. The proton NMR spectrum of this compound showed a doublet at 2.22 ppm, $J = 1.5$ Hz, along with the aromatic protons between 6 and 8 ppm.



Scheme 11: Condensation of Quinoline Reissert Compound with Dihaloalkanes to Yield Novel Polyamides.



Scheme 12: All Possible Products of Methylation of Quinoline Reissert Compound in the Presence of Two Equivalents of Base.

Methylation of **18** was accomplished via the NaH/DMF method. In the first trial, methyl iodide was added 10 minutes after the Reissert anion was generated, distinguished by the intense red color of the solution. Work-up of the reaction yielded 45% of a solid melting at 108-109 °C, whose proton NMR showed a doublet at 2.80 ppm, $J = 1.5$ Hz. The FTIR spectrum confirmed that this was the rearrangement product **33**.⁴⁸ In the second trial and all subsequent trials, methyl iodide was added prior to the addition of base.

Methylation was repeated 3 times affording crude yields of 83%, 86% and 88%. The first crude product was chromatographed so that **19** and **34** could be isolated. The first compound that eluted was **34**, N-benzoyl-4,4-dimethyl-1,4-dihydroquinolidonitrile. No reference to this compound was found in the literature. In fact, one reference stated that "it was considered unlikely" that a structure of type **34** would result from a Reissert compound that had a "blocking group at its 4-position."²⁷ The compound gave satisfactory elemental analysis and had melting point of 134-5 °C. The proton NMR spectrum of **34** (NMR #1, Appendix A) showed a distinctive singlet at 1.55 ppm, assigned to the geminal methyl protons, and a singlet at 6.47 ppm, assigned to the quinolyl H₃ proton. The second compound that eluted was **19**, melting at 136-7 °C. Proton NMR spectrum of this compound (NMR #2, Appendix A) showed a singlet at 1.84 ppm, and a doublet ($J = 1.5$ Hz) at 2.19 ppm, along with aromatic protons from 6.0-7.5 ppm. The singlet was assigned to the 2-methyl protons and the doublet to the 4-methyl protons. Referring back to the crude mixtures obtained from the three trials, the ratio of **19** to **34** was found to be 54:46, 58:42, and 60:40, or an average of $57 \pm 3:43 \pm 3$. None of the crude NMR spectra showed any sign of the methyl doublet (2.80 ppm) of the rearrangement product, **33**. The results of the

methylation of lepidine Reissert compound are summarized in Table 5.

Having determined the regioselectivity of the lepidine Reissert compound, the methylation of the quinoline Reissert compound could be examined. This was done in two reactions: using one equivalent of base, and using two equivalents of base. As before, methyl iodide was used in 3-fold molar excess.

Methylation using two equivalents of base was carried out 2 times. The crude yields were 100% and 97%. In neither case was starting material observed in NMR spectra. A singlet was observed at 1.88 ppm which was ascribed to the 2-methyl protons of **31**, although this compound could not be isolated. Comparing the integration ratios, it was found that $84\pm 2\%$ of the initial methylation occurred at the 4-position and $16\pm 2\%$ at the 2-position. Moreover, the regioselectivity of the second methylation was, as expected from the results described above for the lepidine Reissert compound, $60\pm 2\%$ at the 2-position versus $40\pm 2\%$ at the 4-position. The crude NMR spectra did not show any sign of **29** or **33**, although the former would be hard to detect if it was present. The results of the dimethylation experiments can be found in Table 5.

Finally, monomethylation of quinoline Reissert compound **2** was examined. The reaction was carried out three times, affording crude yield of 100% each time. In addition to the compounds already described, a new product, **30**, was isolated simply by recrystallization of the crude product from ethanol. The ¹H NMR spectrum (NMR #3, Appendix A) of this interesting compound showed a doublet at 1.53 ppm and a multiplet at 3.65 ppm. Irradiation of the doublet at 1.53 ppm caused collapse of the multiplet to a doublet. Undoubtedly, the doublet at 1.53 ppm corresponds to the 4-methyl protons and the

Table 5: Summary of the Results of the Regioselectivity Study:**Starting**

<u>material</u>	<u>Equiv. NaH</u>	<u>Equiv. CH₃I</u>	<u>%18</u>	<u>%30</u>	<u>%31</u>	<u>%19</u>	<u>%34</u>
18	1.10	3.30	--	--	--	54	46
18	1.10	3.30	--	--	--	58	42
18	1.10	3.30	--	--	--	60	40
2	2.20	6.60	--	--	16	51	33
2	2.20	6.60	--	--	15	52	33
2	1.10	3.30	19	48	12	11	10
2	1.10	3.30	14	56	10	10	10
2	1.10	3.30	16	51	11	13	9

multiplet corresponds to the quinolyl H₄ proton of **30**. The pure form of **30** is yellow and melts at 167-8 °C, very close to its isomer, **18**, which melts at 169-170 °C. The product ratio observed by NMR was as follows: 16±4% of **18** (lepidine Reissert compound); 11±4% of **31** (2-methylated); 11±4% of **19** (2,4-dimethylated); 10±4% of **34** (4,4-dimethylated); and 52±4% of **30** (4-methyl-1,4-dihydro). Therefore, the initial methylation occurred to the extent of 89±4% at the 4-position versus 11±4% at the 2-position of the quinoline Reissert compound. The second methylation occurred to the extent of 52±4% at the 2-position, and 48±4% at the 4-position. These results are also summarized in Table 5.

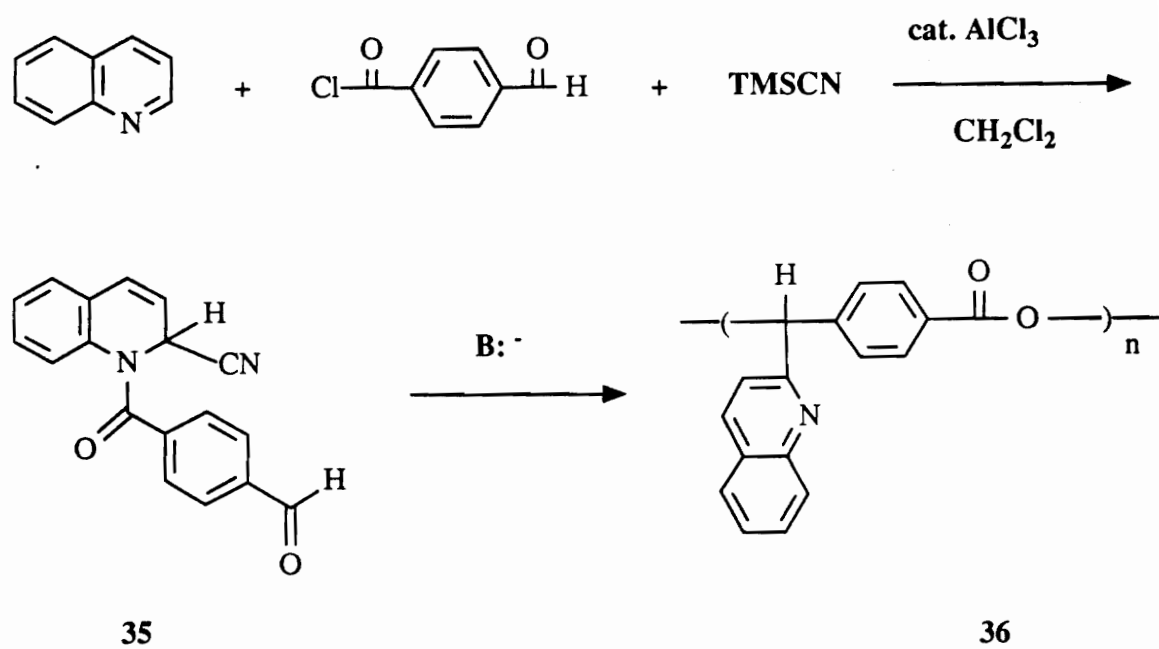
The regioselectivity study was interesting in that it clarified the ambiguous and conflicting reports of the methylation of quinoline Reissert compounds. It was shown that, contrary to popular belief, 1,4-dihydroquinoline Reissert compounds such as **30** exist. More importantly, the study showed that quinoline Reissert compounds cannot be directly used as difunctional monomers in step-growth polymerizations. Clearly, initial alkylation at the 2-position or any rearrangement would terminate chain growth. A possible mechanism by which 2-alkylation could be eliminated is via incorporation of ortho substituents on the aryl group. Presumably, alkylation at the 2-position would become unfavorable by virtue of the steric bulk of ortho groups such as methyl or chloro. Unfortunately, this topic was not examined any further with respect to quinoline Reissert compound, but was examined with isoquinoline Reissert compounds as will be shortly discussed.

2.2. Preparation of Quinoline Reissert A-B Monomer:

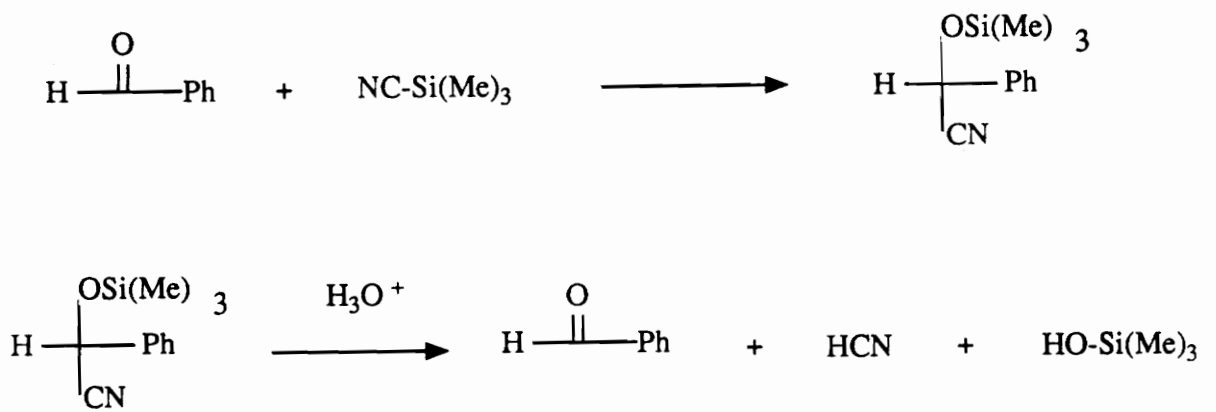
Another approach to difunctional monomers derived from quinoline is via an A-B

monomer where A and B represent different moieties that condense during polymerization. Specifically, we considered the reaction of quinoline Reissert compounds with aldehydes, which typically proceeds to high yields. Therefore, incorporation of a formyl group into the Reissert compound would afford an A-B monomer. The most economical route was via the synthesis of the quinoline Reissert from p-formylbenzoyl chloride, **35**. The synthesis and subsequent polymerization is shown in Scheme 13. The reaction was carried out in CH_2Cl_2 using TMSCN as the cyanide source. After 6.5 hours, the reaction was stopped and washed with water three times. The next step typically is to wash three times with 10% HCl in order to remove any unreacted heterocycle. When the crude product was washed with acid, the solution effervesced, generating some heat in the process. The crude was then washed with saturated NaHCO_3 , followed by 5% NaOH once. The latter base wash formed an emulsion. A gummy solid precipitated, which redissolved in dichloromethane. The overall crude yield was 30%. It seems that the TMSCN had reacted with the aldehyde to form a cyanohydrin silyl ether, depicted in Scheme 14, which would decompose in the presence of acid.

The crude brown solid obtained was the polymer that had formed upon washing with NaOH, i.e., interfacial polymerization. The polymer was precipitated from DMF into methanol. The FTIR spectrum of the polymer showed the amide carbonyl at 1664 cm^{-1} , and the ester carbonyl at 1725 cm^{-1} , 1263 cm^{-1} , and at 1097 cm^{-1} . The FTIR spectrum also showed hydroxyl absorption at 3400 cm^{-1} , which can only arise from lack of rearrangement of the intermediate in the condensation of the Reissert anion with aldehyde shown in Scheme 6 and protonation of the intermediate alkoxide upon workup. The structure of the



Scheme 13: Synthesis and Polymerization of "AB" Quinoline Reissert Monomer.

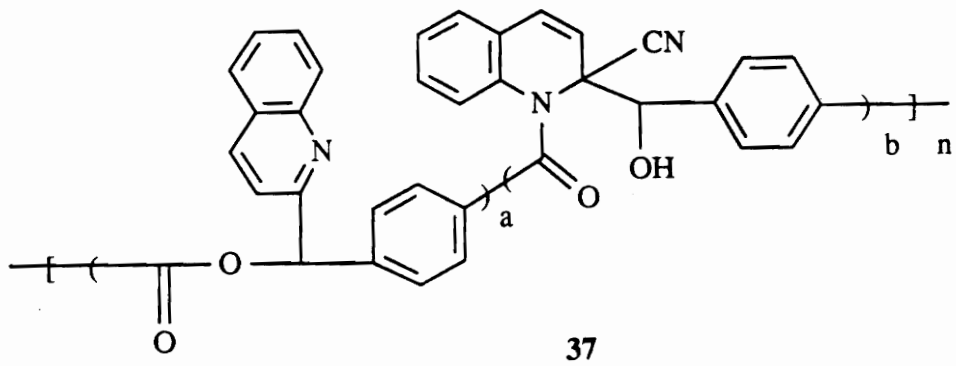


Scheme 14: Reaction of Trimethylsilyl Cyanide with Aldehydes

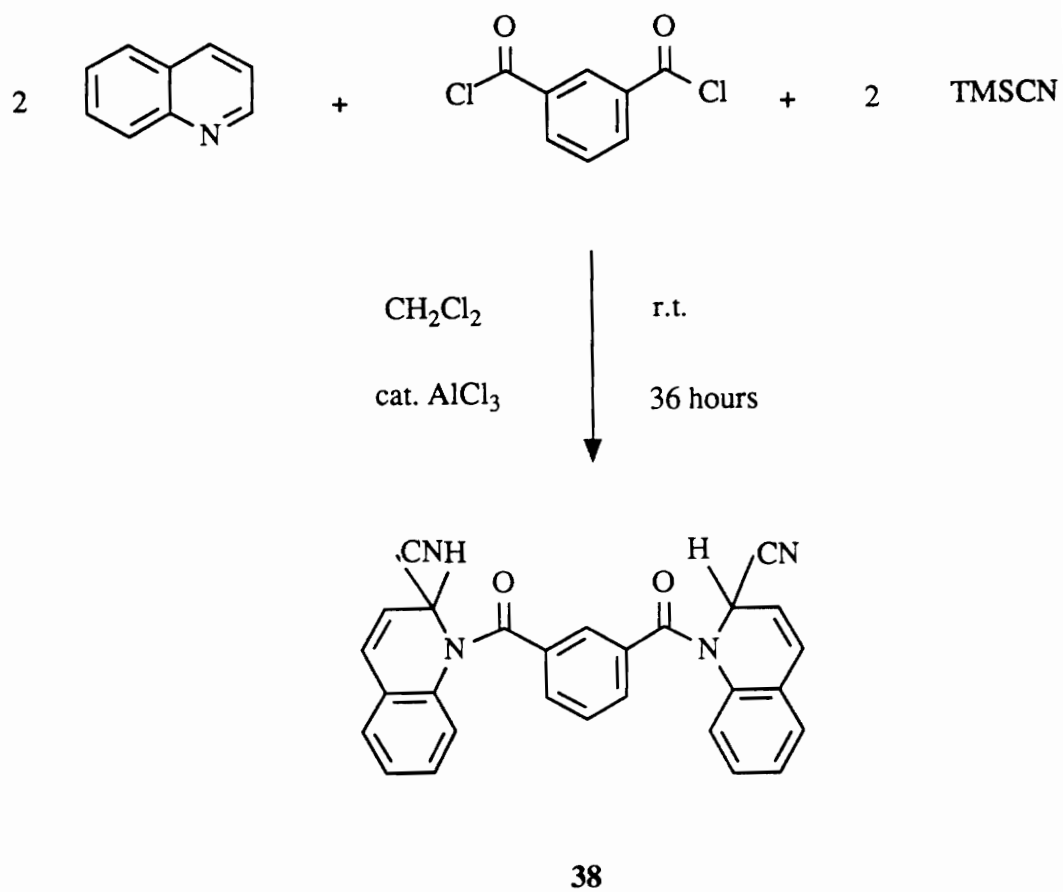
polymer must therefore be the copolymer, **37**, e.g., a poly(ester-amide) shown in Scheme 15. The proton NMR spectrum of the copolymer showed only broad peaks between 6.0 and 8.5 ppm, which could not be resolved by varying the relaxation delay. The aldehydic end groups could be seen at 10.12 ppm, whereas the Reissert end groups are not as easily distinguishable. The GPC of the copolymer reflected $M_n = 3600$ and $M_w = 5500$, the polydispersity ratio being 1.54. The copolymer was found to be stable up to 250 °C. The DSC of the copolymer showed a single Tg at 190 °C. Interestingly, the reaction of isoquinoline with p-formylbenzoyl chloride resulted in an exotherm leading to a dark purple solution. The complexity of these transformations and the high cost of the acid chloride discouraged its further use.

2.3. Preparation of Quinoline Reissert A-A Monomer:

The most general route for incorporation of Reissert compound chemistry into difunctional monomers is via the use of diacid chlorides. The dimeric Reissert compounds prepared as such are called bis-Reissert compounds. The most readily available aromatic diacid chlorides are terephthaloyl and isophthaloyl chloride. Use of aliphatic diacid chlorides is limited by the presence of the acidic protons α to the carbonyls.³⁸ To avoid the symmetry and inherent rigidity that would result from the 1,4-isomer, isophthaloyl chloride was used to prepare the bis-quinoline Reissert compound, **38**, depicted in Scheme 16. As evident, there are two diastereomers, i.e., a meso compound and a pair of enantiomers. The crude yield was 90% after work-up. The base solution used in the work-up was saturated sodium bicarbonate. When recrystallization of the crude was attempted from ethyl acetate,



Scheme 15: Proposed Structure of Poly(ester-amide)



Scheme 16: Synthesis of Novel Bis-quinoline Reissert Compound

approximately 40% of the crude did not dissolve. The soluble portion after the first recrystallization melted at 193.5-194.2 °C. The insoluble portion after recrystallization from acetone, melted at 206.8-207.2 °C. The NMR spectra of the two compounds (NMR #4 lower melting isomer, NMR #5 higher melting isomer, Appendix A) were identical with the exception of the ratio of the pair of doublets at 6.38 and 6.48 ppm which were assigned to acidic protons. Each diastereomer should have one H₂ which is coupled to H₃ (J= 8 Hz). Comparing the integration ratios, the lower melting sample is actually a 46:54 mixture of the two diastereomers, whereas the higher melting compound is a 70:30 mixture. Elemental analysis of the higher melting mixture was satisfactory.

Assuming that the two diastereomers have equal reactivity, a purified mixture of the diastereomers melting at 206.8-207.2 °C was submitted to Ashish Pandya. He was able to synthesize a novel polyester using isophthalaldehyde as the other monomer.⁴⁹ The molecular weight was low, approximately 3600, attributable to the high rigidity that would result in precipitation of the polymer from the reaction medium (DMF). Another explanation for the low molecular weight is the ambidexterity of the quinoline Reissert anion, which by delocalization would decrease the reactivity of the 1-position. Presumably, condensation of the anion with aldehyde at the 4-position would not lead to ester formation, a topic which lacks literature precedence.

3. Use of Isoquinoline as Heterocyclic Base:

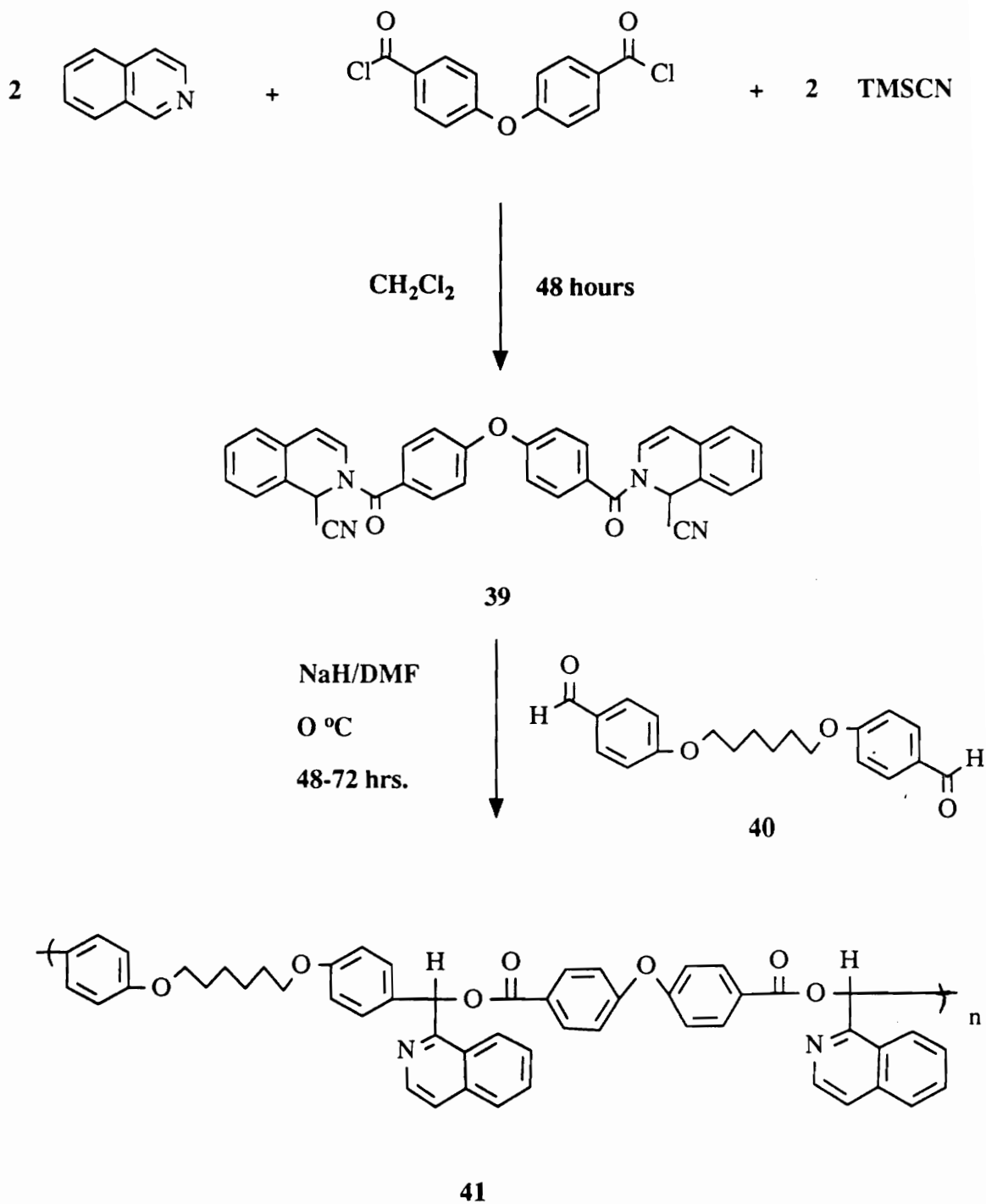
There are considerably more literature references to isoquinoline Reissert compounds than to quinoline Reissert compounds since many more natural products contain

substituted and unsubstituted isoquinoline rings. Moreover, reactions involving isoquinoline Reissert compounds generally give higher yields than those involving quinoline, partly due to the ambidendency of the latter anion (see **15a-b**). The only drawback to using isoquinoline as the heterocyclic base is the higher cost, roughly two to three times more than quinoline.

Attempts at incorporating isoquinoline Reissert compounds as A-B monomers will not be discussed. Only A-A monomers have been considered; these can be achieved in two ways: (a) via diacid chlorides, and (b) via bis-heterocycles.

3.1. Bis-isoquinoline Reissert Compounds Derived from Diacid Chlorides:

Analogous to the quinoline bis-Reissert compound already mentioned, a bis-Reissert compound was prepared from isoquinoline. The diacid chloride chosen was 4,4'-oxydi(benzoyl chloride), the parent acid of which was obtained from Amoco free of charge. The conversion to the acid chloride proceeded smoothly according to the literature procedure.⁵⁰ The product could be either distilled or recrystallized from hexane or heptane. Compared to other readily available aromatic diacid chlorides, i.e., iso- and terephthaloyl dichloride, the ether linkage in 4,4'-oxydi(benzoyl chloride) was expected to add flexibility to the bis-Reissert compound and any polymers derived from it. The flexibility should in turn enhance solubility. The preparation of the bis-Reissert compound derived from isoquinoline and 4,4'-oxydi(benzoyl chloride) and its subsequent polymerization is depicted in Scheme 17. The crude yield of **39** was 92% via the use of trimethylsilyl cyanide/CH₂Cl₂ technique, compared to the yield of 8% by the 2-phase method¹⁷ and 22% by the use of



Scheme 17: Polymerization of 39 with C₆-Dialdehyde

silver cyanide/chloroform method.¹⁷ The proton NMR spectrum of the crude did not show the two diastereomers distinctly, but did show traces of isoquinoline which had been used in a slight excess. Column chromatography afforded the pure bis-Reissert compound, **39**, which crystallized as it eluted from the column. Upon recrystallization from ethyl acetate/hexane, it was noted that part of the solid, melting at 215.2-215.8 °C, was insoluble in ethyl acetate. The PNMR spectrum of this solid agreed exactly with the structure of **39**. Elemental analysis of this solid was satisfactory. The soluble portion of the product recrystallized upon cooling and melted at 205.5-206.5 °C. The proton NMR spectrum of this solid matched that of the higher melting compound. The reported melting point was 140-163 °C, a 23 degree range.¹⁷

Having purified the above bis-Reissert compound, a difunctional electrophile had to be selected. Rather than a dihalide, the dialdehyde depicted in Scheme 17 was selected to yield the novel poly(N-heteroaryl ester), **41**. The dialdehyde, 1,6-bis(p-formylphenoxy)hexane (or C₆-dialdehyde), **40**, was prepared according to a literature procedure,⁵¹ affording 58% of the dialdehyde melting at 101-103 °C (lit.⁵¹ m.p., 106-107). Two additional recrystallizations from ethanol afforded analytically pure compound melting at 107-108 °C.

Condensation of the above dialdehyde and the higher melting bis-Reissert compound was performed twice in DMF using sodium hydride as the base. The first trial resulted in 38% of a powdery solid after 42 hours of reaction time and one precipitation from chloroform into methanol. Extending the reaction time to 67 hours in the second trial improved the crude yield of polymer to 57%. The FTIR of the second polymer, cast as a

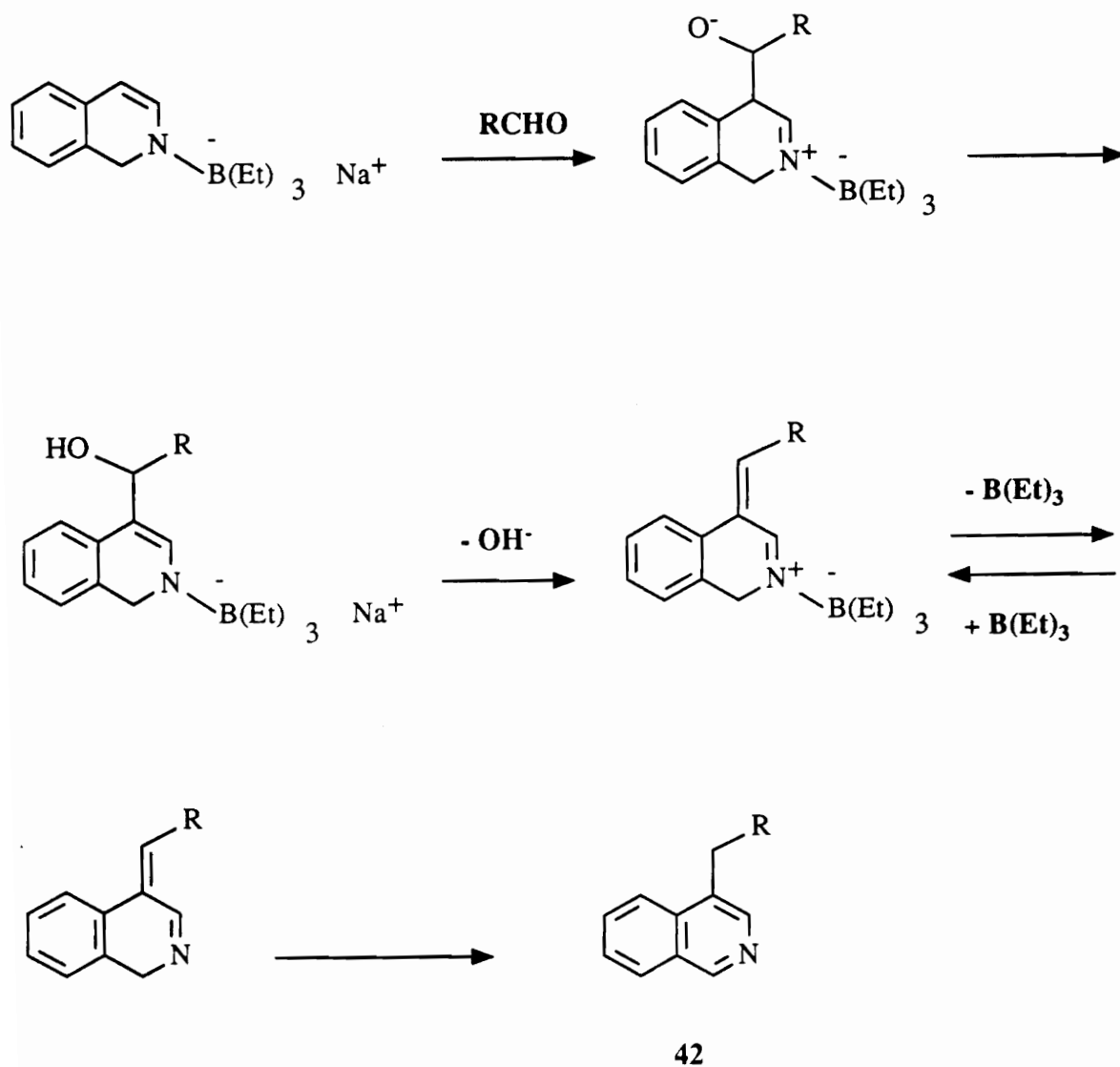
film from chloroform, showed loss of amide carbonyl, and appearance of ester carbonyl at 1715 cm^{-1} . The GPC of the polymer showed $M_n = 2800$, which corresponds to a d.p. of approximately 4. The M_w was 6600, so that the polydispersity ratio was 2.32. The TGA of the polymer in air showed stability up to $260\text{ }^\circ\text{C}$. The DSC of the polymer, showed Tg at $122\text{ }^\circ\text{C}$. Films cast from chloroform were transparent, yellow, and brittle. It is believed that the ether linkage present in the bis-Reissert monomer deactivated the Reissert anion, leading to lower extents of reaction and low molecular weights.

3.2. Bis-isoquinoline Reissert Compounds Derived from Bis-isoquinolines:

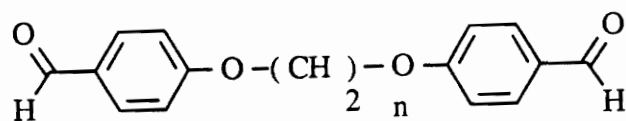
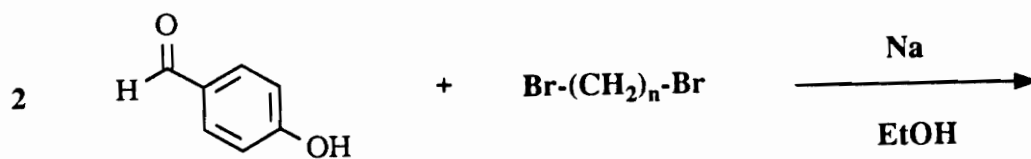
Condensation of bis-Reissert compounds derived from diacid chlorides produces polymer structures in which the heterocyclic units are pendant from the backbone, as shown in Scheme 17. Alternatively, the heterocyclic rings may be part of the backbone, as is the case with some of the technologically important polymers mentioned in the Historical Section. The most obvious route to incorporation of heterocycles into the polymer backbone is via bis-Reissert compounds prepared from bis-heterocycles. Until recently, the most readily available or accessible bis-heterocycles were based on quinoline. As mentioned, however, reactions involving quinoline Reissert compounds do not proceed to as high conversions as those involving isoquinoline Reissert compounds. The need for easily preparable bis-isoquinolines led to the synthesis of five novel bis-isoquinolines via the enamine reaction reported by Minter and Re.⁵² The same reaction was used in the synthesis of a novel difluorodiketone that will be discussed shortly and hence merits considerable attention.

Minter and Re⁵² reported that an enamine could be prepared from isoquinoline by addition of sodium triethylborohydride (Scheme 18). The formation of the enamine was instantaneous as found by ¹¹BNMR. Addition of an aldehyde, followed by quenching of the reaction after 2 hours afforded the 4-substituted isoquinoline, **42**. The proposed mechanism is outlined in Scheme 18. The isolated yield of 4-benzylisoquinoline was 65%, although the crude NMR spectrum reportedly showed purity greater than 90%. The process was not as efficient when aliphatic aldehydes were used, however. The yield of 4(*n*-propyl)isoquinoline from the reaction of the enamine with propionaldehyde was only 28%.⁵²

Capitalizing on the above reaction, use of aromatic dialdehydes should yield novel bis-isoquinolines. The most readily available aromatic dialdehyde, terephthalaldehyde, was purchased from Aldrich and used without further purification. Three other dialdehydes, **40**, **43**, and **44**, were easily prepared from *p*-hydroxybenzaldehyde using known literature methods,⁵⁰ depicted in Scheme 19. The C₄-dialdehyde, **43**, was prepared by Dr. Hermann. As already mentioned, the C₆-dialdehyde, **40**, was obtained in 58% isolated yield using dibromohexane in the reaction shown. The C₁₀-dialdehyde, **44**, was prepared by Melvin Rasco and used after one recrystallization. Another interesting dialdehyde, **45**, also shown in Scheme 19 was prepared from 4,4'-oxydi(benzoylchloride) using lithium tri-*t*-butoxyaluminumhydride as the reducing agent.⁵³ The synthesis of the novel series of bis-isoquinolines, **46-50**, is shown in Scheme 20, along with the crude yields and melting points. The procedure reported by Minter and Re was followed with the exception that a slight excess of the isoquinoline enamine was used. Minter and Re had used a slight excess



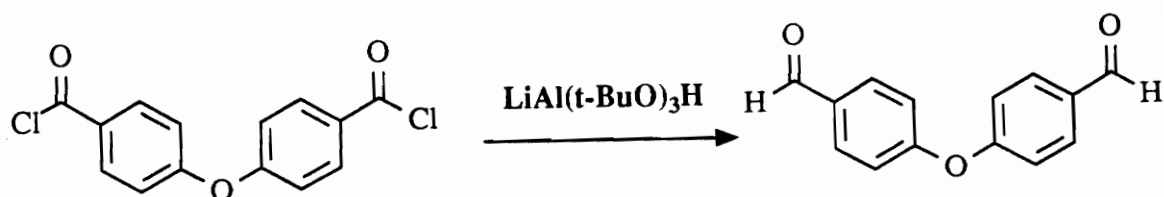
Scheme 18: Reported Mechanism of 4-Alkylation of Isoquinoline⁵²



40: $n=6$

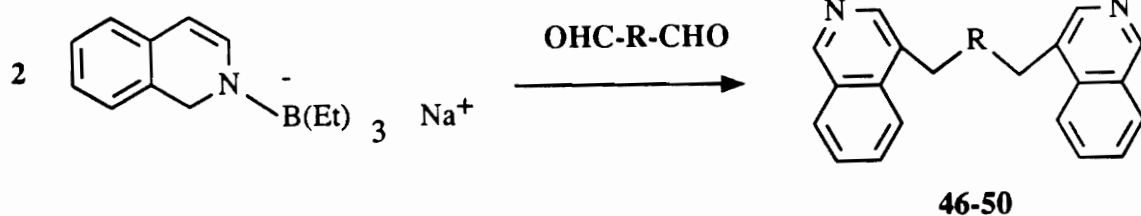
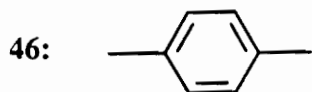
43: $n=4$

44: $n=10$



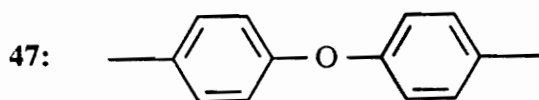
45

Scheme 19: Synthesis of Aromatic Dialdehydes

Bis-isoquinoline, -R-Crude Yieldm.p. °C

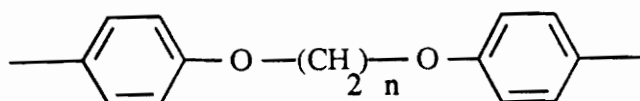
74%

186.5-187.5



88%

117.5-118.5



48:

n = 4

90%

167-168

49:

n = 6

87%

162-163

50:

n = 10

76%

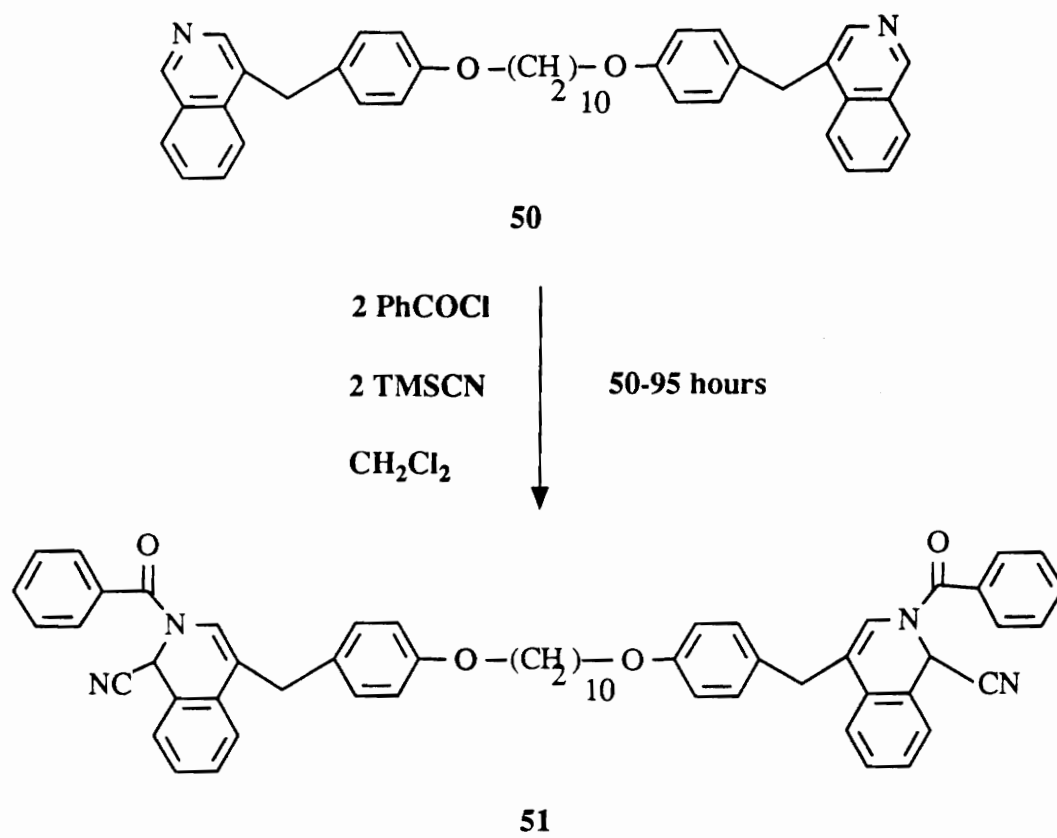
110-112.5

Scheme 20: Synthesis of Novel Bis-isoquinolines

of the aldehyde to favor the mono product formation.

Using the bis-isoquinolines shown in Scheme 20, a novel series of bis-Reissert compounds can be prepared. Only the C₁₀-bis-isoquinoline, **50**, was selected for the synthesis of the bis-Reissert compound, **51**, shown in Scheme 21, considering the enhanced solubility that can be expected from the decamethylene group. The preparative method chosen was the TMSCN method using a slight excess of benzoyl chloride and TMSCN. The reaction was performed twice: once for 50 hours of reaction time, a second trial for 95 hours of reaction time. At the end of both trials, only one spot was detected by TLC. After a standard work-up, the crude yield was >100% for the first trial and 97% for the second trial. In neither case could the product be purified by recrystallization; therefore, column chromatography was performed. The bis-Reissert compound after chromatography could be recrystallized from ethanol or ethyl acetate/hexane. The former solvent yielded crystals that melted at 100-105 °C, whereas the latter solvent system yielded crystals that melted at 175-177 °C. The variance in the melting points may be due to different diastereomers or to crystalline modifications that could arise from the solvents used. The ¹H NMR spectrum of the analytical sample, mp 100-105 °C (NMR #6, Appendix A), was in perfect agreement with the structure of the product.

Having prepared the above bis-Reissert compound, three polymerizations were performed. Again, considering the importance of polymer solubility, the C₁₀-dialdehyde, **44**, and the C₆-dialdehyde, **40**, were selected. The base/solvent system used in the first two trials was sodium hydride/DMF. As a comparison, n-butyllithium/THF was used in the third trial.

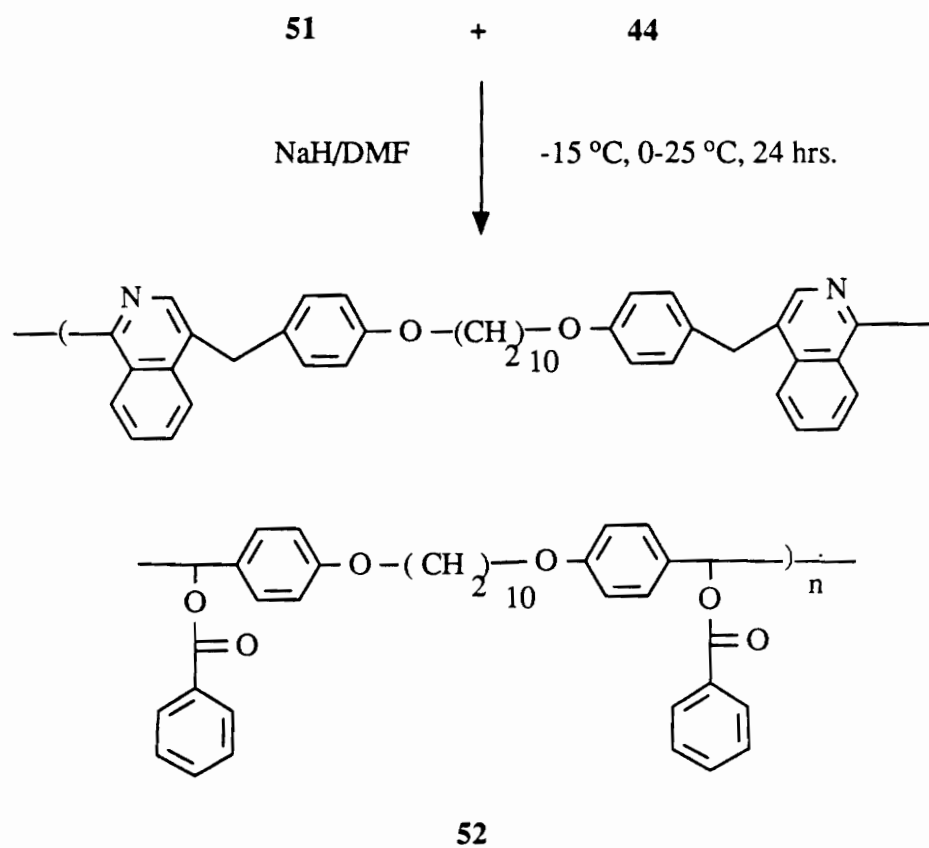


Scheme 21: Synthesis of C₁₀-bis-isoquinoline Benzoyl Reissert Compound

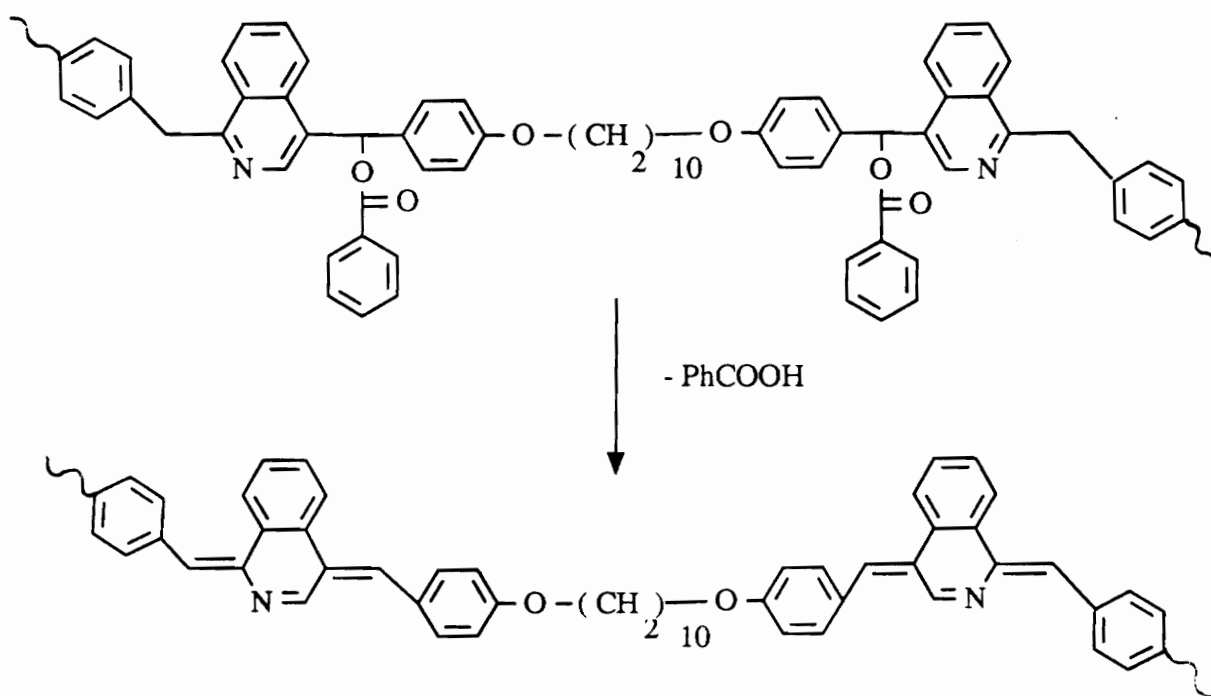
The polymerization of the C₁₀-bis-Reissert compound **51** with the C₁₀-dialdehyde is shown in Scheme 22. The bis-Reissert compound was dissolved in DMF and cooled to -15 °C. Sodium hydride was added, resulting in the generation of the intensely red color characteristic of Reissert anions. After 15 minutes, the dialdehyde was added in one portion. The solution was allowed to warm to 0 °C and kept there for 12 hours, followed by gradual warming to room temperature for 12 hours. At the end of the reaction, the solution was somewhat viscous and green in color. The reaction was quenched by precipitation into water. After 2 further precipitations from DMF into 60:40 water:ethanol, the yield of polyester **52** was 61%. The FTIR spectrum of the dried polymer (IR #1, Appendix B) showed the ester carbonyl absorption at 1720 cm⁻¹, and complete loss of the amide carbonyl absorption of the Reissert compound. The GPC of the polymer indicated intrinsic viscosity of 0.31 dl/gram in chloroform at 30 °C, and M_w= 35,000. However, the presence of low molecular weight species caused M_n= 4100. The polydispersity was 8.56, far greater than the theoretical value of 2.0.⁶⁶ A possible explanation for the observed large polydispersity will be presented shortly.

The thermal properties of the polymer were rather interesting. The DSC of the polymer (DSC #1, Appendix C) showed T_g= 79 °C; no T_m was observed. The TGA of the polymer (TGA #1, Appendix D) revealed stability up to 260 °C in air, with an approximately 20% weight loss occurring between 260-325 °C. This is likely due to the loss of benzoic acid leading to the quinoidal structure shown in Scheme 23. Since very little of the polymer was available, a model study was performed to confirm the proposed loss of benzoic acid.

Scheme 24 shows the synthetic route to the model compound. The first step



Scheme 22: Polymerization of C₁₀-bis-Reissert Compound with C₁₀-Dialdehyde

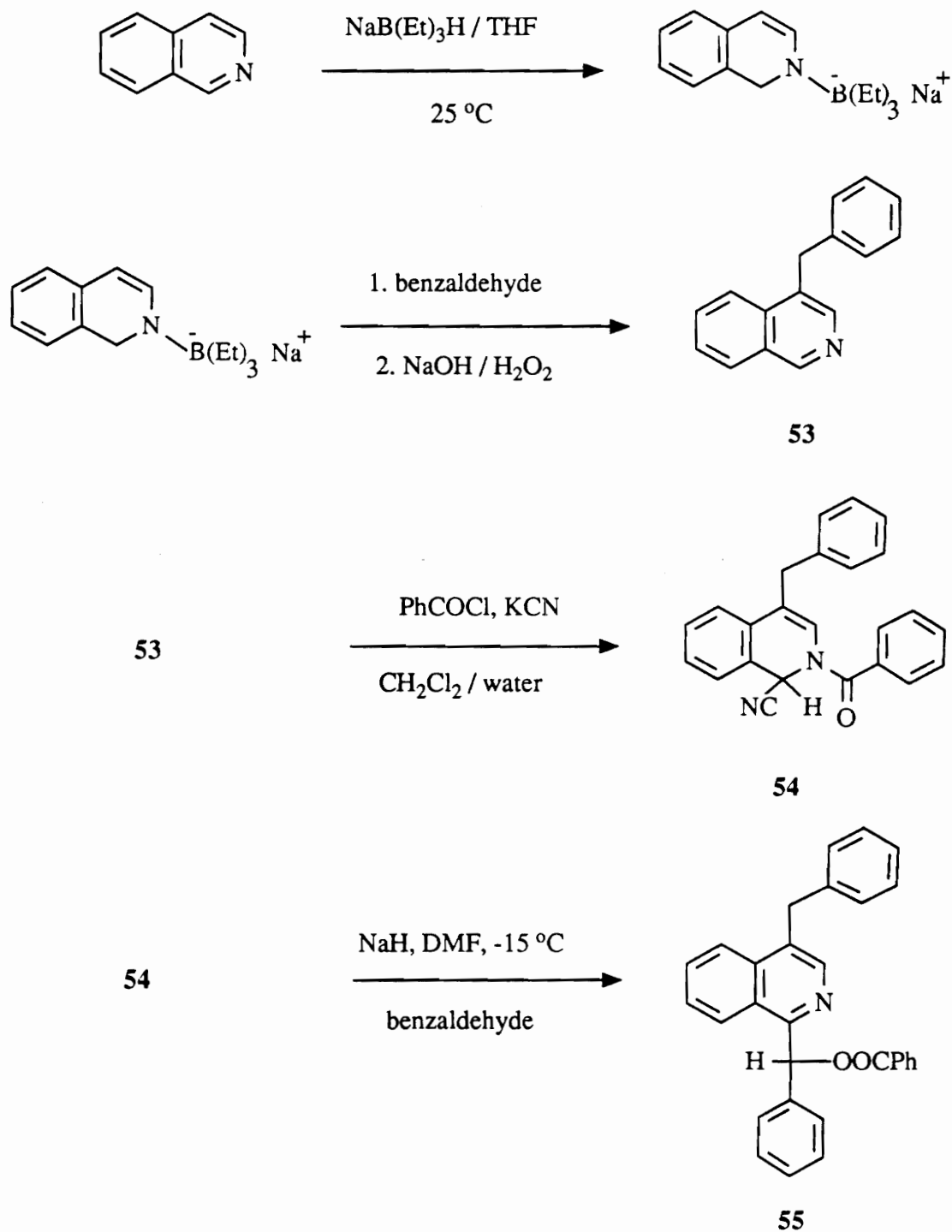


Scheme 23: Proposed Thermolytic Loss of Benzoic Acid

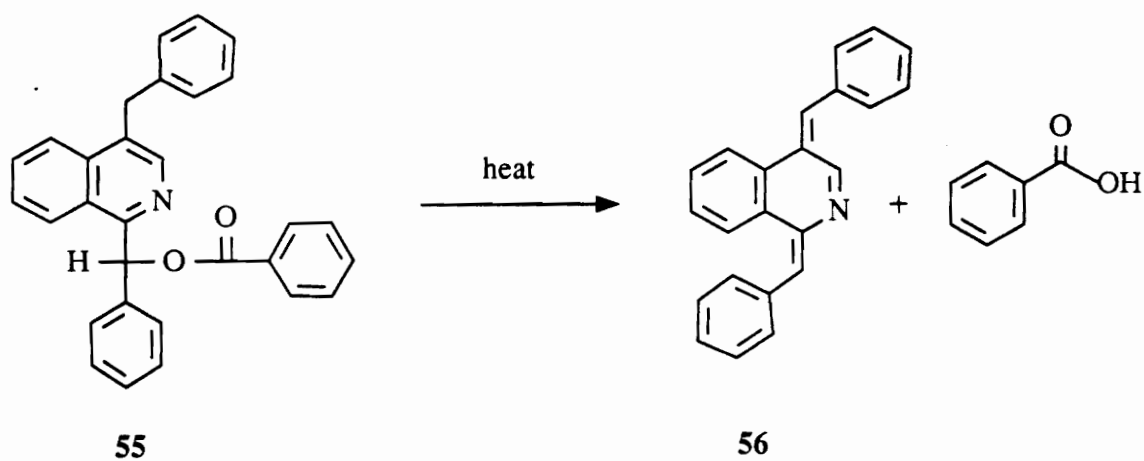
involved the preparation of 4-benzylisoquinoline, **53**, via the already mentioned reaction reported by Minter and Re.⁵² The crude yield of the product was 87%, melting at 115-118 °C (lit.⁵² m.p.: 117.5-118.5 °C). The NMR spectrum of the crude corresponded exactly with the reported spectrum and indicated purity greater than 95%. The Reissert compound, **54**, was prepared using crude **53** and the 2-phase method. After work-up and three recrystallizations from ethanol, an analytically pure sample melting at 186.2-187.2 °C was obtained. The PNMR spectrum of the pure sample showed an AB-pattern at 3.81 ppm, $J_{ab}=16$ Hz, corresponding to the methylene protons. The compound gave satisfactory elemental analysis.

The final step in the synthesis of the model compound **55** was condensation with benzaldehyde. The reaction was carried out in the same manner as the polymerization, i.e., in DMF at -15 °C and under nitrogen. At the end of the reaction, the solution was chalky yellow in color. After quenching by precipitation into water, the crude yield was found to be 94%. Recrystallization from ethanol afforded the pure ester **55** melting at 137.5-138.2 °C. The FTIR spectrum of the product showed the ester carbonyl at 1702 cm^{-1} . The PNMR spectrum of the compound corresponded exactly with the structure of **55**.

The TGA of the pure ester was then performed. Scheme 25 shows the proposed reaction products, including the quinoidal structure **56**. Benzoic acid calculates to be 28% of the ester by weight. Therefore, the TGA should reflect this loss between 260-320 °C. Instead, the TGA in air (TGA #2, Appendix D) showed loss of 90% between 250-350 °C. Moreover, TGA under nitrogen showed the same loss behavior. It is possible that the ester simply distilled at that temperature, or that the quinoidal structure **56** is volatile and either



Scheme 24: Synthesis of Model 4-Benzylisoquinolyl Ester

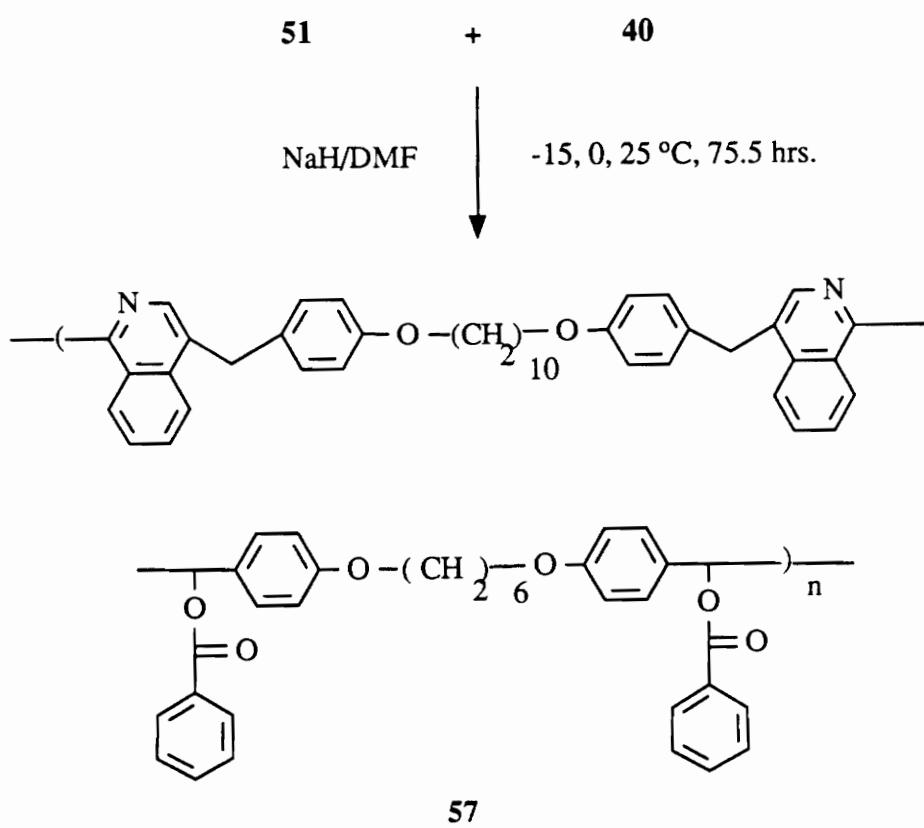


Scheme 25: Proposed Reaction Products of Thermolysis of Model Compound.

distilled or sublimed at higher temperatures.

To determine whether the conditions could be optimized, another polymerization was attempted using the C₁₀-bis-Reissert compound and C₆-dialdehyde, **40**, depicted in Scheme 26. The base/solvent system again was NaH/DMF. The reaction time was extended to 75.5 hours. After quenching and precipitation from chloroform into methanol, the yield of polyester **57** was 71%. The FTIR of the polymer showed ester carbonyl at 1721 cm⁻¹ and complete loss of the amide carbonyl. The DSC of the polymer showed T_g at 93 °C in the first heat; again, no T_m was observed. The TGA of the polymer revealed stability up to 200 °C in air, losing approximately 18% by weight between 200 and 325 °C. Benzoic acid constitutes 21% of the repeat unit by weight.

The GPC of the above polymer (GPC #1, Appendix E) showed the presence of low molecular weight species which caused M_n= 1200 and M_w= 40,000, i.e., polydispersity of 33.8! The low value of M_n and large value of the polydispersity may be attributed to rearrangement of the Reissert anion which would terminate polymer growth. The polymer was fractionated using CHCl₃ and methanol. After two fractionations, the polymer was dried and resubmitted for GPC (GPC #2, Appendix E). The molecular weight distribution did in fact improve: M_n was found to be 31,000, M_w= 69,000, the polydispersity ratio being 2.21. The intrinsic viscosity improved to 0.36 dl/gram, compared to 0.30 dl/gram for the unfractionated sample. A film of the unfractionated sample was solution cast from chloroform and submitted for mechanical testing. The tensile strength was found to be 13 MPa for a maximum strain of 3%, which are not very impressive values. The low molecular weight species present in the sample may have behaved as plasticizers,

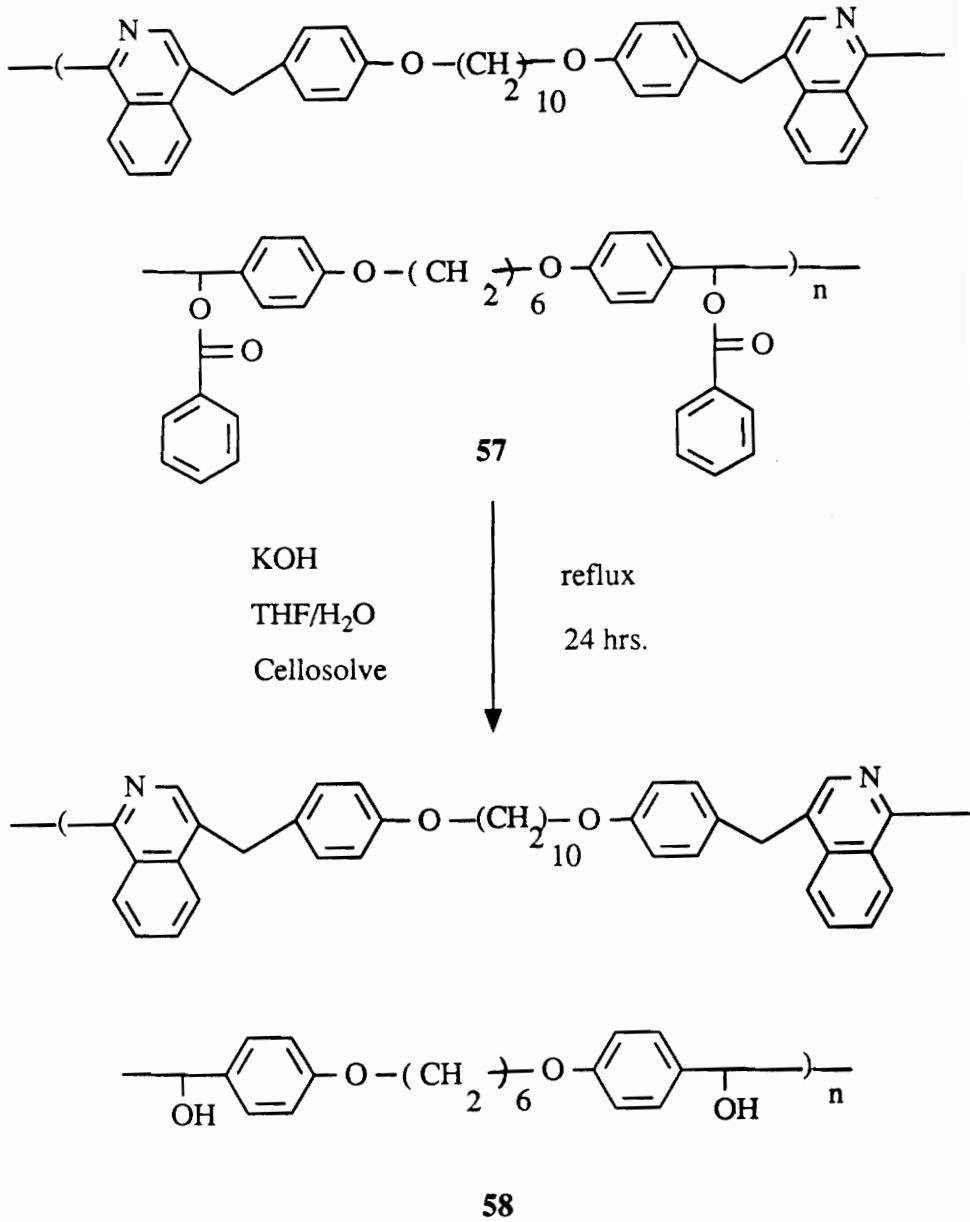


Scheme 26: Polymerization of C₁₀-bis RC with C₆-dialdehyde

weakening the polymer sample. The mechanical properties of the fractionated sample were not determined.

Analogous to the monomeric ester hydrolysis, the ester groups of the above polyester could be hydrolyzed using KOH as base by a procedure reported by Gibson and Bailey.⁵⁴ The polyester would then yield the novel polyalcohol, **58**, as depicted in Scheme 27. Polyester **57** was dissolved in THF and the theoretical amount of KOH was added, along with a few drops of water and 2-ethoxyethanol (Cellosolve). The solution was refluxed for 18 hours and precipitated thereafter. The FTIR spectrum of the polyalcohol (IR #2, Appendix B) showed complete loss of ester carbonyl at 1720 cm^{-1} . The TGA of the polymer showed stability up to $300\text{ }^{\circ}\text{C}$. The loss of 18% mass between $200\text{-}300\text{ }^{\circ}\text{C}$ was absent, supporting the presumption that the ester groups were thermolytically cleaving. DSC of the polyalcohol showed T_g at $86\text{ }^{\circ}\text{C}$, which is lower than the ester. The polyalcohol had a tensile strength of 38 MPa for a maximum strain of 6%. Compared to the parent polyester, the polyalcohol is a tougher, more extensible material, largely due to the effects of hydrogen bonding in the latter.

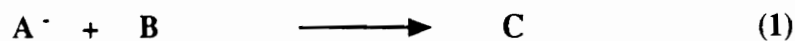
To determine whether a different base/solvent system would lead to higher molecular weight, the polymerization shown in Scheme 26 was repeated using n-butyllithium/THF on a small scale. The bis-Reissert compound, **51**, was dissolved in THF and cooled to $-78\text{ }^{\circ}\text{C}$. Keeping approximately 1 gram of **51** in solution at $-78\text{ }^{\circ}\text{C}$ required 30 ml THF, or a 3.3% solution by weight. The n-butyllithium was then added in one portion, followed after 15 minutes by the addition of the dialdehyde, **40**. The reaction was continued for 26.5 hours at -78°C , at the end of which, the solution was light brown and



Scheme 27: Hydrolysis of Polyester to Yield Novel Polyalcohol

slightly viscous. After work-up, the yield of light yellow powdery polymer was 44%. The FTIR spectrum of the polymer was identical to that prepared by NaH/DMF, showing complete loss of amide carbonyl absorption. However, the intrinsic viscosity was found to be 0.16 dl/gram in chloroform at 25 °C. Clearly then, NaH/DMF is the base/solvent system of choice. One possible reason why NaH yields higher molecular weights than n-BuLi is that the latter base is more nucleophilic and therefore is more likely to attack the amide carbonyl. Such a reaction would upset the reaction stoichiometry and therefore lead to lower molecular weights. The solvent also plays an important role in polymerizations. Condensation polymerizations are typically run at solution concentrations of 15-30 weight percent with respect to the monomers. Dilute concentrations generally lead to longer reaction times, cyclic polymers, and therefore lower molecular weights. Comparing the two solvents in the above polymerizations, DMF seems to be a better solvent because higher concentrations are possible when it is used. The results of the polymerization of C₁₀-bis-Reissert compound **51** with dialdehydes are summarized in Table 6.

As mentioned, the high polydispersity in the preceding polyester was attributed to rearrangement of the Reissert anions prior to condensation with the aldehyde groups. This phenomenon can be explained in terms of the kinetics of the polymerization. The reactions of interest are:



A⁻ represents the Reissert anion, B represents the aldehyde moiety, C represents the ester,

Table 6: Summary of Results of Polymerization of 51 with Dialdehydes:

<u>Trial</u>	<u>Bis-RC</u>	<u>Dialdehyde</u>	<u>[η]^a</u>	<u>T_g</u> ^{°C}	<u>M_w</u>	<u>M_n</u>	<u>M_w/M_n</u>
1 ^b	51	44	0.31	79	35K	4.1K	8.56
2	51	40	0.30	83	40K	1.2K	33.8
2 ^c	51	40	0.36	--	69K	31K	2.27
3 ^d	51	40	0.16	--	--	--	--

(a) intrinsic viscosities were determined in chloroform at 25 °C and given in units of dl/gram,

(b) trials 1 and 2 were done using sodium hydride/DMF at -15-0 °C, (c) trial 2 fractionated using chloroform and methanol, (d) base/solvent was n-butyllithium/THF at -78 °C.

and **D** represents the rearranged ketone. The rate expressions for reactions **1** and **2** are:

Rate of **1** (polymerization): $-d[A^-]/dt = k_1[A^-][B]$

Rate of **2** (termination): $-d[A^-]/dt = k_2[A^-]$

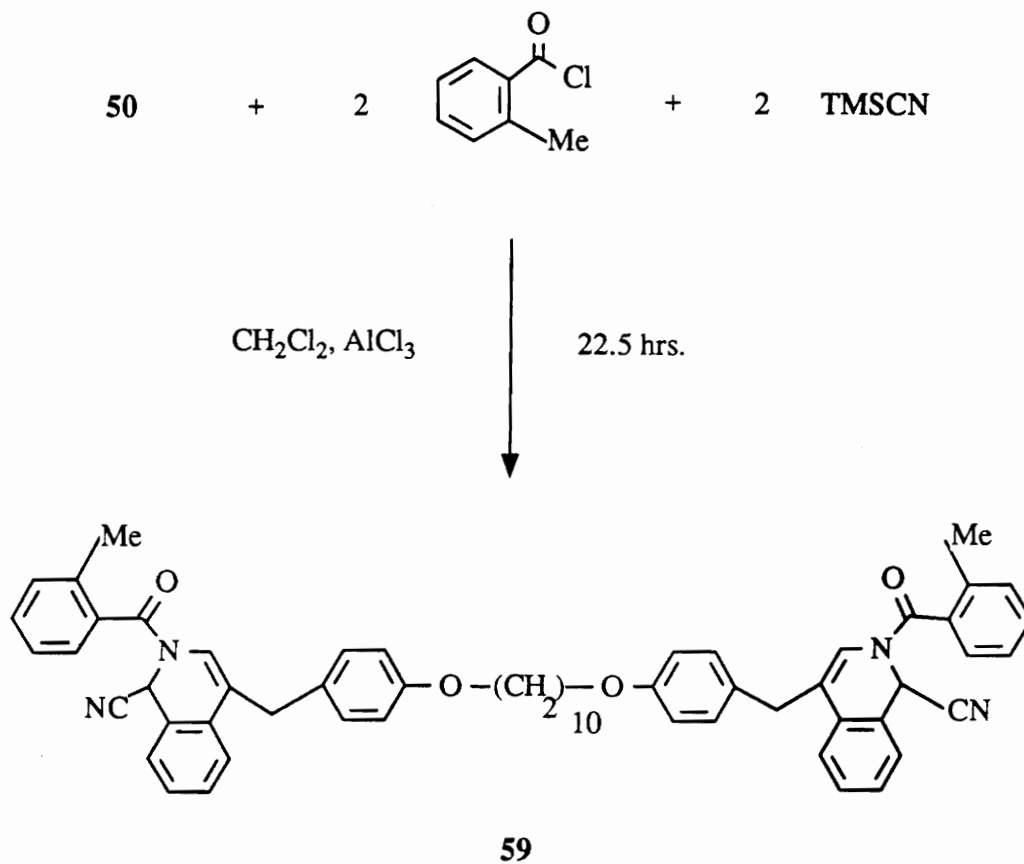
The ratio of the rate of polymerization to the rate of termination then is:

$$\text{Rate 1/Rate 2} = k_1[B]/k_2$$

High molecular weight polymer will be formed only if $k_1[B] \gg k_2$, naturally. However, as the reaction proceeds, **[B]** will decrease, which means that the unimolecular rearrangement will become more significant, leading to termination of the growing polymer chains, which explains the large polydispersity observed in the preceding polyester.

Eliminating the rearrangement reaction should therefore lead to higher molecular weight and lower polydispersity. As mentioned in the Historical section, Gibson found that the anion of the Reissert compound **28**, derived from isoquinoline and *o*-toluoyl chloride, does not rearrange at room temperature due to the steric effects induced by the *o*-methyl group.³⁰ Extending to the present work, the bis-Reissert compound **59** was prepared from bis-isoquinoline **50** and *o*-toluoyl chloride, as indicated in Scheme 28. The preparative method was the familiar TMSCN method, which afforded a crude yield of 96% after work-up. The pure compound was isolated by chromatography followed by recrystallization from ethyl acetate/hexane. The ¹H NMR spectrum of the analytical sample showed the *o*-toluoyl methyl protons as a doublet, *J* = 1.5 Hz, at 2.25 ppm. The diastereotopic diaryl methylene protons were observed as an AB-pattern at 3.68 ppm, *J*_{ab} = 15 Hz.

The bis-Reissert compound **59** was used in two small scale polymerizations. The



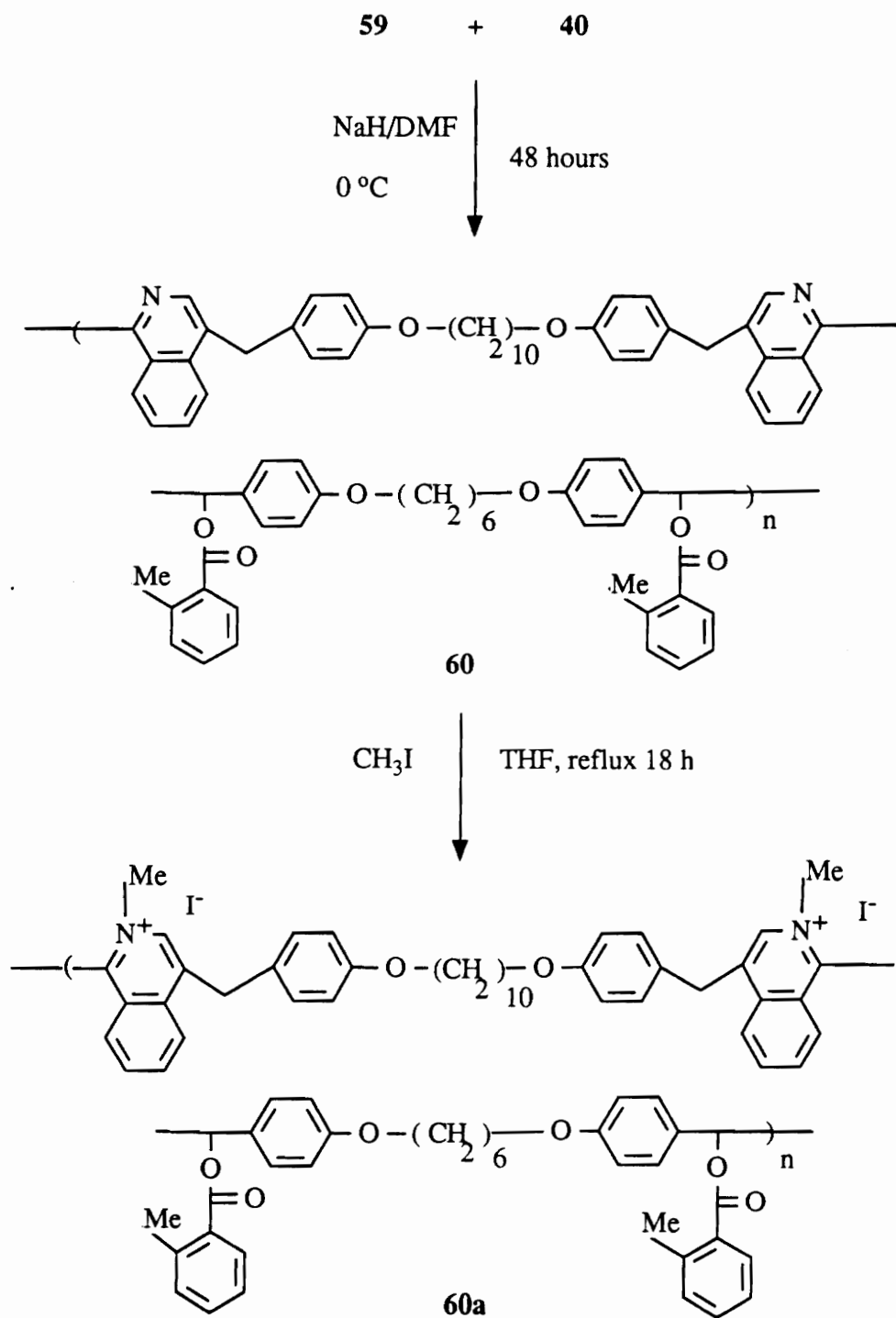
Scheme 28: Synthesis of *o*-Toluoyl C_{10} -bis-Reissert Compound

dialdehyde in both trials was the C₆-dialdehyde, **40**; the base/solvent system was NaH/DMF, and the reaction time was 48 hours, shown in Scheme 29. However, the technique was varied in order to examine an overlooked parameter. In the first trial, the dialdehyde was added *after* the base, whereas in the second trial, the dialdehyde was added *before* the base. If the second trial produced lower molecular weight polymer, it would be safe to assume that the base had reacted with the aldehyde groups thus upsetting the stoichiometry. For comparison, the polymer shown in Scheme 22 was prepared by the first technique, whereas the polymer shown in Scheme 26 was prepared by the second technique. The latter yielded the polydispersity of 33.8, as already mentioned.

The stoichiometry of the monomers in both polymerizations was 0.984:1.000 due to an error in the calculation of the bis-Reissert compound molecular weight. Hence, there was a slight excess of the dialdehyde. The maximum degree of polymerization could be calculated via the equation:

$$X_n = (1+r)/(1-r),$$

where *r* is the monomer imbalance ratio, e.g., 0.984/1.000. The value of *X_n* calculates to be 124, which corresponds to the number average molecular weight of approximately 145,000 assuming that the condensation reaction was quantitative. The two polymerizations were subjected to identical work-ups. The first trial, where the dialdehyde was added *after* the base, yielded 75% of an off-white polymer with an intrinsic viscosity of 0.60 dl/gram in chloroform at 25 °C. The second trial, where the dialdehyde was added *before* the base yielded 67% of an off-white polymer with an intrinsic viscosity of 0.58. Both polymers had T_g of 87 °C and lost 20% by weight between 225-350 °C in air.



Scheme 29: Polymerization of *o*-Toluoyl Bis-Reissert Compound
with C₆-dialdehyde and Subsequent Methiodide Formation

The GPC's of both polymers were determined in THF using a Styragel column and polystyrene standards. The molecular weights were determined manually by dividing the raw elution curve into 50 segments and reading the peak height at each increment. The data was then fed into a MacIntosh computer which calculated M_w , M_n , and polydispersity ratios. The results are summarized in Table 7. As evident, the polydispersity ratios improved to near the theoretical value of 2. Thus, eliminating the rearrangement led to higher molecular weights and better polydispersities, even though there was an imbalance of the monomers. Also, addition of base before or after the aldehyde has no effect on the polymerization.

The isoquinolyl rings in the above polyesters were quaternized on a small scale with methyl iodide using a procedure reported by Gibson and Bailey.⁷⁰ After 18 hours of reflux, an orange polymer precipitated from THF. The polymethiodide was found to be slightly soluble in chloroform, and soluble in dichloromethane and in DMF. Once in solution, the polymer did not precipitate from methanol. The crude polymer was dissolved in CH_2Cl_2 and precipitated into hexane. The final polymer was dried for 2 days under vacuum at 67 °C to yield 66% of an orange solid. The FTIR spectrum of the polymer showed a broad baseline absorption between 2200 and 2600 cm^{-1} supporting the presence of quaternary salts. The DSC of the polymer did not show any transitions before 110 °C, the point at which the polymer showed weight loss in TGA under air. The NMR spectrum of the polymer showed two *o*-toluoyl methyl signals, indicating incomplete methiodide formation. The methyl protons of the methiodide were observed at 4.85 ppm. The product must therefore be a random copolymer containing quaternized and unquaternized isoquinolyl

Table 7: GPC Results of Polymerization of 59 with 40:

<u>Trial</u>	<u>[n]^a</u>	<u>T_g °C</u>	<u>M_n</u>	<u>M_w</u>	<u>M_w/M_n</u>
1 ^b	0.60	87	22.4K	54.7K	2.43
2 ^c	0.58	87	22.5K	57.3K	2.54

(a) units of dl/gram, in chloroform at 25 °C; (b) NaH/DMF method: dialdehyde added after NaH; (3) NaH/DMF method: dialdehyde added before NaH.

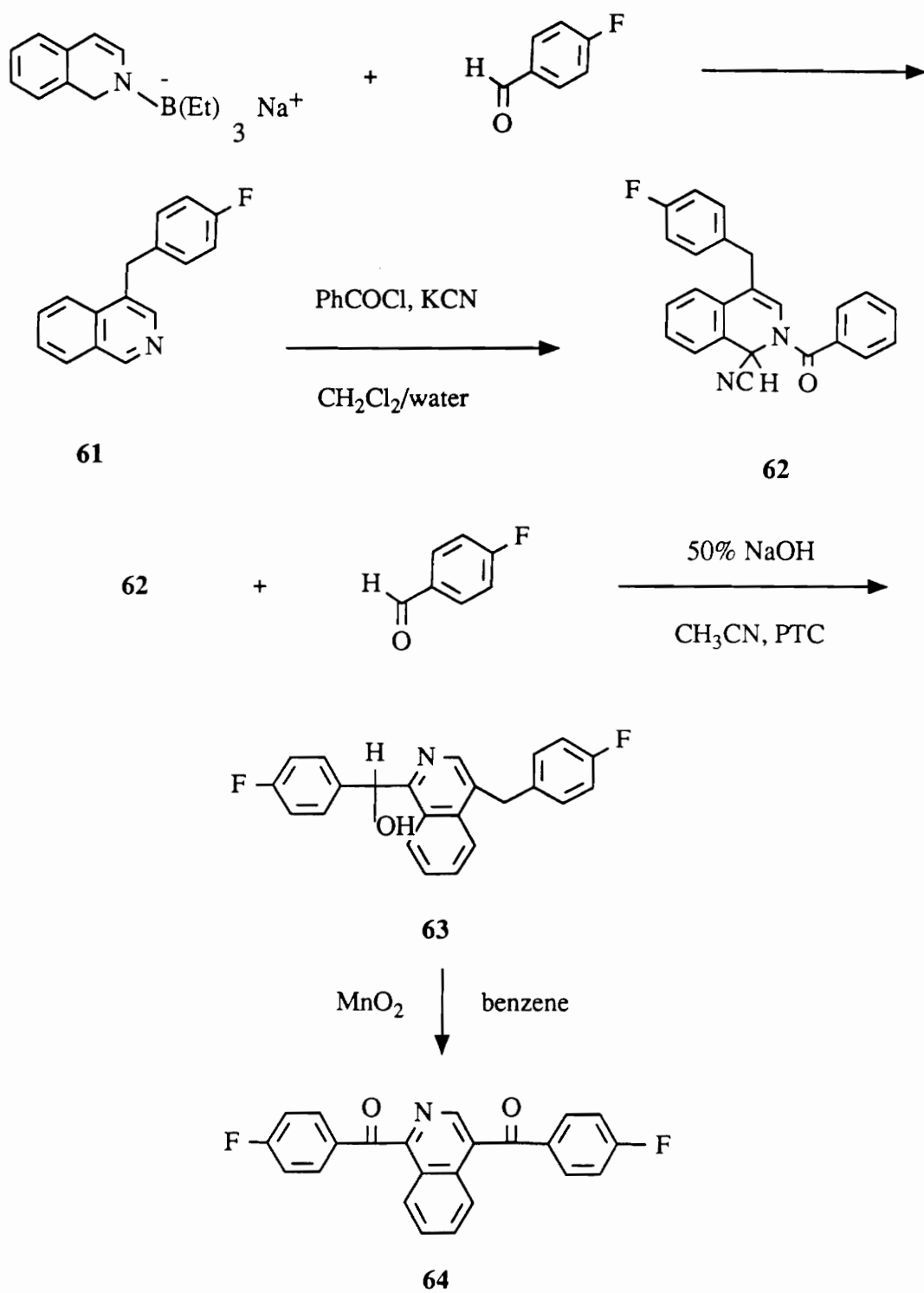
rings.

3.3. Synthesis of Novel Isoquinolyl Difluorodiketone:

Another extension of the reaction reported by Minter and Re is the synthesis of 4-substituted isoquinolines containing a reactive functionality on the benzyl ring. Subsequent formation of the Reissert compound, followed by condensation with an aldehyde that contains another reactive moiety leads to a difunctional monomer containing an isoquinoline ring. The reactive functionality examined was fluorine, as depicted in Scheme 30, leading to a novel isoquinolyl difluorodiketone. The individual steps in the synthetic scheme will be discussed below.

The first step in the synthesis of the difluorodiketone was the preparation of 4-(p-fluorobenzyl)isoquinoline, **61**. The reaction, which was run on a 62 gram scale, afforded 97% of a crude viscous orange oil. The ¹H NMR spectrum showed that the actual yield of the desired product was 80% by comparing the integration ratios of the methylene protons to the aromatic protons. After column chromatography and recrystallization from ethanol/water, pure **61** was obtained. The results of the elemental analysis were satisfactory. The ¹H NMR spectrum of the analytical sample of **61** showed the methylene protons as a singlet at 4.34 ppm.

The next step was the preparation of the benzoyl Reissert compound, **62**, via the 2-phase method. The crude 4-substituted isoquinoline from the previous step was used, correcting the stoichiometry for the 80% purity. After work-up, the crude yield of the Reissert compound was >100%. Recrystallization from ethanol afforded the desired



Scheme 30: Synthesis of Novel Difluorodiketone Monomer

product in 70% isolated yield (3 crops). Repeating this reaction, the isolated yield of the Reissert compound was 78% (3 crops). Further recrystallizations from ethanol yielded the pure compound, which gave satisfactory elemental analysis. The ¹H NMR spectrum of **62** is interesting in that it shows an AB-pattern at 3.80 ppm, $J_{ab} = 15$ Hz, corresponding to the diastereotopic methylene protons. The FTIR spectrum of **62** showed the amide carbonyl absorption at 1676 cm⁻¹.

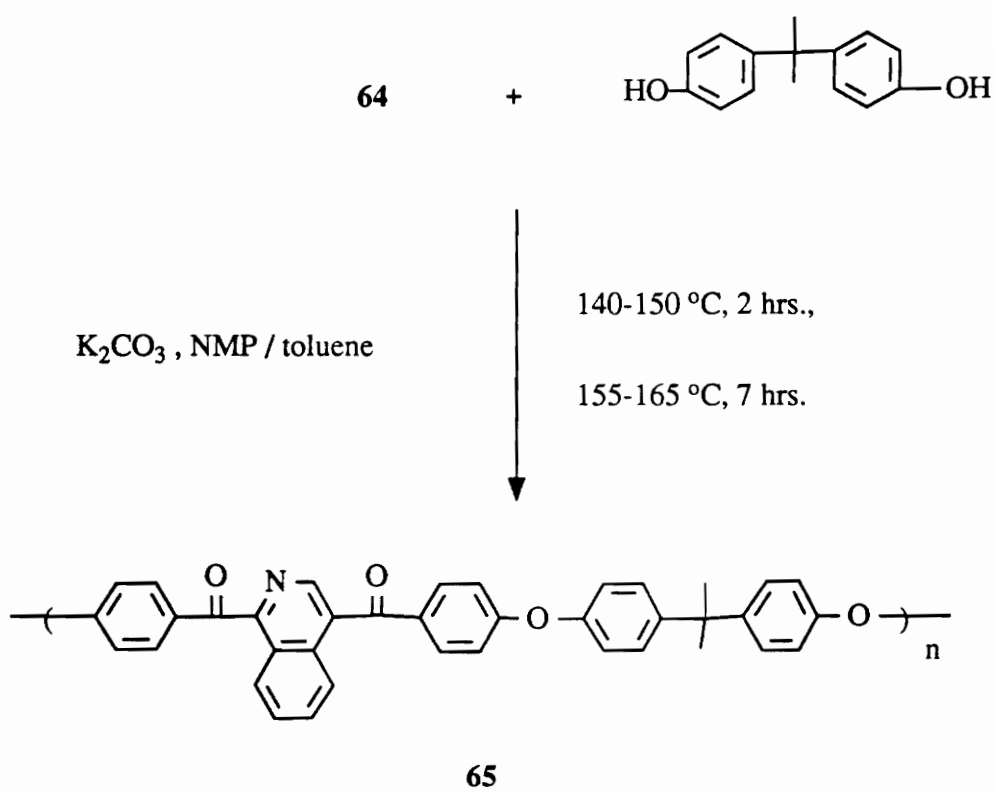
Condensation of **62** with 4-fluorobenzaldehyde yielded the alcohol, **63**, shown in Scheme 30. The preparative method chosen was the 2-phase method initially reported by Jonczyk.³⁵ The only modification was applied heat to ensure complete hydrolysis of the ester to the alcohol. In the first trial, the FTIR spectrum of the crude product showed ester carbonyl at 1720 cm⁻¹, signifying incomplete reaction. Using the hydrolysis method reported by Gibson,⁵⁴ the desired alcohol, **63**, was obtained in 87% total yield, confirmed by the disappearance of the ester carbonyl absorption and the appearance of the hydroxyl absorption of the alcohol in FTIR spectrum. In the second trial, the reaction was allowed to continue longer; the crude yield became quantitative and contained only **63** as evident by the FTIR spectrum. After two recrystallizations from ethanol, pure **63**, mp 127-8 °C, was obtained. The results of elemental analysis were satisfactory. The ¹H NMR spectrum of the pure sample showed methylene protons as a singlet at 4.40 ppm, methine proton at 6.35 ppm, and hydroxyl proton at 6.20 ppm.

The final step in the synthesis of the difluorodiketone **64** was oxidation of the alcohol and methylene moieties to ketones. Attempts using sodium dichromate/acetic acid resulted in complete oxidation of the alcohol, but only partial oxidation of the methylene

even after extended reaction times. A brief survey of known oxidative methods in the literature revealed that $\text{MnO}_2/\text{benzene}$ ⁵⁶ was the most economical method to effect the desired oxidations, compared to other more exotic and more expensive reagents. Oxidation of the alcohol using $\text{MnO}_2/\text{benzene}$ was therefore carried out. In the first trial, the crude yield was 54% and contained the desired diketone **64** exclusively. A second trial produced the same yield; however, when the MnO_2 at the end of the reaction was extracted with chloroform in a Soxhlet apparatus for 24 hours, the yield of **64** improved to 70%.

Recrystallization of the diketone from ethanol afforded the pure compound which gave satisfactory elemental analysis. The PNMR spectrum of the analytical sample (NMR #7, Appendix A) showed the isoquinolyl H_3 proton at 8.65 ppm. The FTIR spectrum of **64** showed both ketone absorptions at 1667 cm^{-1} . Apparently, the difference in absorptions between the two ketones is less than the instrument's resolution.

After purification of the difluorodiketone, several polymerizations were carried out using readily available diphenols. The first diphenol employed was bis-phenol-A, using NMP/toluene as solvent/azeotroping agent and potassium carbonate as base.⁷² The polymerization is depicted in Scheme 31. The mixture was heated for 2 hours at 140-150 °C to ensure removal of the water/toluene azeotrope. Heating was then continued for an additional 9 hours. At the end of the reaction, the solution was moderately viscous and dark brown. The solution was diluted with CH_2Cl_2 , filtered to remove the salts, and acidified with glacial acetic acid. Precipitation of the polymer twice into methanol yielded 63% of tan-colored polymer, which was dried for 1.5 days at 100 °C under vacuum. The PNMR spectrum of the polymer supported the repeat unit structure and did not show any phenolic

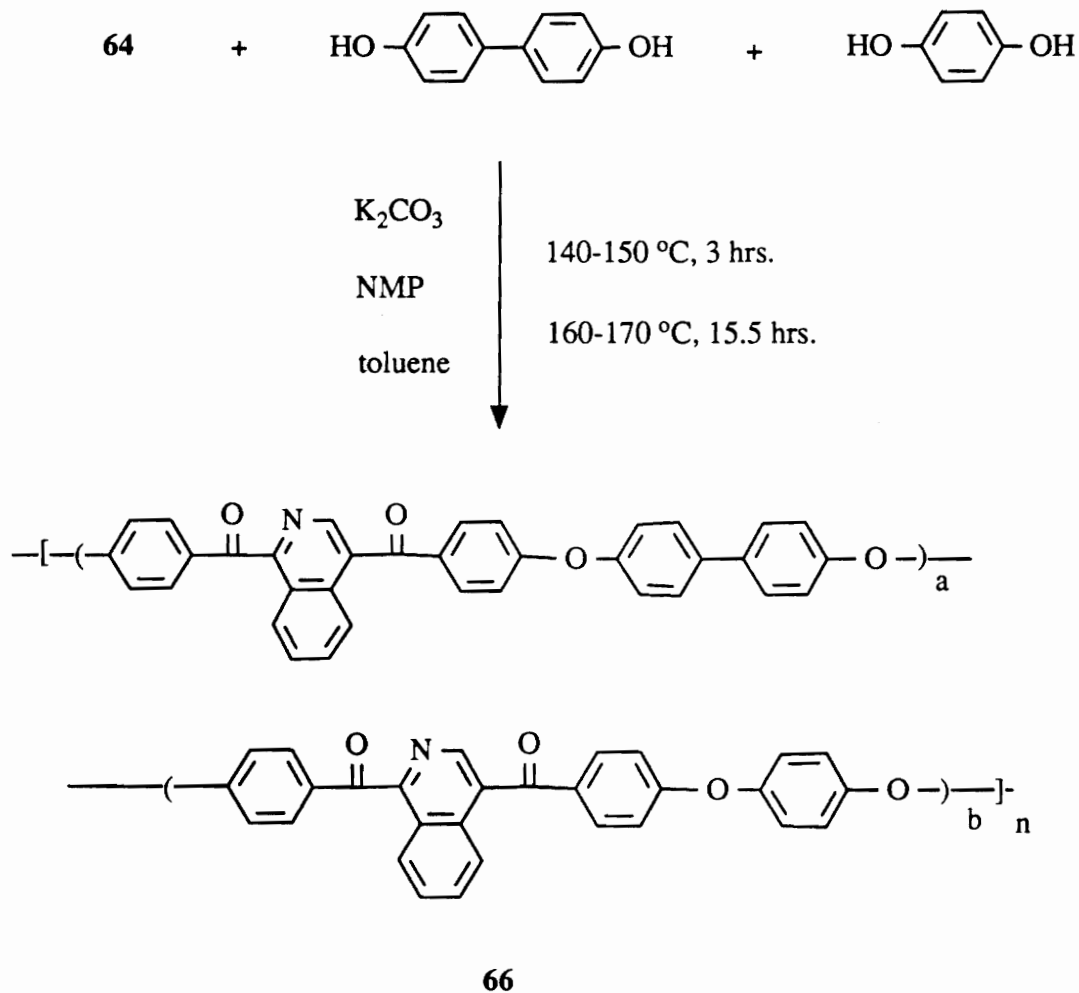


Scheme 31: Polymerization of **64** with Bis-Phenol-A

or fluoroaryl end-groups. The intrinsic viscosity of the polymer was 0.39 dl/gram in chloroform at 25 °C. The thermal properties of the polymer are as follows: T_g observed at 181 °C, no T_m was observed; stable up to 450 °C in air.

Other than bis-phenol-A, the most readily available and economical diphenols are hydroquinone and biphenol. It was assumed that the homopolymers resulting from both diphenols and the mentioned difluoroketone would be crystalline and would therefore precipitate during the polymerization. To avoid this problem, a copolymer was synthesized utilizing a mixture of hydroquinone and biphenol. It is well known that using mixed monomers, one can generally avoid crystallinity in the polymer by reducing the symmetry of the repeat unit structure. This holds true for random copolymers only, and not necessarily for alternating and block copolymers.

The copolymerization was carried out using a 1:1 mixture of hydroquinone and biphenol, as shown in Scheme 32. As before, the solvents and base used were NMP/toluene and potassium carbonate. The reaction was heated to 145 °C and kept there for 3.5 hours to ensure removal of toluene/water, aided by a strong flow of nitrogen. The temperature was then raised to 165-170 °C and the reaction was continued for 15.5 hours. At the end of the reaction, the mixture was noticeably viscous and dark brown in color. After work-up, the yield of tan-colored fibrous copolymer, **66**, was 50%. The ¹H NMR spectrum of the copolymer (NMR #8, Appendix A) indicated that the molar composition of the copolymer was approximately 50:50, as expected. The GPC of the copolymer in chloroform showed M_n = 4300, M_w = 17,000, the polydispersity being 3.94. The intrinsic viscosity was found to be 0.28 dl/gram. The TGA of the polymer revealed stability up to 400 °C in air, losing



Scheme 32: Copolymerization of **64** with Hydroquinone and Biphenol

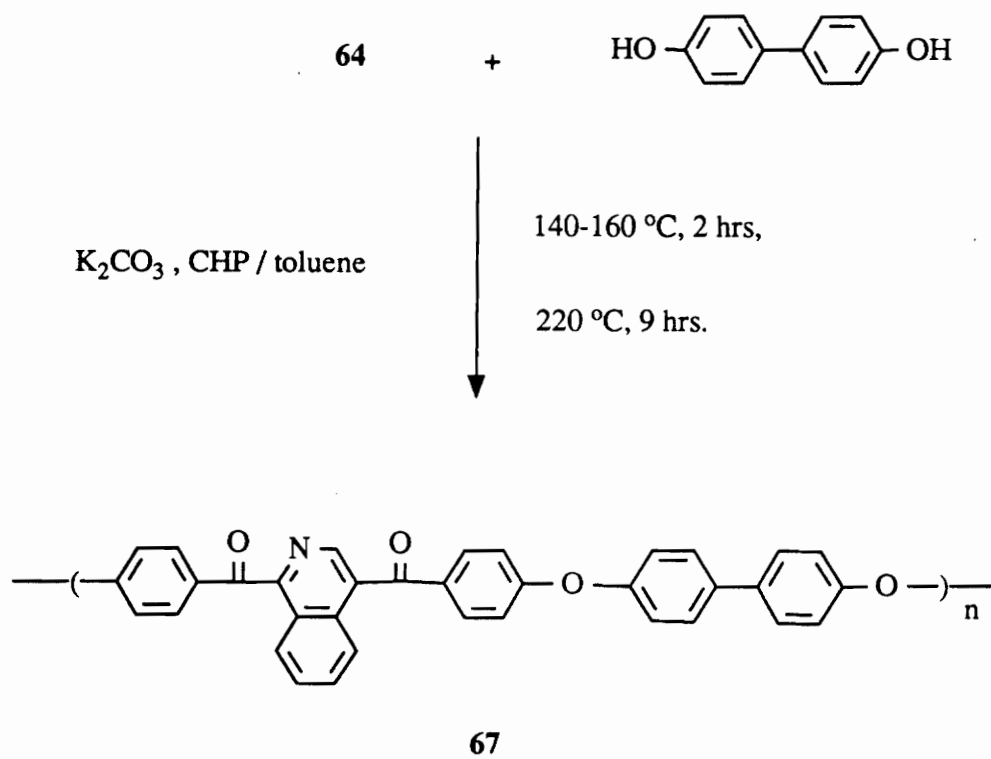
approximately 18% of its weight between 400-500 °C. The DSC of the copolymer showed T_g at 199 °C; no T_m was observed as expected.

Having successfully prepared the above copolymer, the homopolymers could be prepared. Limited supply of the difluoro monomer allowed the preparation of only one homopolymer. Biphenol was selected, rather than hydroquinone, for the polymerization depicted in Scheme 33. It was assumed that this polymer would be crystalline and therefore require higher reaction temperatures. Rather than diphenyl sulfone as solvent, 1-cyclohexyl-2-pyrrolidinone (CHP) was used since it is stable up to 230 °C under nitrogen. The reaction was allowed to reach 220 °C and kept there for 9 hours. At the end of the reaction, the solution was dark brown and moderately viscous. After 2 precipitations from THF into 50:50 acetone:methanol, a tan fibrous polymer was obtained in 52% yield. The intrinsic viscosity of the polymer was 0.34 dl/gram in chloroform at 25 °C. The TGA of the polymer in air revealed stability up to 480 °C. DSC of the polymer (DSC #2, Appendix C) showed T_g at 209 °C; no T_m was observed. The lack of crystallinity can be attributed to the lack of symmetry arising from the nitrogen of the diketone.

From the data obtained from the copolymer and the preceding homopolymer, an estimation can be made of the properties of the remaining homopolymer that can be prepared from hydroquinone. Assuming that the copolymer composition was random, the glass transition of the copolymer should fall between those of the corresponding homopolymers. The T_g of the copolymer often is a weighted average, given by:⁵⁷

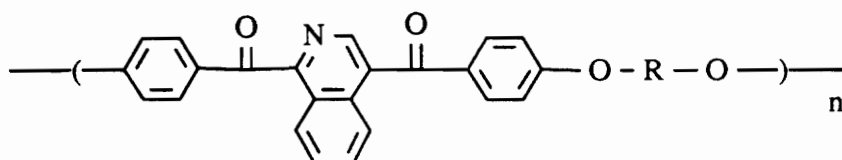
$$a_1 w_1 (T_g - T_{g1}) + a_2 w_2 (T_g - T_{g2}) = 0$$

where T_{g1} and T_{g2} represent the T_g of the homopolymers, w₁ and w₂ represent the weight



Scheme 33: Polymerization of 64 with Biphenol

fractions of the two monomers in the copolymer, and a_1 and a_2 are variables that depend on the type of monomers. The copolymer as mentioned was made using a 1:1 molar ratio of the two diphenols, which corresponds to the weight fractions of 37% for hydroquinone and 63% for biphenol. Solving the above equation and assuming that a_1 and a_2 are equal, the T_g of the homopolymer prepared from hydroquinone calculates to be 183 °C. Table 8 is a summary of the results of the novel poly(N-aryl-ether-ketones).

Table 8: Summary of the Properties of Novel Poly(N-aryl-ether-ketones):

<u>R</u>	<u>[n]* (dl/g)</u>	<u>Tg (°C)</u>
	0.39	181
	0.34	209
	0.28	199

* At 25 °C in chloroform

V. CONCLUSIONS AND FUTURE WORK:

The regioselectivity study of alkylation of quinoline Reissert compound showed that 1,4-dihydroquinoline Reissert compounds exist, contrary to popular belief. The initial alkylation was found to occur 86% at the 4-position and 14% at the 2-position. The second alkylation occurred at the 2- and 4-positions to nearly the same extent. More importantly, the study showed that quinoline Reissert compounds could not be directly used as difunctional monomers in step-growth polymerizations. Initial alkylation at the 2-position, as well as rearrangement to the ketone would lead to inactive terminal groups and lead to low molecular weights.

It was found that the A-B monomer prepared from quinoline and 4-formylbenzoyl chloride could be polymerized interfacially (by accident) to yield a poly(ester-co-amide). The T_g of the copolymer was 190 °C, even though the molecular weight was low. The poor yields of the Reissert compound were a consequence of the attack of TMSCN on the aldehyde groups. The resulting cyanohydrin silyl ether decomposed under acidic workup conditions to yield back the aldehyde groups.

An A-A monomer was prepared from isoquinoline and 4,4'-oxydi(benzoyl chloride). The resulting bis-Reissert compound could be polymerized with 1,6-bis(*p*-formylphenoxy)hexane to yield a novel polyester exhibiting T_g at 122 °C. The molecular weights were low as a consequence of the destabilizing effect the ether linkage would have on the Reissert anion.

The need for easily preparable bis-isoquinolines led to the synthesis of five such

compounds by adaptation of an efficient reaction reported by Minter and Re.⁵² Two novel bis-Reissert compounds were prepared from C₁₀-bis-isoquinoline. Condensation of the bis-Reissert compounds with dialdehydes afforded three novel high molecular weight N-heterocyclic polyesters. The optimum base/solvent system was found to be NaH/DMF rather than n-BuLi/THF. The optimum reaction temperature for the NaH/DMF system was found to be -15 to 0 °C. It was also observed that elimination of rearrangement via ortho substitution on the aroyl group led to higher molecular weights and lower polydispersities.

The polyesters prepared from the above bis-Reissert compounds exhibited a mass loss of 18-21% in TGA. A model study was performed to examine whether the ester groups were thermally cleaving; this study gave inconclusive results. However, when the ester groups were chemically hydrolyzed to yield the polyalcohol, the weight loss in TGA was absent, supporting the hypothesis that the ester groups underwent thermolytic cleavage, eliminating the carboxylic acid and forming quinoidal backbone elements. The isoquinoline rings in one of the above polyesters could be partially quaternized with methyl iodide. The resulting polymethiodide was insoluble in THF, and would not precipitate from methanol or water.

A novel heteroaryl difluorodiketone was prepared using Reissert compound chemistry and the mentioned enamine reaction. This monomer could be polymerized with diphenols via standard techniques to yield a series of novel poly(N-arylene-ether-ketones) exhibiting T_g as high as 209 °C. Although no similar polymers exist for comparison, it is believed that the high thermal properties of these polymers are a consequence of the

inclusion of isoquinolyl rings in the polymer backbone.

The future work pertaining to the results contained in this thesis must include a scale-up of the difluorodiketone synthesis. Polymerizations using this monomer should then be attempted on larger scales in order to avoid the weighing errors and resultant stoichiometric imbalances associated with the small scale polymerizations reported herein. Increases in the viscosities of the same polymers will be anticipated. Most importantly, hydroquinone should be polymerized with the above difluorodiketone to verify the calculated T_g of 183 °C. Other base/solvent systems should be considered, as well. For example, use of diphenylsulfone as solvent would allow reaction temperatures as high as 275 °C.

The poly(N-arylene-ether-ketones) reported in this thesis should be considered for high temperature adhesive applications. The presence of polar moieties, such as imines and ketones, would favor strong interactions between the polymer and substrate, and therefore lead to high adhesive strengths. To evaluate the feasibility of their use in adhesive applications, mechanical testing of the polymers must be initially performed. Such tests must include single lap-shear and stress-strain measurements.

Of the bis-isoquinolines reported in this thesis, only the C₁₀-bis-isoquinoline has been converted to the bis-Reissert compound. Bis-Reissert compounds can be prepared using the remaining four, which may then be polymerized with other readily available dialdehydes, such as iso- and terephthalaldehyde. Some crystallinity would be expected from the use of the latter dialdehyde.

The 4-alkylation reaction reported by Minter and Re⁵² may be exploited further.

Use of aldehydes with functionalities other than fluoro-, e.g., hydroxy, carboxy and nitro, would produce other novel 4-substituted isoquinolines that may be used as monomeric precursors. For example, incorporation of nitro groups in the diketone monomer could lead to the synthesis of a novel diamine by careful reduction of the nitro groups. The diamines could then be used to prepare polyimides that should exhibit high Tg's and thermal stabilities.

VI. EXPERIMENTAL SECTION:

General:

Melting points were determined in a Thomas-Hoover hot oil capillary melting point apparatus and are corrected unless otherwise indicated. The IR spectra were determined on KBr pellets or films cast from dichloromethane on a Nicolet MX-L FTIR spectrophotometer. The NMR spectra were recorded on a Bucker 270-MHz FT instrument. All proton NMR spectra were done in CDCl_3 with TMS as internal standard. The following abbreviations have been used in describing NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, or by Atlantic Microlab, Norcross, Georgia. Mass spectra were determined by VG Analytical 7070 EMS. Differential scanning calorimetry was performed by Paul S. Vail on a DuPont 912 Dual-Sample DSC interfaced with an IBM PS-2 Model 60. All DSC runs were performed under a nitrogen atmosphere. Unless specified, the heating rate for all DSC's was 10 °C/minute. Thermogravimetric analyses were performed by Paul S. Vail on a DuPont TGA 951 interfaced same as DSC. Atmospheres and heating rates/ranges for TGA are specified for each sample. Intrinsic viscosities were determined by David DeSante. Gel permeation chromatography (GPC) of polymeric samples were performed by Dr. Mia Siochi on a Waters 150-C Gel Permeation Chromatograph using a Viscotek 100 viscosity detector; this instrument provides absolute molecular weights (M_n , M_w) and Mark-Houwink constants. Some GPC's were performed by Charles Gutberlet on a Waters Model 590 GPC using a refractive index (RI) detector.

The universal calibration curve for this GPC was developed using polystyrene standards. Mechanical analyses were performed by Carl Anthony Williams on a Polymer Laboratories' Mini Mat. Dichloromethane was obtained as reagent grade from Fisher and used without drying. DMF (N,N-dimethylformamide), NMP (1-methyl-2-pyrrolidinone), and CHP (1-cyclohexyl-2-pyrrolidinone) were distilled from calcium hydride, and THF (tetrahydrofuran) from sodium/benzophenone prior to use. Sodium hydride was used as 55% or 60% dispersion in light mineral oil, as obtained from Aldrich Chemicals.

N-benzoyl-1,2-dihydroquinaldonitrile, 2, and

N-benzoyl-1,2-dihydroisoquinaldonitrile, 18: These were prepared via the methylene chloride/water method from quinoline (for **2**) and lepidine (for **18**), following the procedure of Popp, Blount, and Melvin.¹³ The crude yields were 78% and 63%, respectively. The observed melting points were: 149-151 °C for **2** (lit.²⁴ mp: 154-5), and 169-170 °C for **18** (lit.¹³ mp: 173-175 °C). The PNMR spectrum of **2** showed H₂ (d, J= 6 Hz, 6.19 ppm), H₃ (dd, J= 8, 6 Hz, 6.10 ppm), and H₄ (d, J= 8 Hz, 6.56 ppm). The PNMR spectrum of **18** showed a doublet at 2.22 ppm, J=1.5 Hz, along with the aromatic protons between 6 and 8 ppm.

Methylation of Lepidine Reissert Compound, 18: The procedure was based on that described by J. M. Wefer.²³ A mixture of 1.92 g (7.0 mmole) of **18** and 2.98 g (21.0 mmole) of methyl iodide was allowed to stir in 25 ml DMF for 30 minutes at 0 °C under nitrogen. Sodium hydride, 0.367 g (8.4 mmole, 55% dispersion), was added in one

portion. The resulting yellow mixture was allowed to stir at 0 °C for 4 hours, followed by four hours at room temperature. The mixture was poured over crushed ice and extracted with dichloromethane. The extract was washed 3 times with water and allowed to dry over magnesium sulfate. Removal of solvent afforded 1.67 g (83%) of a dark brown gummy solid. Thin layer chromatography (TLC) of the crude product using dichloromethane/silica gel revealed two spots, $\Delta R_f < 0.1$. Flash chromatography using dichloromethane/silica gel yielded 0.4 g (20%) of **19** and 0.4 g (20%) of **34**. Compound **19** was obtained pure from the column, mp 136-7 °C (lit. m.p.²⁶: 134-6). PNMR of **19** (NMR #2, Appendix A) showed: s, 1.84 ppm, 3H, 2-CH₃ protons; d, 2.19 ppm (J=1.5 Hz), 3H, 4-CH₃ protons; d, 5.88 ppm (J=1.5 Hz), 1H, quinolyl H₃; dd, 6.45 ppm (J=8 Hz, 1 Hz), 1H, quinolyl H₅; td, 6.85 ppm (J= 8 Hz, 1 Hz), 1H, quinolyl H₆; td, 7.02 ppm (J= 8 Hz, 1 Hz), 1H, quinolyl H₇; m, 7.2-7.5 ppm, 5H; dd, 7.58 ppm (J= 8 Hz, 1 Hz), 2H, aroyl 2,6 protons. Compound **34** was recrystallized from ethanol to mp 134-5 °C. PNMR of **34** (NMR #1, Appendix A) showed: s, 1.55 ppm, 6H, gem dimethyl protons; s, 6.47 ppm, 1H, quinolyl H₃; m, 7.0-7.5 ppm, 9H. Results of elemental analysis for **34**: C₁₉H₁₆N₂O, calc'd (found); %C, 79.14 (78.75); %H, 5.59 (5.57); %N, 9.72 (9.67); performed by Galbraith Laboratories.

The reaction was performed 2 additional times by the above procedure. Using 2.47 g (9.0 mmole) of **18**, 3.83 g of CH₃I (27.0 mmole), and 0.259 g (24.0 mmole) of 55% NaH, the crude yield was 2.28 gram (88%). Using 2.01 g (7.33 mmole) of **18**, 3.12 g (22.0 mmole) of CH₃I, and 0.35 g (8.80 mmole) of 60% NaH, the crude yield of 1.82 g (86%) was obtained. In all three trials, the percent compositions of the crude products were

determined in the following manner: two integrations were performed for each sample; the methyl regions in the spectra (1.00-4.00 ppm) were made full scale (25 cm); individual peaks were measured to the nearest 0.5 mm by ruler; estimated error in percent compositions is 2% or less. The relaxation delay in all proton NMR spectra was set at 2.0 seconds. The ratio of **19** to **34** was found to be 54:46, 58:42, and 60:40, or an average of $57 \pm 3:43 \pm 3$.

Dimethylation of Quinoline Reissert Compound, 2: A mixture of 2.60 g (10.0 mmoles) of **2** and 8.52 g (60.0 mmoles) of CH_3I in 30 ml DMF was cooled to 0 °C and stirred under nitrogen for 30 minutes. Then 0.96 g (22.0 mmoles) of 55% NaH was added in one portion. Reaction was continued 4 hours at 0 °C and 4 h at room temperature. The mixture was poured over crushed ice and extracted with dichloromethane. The CH_2Cl_2 layer was washed five times with water and dried over magnesium sulfate. Removal of solvent afforded 3.13 g (100%) of a dark brown gum. The reaction was repeated using 7.81 g (30.0 mmoles) of **2**, 25.55 g (180.0 mmoles) of CH_3I , and 2.64 g (66.0 mmoles) of 60% NaH. The crude yield of a dark brown gummy solid was 97%. The ¹H NMR spectra of the crude products showed: absence of **2** and **18**, peaks of **19** and **34**, and a singlet at 1.88 ppm which was assigned to **31**, the 2-methylated product. Attempted isolation of **31** by column chromatography using gravity silica and 80:20 hexane:ethyl acetate was unsuccessful. The percent compositions in the crude products were determined by the method already described; ratio of **19** to **34** to **31** was found to be: 51:33:16 and 52:33:15.

Monomethylation of Quinoline Reissert Compound, 2: A mixture of 4.69 g (18.0 mmoles) of **2** and 7.66 g (54.0 mmoles) of CH₃I was dissolved in 35 ml DMF, cooled to 0 °C and stirred under nitrogen. After 30 minutes, 0.76 g (19.0 mmoles) of 60% NaH was added in one portion. Reaction was continued for 5 hours at 0 °C and 5 hours at room temperature. After quenching and work-up, the crude yield of a dark brown gum was 5.15 g (>100%). Recrystallization of the crude gum from ethanol afforded 1.70 g (34%) of a dark brown solid, which was recrystallized three additional times from ethanol to afford pure **30**, melting at 167-8 °C. PNMR of **30** (NMR #3, Appendix A) showed: d, 1.55 ppm (J= 6 Hz), 3H, methyl; m, 3.65 ppm 1H, quinolyl H₄; d, 6.62 ppm (J= 6 Hz), 1H, quinolyl H₃; m, 7.0-7.5 ppm, 9H. Irradiation of the doublet at 1.55 ppm caused collapse of the multiplet at 3.65 ppm to a doublet (J= 6 Hz). Mass spectrum, m/e=274 (mw: 274.32). Elemental analysis for C₁₈H₁₄N₂O, calc'd (found): %C, 78.81 (78.70); %H, 5.14 (5.16); %N, 10.21 (10.24); performed by Atlantic Microlab.

The reaction was performed 2 additional times, both times using 5.20 g (20.0 mmoles) of **2**, 9.37 g (66.0 mmoles) of CH₃I, and 0.88 g (22.0 mmoles) of 60% NaH. The crude yields of a dark brown gummy solid were: 5.46 grams (99%), and 5.60 g (>100%). The compositions of both crude products were analyzed via PNMR by the method already described. The average of the ratio of **18:31:19:34:30** was: 16:11:11:10:52, the uncertainty in the figures being ±4.

N-(4-Formylbenzoyl)-1,2-dihydroquinaldonitrile, 35: To 100 ml of CH₂Cl₂ were added 19.40 g (0.150 mole) of quinoline and 28.56 g (0.169 mole) of 4-formylbenzoyl chloride.

The mixture was stirred at 0 °C under nitrogen for 1 h, after which time 22.0 ml (0.165 mole) of trimethylsilyl cyanide (TMSCN) were added gradually. An additional 50 ml solvent were added along with half a microspatula of aluminum chloride. The flask was stoppered and stirring was continued for 6.5 hours. The crude mixture was washed 3 times with water. Washing the crude mixture with 10% HCl caused the solution to effervesce, generating a slight exotherm. After the acid wash, the organic solution was washed with water three times, once with saturated NaHCO₃, and then washed with 5% NaOH which resulted in an emulsion and the precipitation of a gummy solid. The mixture was washed with water 4 additional times and dried over magnesium sulfate. Removal of solvent afforded 12.09 g (30%) of a brown solid, m.p. 185-190. The crude solid was extracted with boiling ethyl acetate and filtered to remove 3.5 grams of a gummy solid, mp 180-195 °C. The FTIR spectrum of the insoluble material showed: hydroxyl absorption at 3400 cm⁻¹; ester carbonyl at 1725 cm⁻¹, 1263 cm⁻¹, and 1097 cm⁻¹; and amide carbonyl at 1662 cm⁻¹. The NMR spectrum of the polymer showed only broad peaks between 6.0-8.5 ppm, which could not be resolved by varying the relaxation delay. The aldehydic end groups could be seen at 10 ppm. GPC of the polymer indicated M_w= 5500 and M_n= 3600, polydispersity being 1.54. The T_g of the polymer was found to be near 190 °C from DSC. The polymer was thermally stable to 250 °C in air.

Upon cooling the ethyl acetate extract, 0.22 g of a brown powder crystallized, mp 170-180 °C. The IR spectrum of this solid was identical to the spectrum of the insoluble material. Removal of ethyl acetate afforded a brown gummy solid whose IR spectrum was again identical to the insoluble solid. It was obvious that very little of the desired

product, **35**, could be recovered; therefore, the work-up was terminated.

N,N'-isophthaloyl-bis(1,2-dihydroquinaldonitrile), 38: Quinoline, 29.84 g (0.240 mole), and isophthaloyl dichloride, 24.00 g (0.117 mmole), were dissolved in 100 ml CH_2Cl_2 and stirred at 10 °C for 30 minutes. Then, 33 ml (0.247 mole) of TMSCN were added slowly, followed by 50 ml additional CH_2Cl_2 . After 2 hours of stirring under nitrogen, the flask was stoppered and stirred for 36 hours. The crude mixture was then vigorously stirred with 100 ml water for 6 hours. Layers were separated and the organic layer washed with water 2x, 10% HCl 2x, water 2x, sat'd NaHCO_3 2x, and water 2x. Removal of solvent afforded 45.79 g (90%) of a light brown solid, mp 158-165 °C. Recrystallization was attempted from ethyl acetate. Of the crude product, 20.15 g (40%), mp 207.5-208.5 °C, did not dissolve in ethyl acetate. Recrystallization of the insoluble solid from acetone yielded a white solid, mp 206.8-207.2 °C. The PNMR spectrum of this compound (NMR #5, Appendix A) showed: m, 6.0-6.2 ppm, 4 H, quinolyl H_3 and H_4 protons; dd, 6.38, 6.48 ppm ($J=7$ Hz, 7 Hz), 2H, quinolyl H_2 protons; m, 6.8-7.5 ppm, 12H.

Upon cooling the ethyl acetate solution, 15.60 g (34%) of a crema colored solid, mp 190-193 °C, recrystallized. After a second recrystallization, 6.56 grams of an off-white solid, mp 193.5-194.2 °C, were obtained. The PNMR spectrum of this solid (NMR #4, Appendix A) was identical to NMR #5, with the exception of the pair of doublets at 6.38 and 6.48 ppm, assigned to the acidic protons of the diastereomers. Comparing the integration ratios, the lower melting solid was actually a 46:54 mixture of the two diastereomers, whereas the higher melting solid was a 70:30 mixture. Elemental

analysis of the lower melting mixture, $C_{28}H_{18}N_4O_2$, calc'd (found): %C, 76.01 (75.34); %H, 4.10 (3.96); %N, 12.66 (12.55); performed by Galbraith Laboratories.

4,4'-Oxybis(benzoyl chloride): In a 1 liter flask fitted with a condenser and a drying tube were mixed 154.94 g (0.60 mole) of 4,4'-oxybis(benzoic acid) and 450 ml (6.2 moles) of thionyl chloride. After refluxing for 24 hours, the solution had turned dark brown. Most of the thionyl chloride was distilled off under nitrogen. The balance was removed on Rotavap fitted with a magnesium sulfate drying tube. Distillation of the crude product at 194-5 °C and 0.10 mmHg yielded 148 g (84%) of product, mp 89.5-91.5 °C (lit.⁵⁰ m.p., 82-3 °C). The FTIR spectrum of the product showed absence of hydroxyl, and showed carbonyl absorptions at 1750 and 1710 cm^{-1} .

N,N'-[4,4'-Oxybis(benzoyl)]bis(1,2-dihydroisoquinaldonitrile), 39: 16.95 g (0.131 mole) of freshly distilled isoquinoline and 18.89 g (0.064 mole) of 4,4'-oxybis(benzoyl chloride) were dissolved in 125 ml dry CH_2Cl_2 . After 15 min. of stirring under nitrogen at room temperature, 17.92 ml (0.134 mole) of TMSCN were added along with a small amount of $AlCl_3$. The reaction was stoppered, stirred for 1 week, and quenched by addition of water. The organic phase was washed with water 3x, 10% HCl 3x, water 3x, 10% $NaHCO_3$ 3x, and water 3x, and dried over sodium sulfate. Removal of solvent afforded 31.63 g (92%) of **39** as a yellow solid, m.p. 151-167 °C. Recrystallization was attempted from ethyl acetate/hexane. 0.90 gram of a tan solid, mp >230 °C, did not dissolve. To the mother solution hexane was added until the cloud point. On cooling, the

product would not crystallize. Column chromatography was performed on 5.34 grams of crude solid using silica gel and 50:50 hexane:ethyl acetate. From the column, 2.20 g (41%) of product was collected. The chromatographed product was partly soluble in ethyl acetate. The insoluble portion melted at 215.2-215.8 °C. The FTIR spectrum of the insoluble portion showed amide carbonyl at 1668 cm^{-1} and ether absorption at 1237 cm^{-1} . The PNMR spectrum of the insoluble portion showed: d, 6.11 ppm ($J = 8$ Hz), 2H, isoq. H_4 ; s, 6.53 ppm, 2H, isoq. H_1 ; d, 6.69 ppm ($J = 8$ Hz), 2H, isoq. H_3 ; d, 7.12 ppm ($J = 8$ Hz), 4H, aroyl H_3 protons; m, 7.2-7.5 ppm, 8H; d, 7.67 ppm ($J = 8$ Hz), 4H, aroyl H_2 protons. Elemental analysis of the insoluble portion, $\text{C}_{34}\text{H}_{22}\text{N}_4\text{O}_3$, calc'd (found): %C, 76.39 (76.23); %H, 4.15 (4.29); performed by Atlantic Microlab.

The soluble portion of the product recrystallized from ethyl acetate/hexane had melting point 205.5-206.5 °C. The FTIR and PNMR spectra of this solid were identical to those of the higher melting solid. Elemental analysis of the lower melting compound, calc'd (found): %C, 76.39 (75.86); %H, 4.15 (4.24). It was not clear whether the two compounds were pure diastereomers or eutectic mixtures of the two diastereomers, since the PNMR spectra were identical. The reported¹⁶ melting point for **39** was 140-163 °C.

1,6-Bis(*p*-formylphenoxy)hexane, 40:⁵⁰ To 600 ml of absolute ethanol were added 7.01 g (0.305 mole) sodium metal. After 10 minutes, 37.25 g (0.305 mole) *p*-hydroxybenzaldehyde were added followed by 36.60 g (0.150 mole) dibromohexane. The reaction was allowed to reflux for 10 hours, after which it was poured into 1.5 l of ice/water and allowed to stand for 12 hours. The solution was filtered and the precipitate

washed with warm water and hexane. After drying in air, the crude yield was 46.96 g (96%). One recrystallization from ethanol afforded 28.60 g (58%) of the bis-aldehyde melting at 98.5-100.0 °C. Two further recrystallizations from ethanol afforded the pure bis-aldehyde, mp 107-8 °C (lit.⁵¹mp, 106-7 °C).

Condensation of Bis-Reissert Compound 39 with 1,6-Bis(*p*-formylphenoxy)hexane,

40: To 15 ml of DMF were added 1.2157 g (2.274 mmoles) of bis-Reissert compound **39** and 0.7423 g (2.274 mmoles) of bis-aldehyde **40**. The mixture was cooled to 0 °C and stirred for 30 minutes under nitrogen. Then, 0.191 g (4.78 mmoles) of 60% NaH was added in one portion. Color of solution turned from light yellow to dark brown over 15 minutes. Reaction was continued for 42 hours at 0 °C. At the end of the reaction, the solution was cloudy, light brown, and slightly viscous. The reaction was quenched by precipitation into water, followed by precipitation of the crude solid from CHCl₃ into methanol. The yield of white powdery polymer was 0.70 g (38%). The reaction was repeated using 1.1243 g (2.103 mmoles) of **39**, 0.6865 g (2.103 mmoles) of **40**, and 0.177 g (4.42 mmoles) of 60% NaH. The reaction time was extended to 67 hours. After identical work-up, 0.97 g (57%) of the polymer was obtained as a white and slightly fibrous solid. The FTIR spectrum of the polymer, cast as a film from CHCl₃, showed: aliphatic C-H at 2940 cm⁻¹, ester carbonyl at 1715 cm⁻¹, ether at 1247 cm⁻¹, and methylene at 754 cm⁻¹. No trace of amide or formyl carbonyl could be seen in the IR spectrum. GPC of the polymer in chloroform showed M_n= 2800 and M_w= 6600, the polydispersity being 2.32. The TGA of the polymer in air showed stability up to 260 °C. DSC of the polymer

(DSC #1, Appendix C) showed T_g at 122 °C. Films cast from chloroform were transparent, yellow, and brittle.

4,4'-Diformyldiphenyl Ether, 45: 28.92 g (0.098 mole) 4,4'-oxybis(benzoyl chloride) were dissolved in 250 ml THF and cooled to -78 °C under nitrogen. After 30 minutes, 200 ml (0.200 mole) of 1.0 M lithium tri-*t*-butoxyaluminumhydride were added over the period of 1 hour. Stirring was continued for 7.5 hours. Some THF was then removed via Rotavap, and the resulting yellow solution was precipitated into 7-fold excess water. The product was extracted with chloroform. The combined extracts were washed twice with water and dried over Na₂SO₄ for two days. The solvent was then removed; crude yield 16.37 g (74%). The crude solid was stored under nitrogen at 5 °C for 12 days. Chromatography was then performed on 15 g of the crude using silica and ether. The first compound to elute was the desired dialdehyde. Total yield of the dialdehyde was 28%. After one recrystallization from ether/hexane, the melting point was 59.5-64.0 °C, compared to the reported mp of 61.0-62.5 °C.⁷¹ The NMR spectrum of the purified product showed: d, 7.10 ppm (J= 8 Hz), 4H, H₂; d, 7.95 ppm (J= 8 Hz), 4H, H₃; s, 10.0 ppm, 2H, aldehydic protons.

α,α'-Bis(4-isoquinolyl)-*p*-xylene, 46: 10.33 g (0.080 mole) isoquinoline were dissolved in 150 ml dry THF. Sodium triethylborohydride was added gradually in three portions 45 ml, 25 ml, 10 ml of a 1.0 molar solution (total 80 ml, 0.080 mole). The reddish-brown solution was allowed to stir at room temperature for 30 minutes under nitrogen, after

which terephthalaldehyde, 5.10 g (0.038 mole), was added in one portion. The solution turned black and faded to a dark green color over 2.6 hours. The reaction was cooled to 0 °C and 160 ml 0.5 N NaOH were added. Three minutes later, 80 ml of 30% H₂O₂ were added gradually. Color of the solution became yellow, containing a white solid. Stirring was continued for 18 hours at fast speed, at the end of which time the precipitate was collected and dried in air. Yield: 10.12 g (74%), melting point 176-181 °C. After three recrystallizations from ethanol/water, the pure product was obtained, mp 186.5-187.5 °C. The PNMR spectrum of the pure product showed: s, 4.33 ppm, 4H, methylene protons; s, 7.10 ppm, 4H, phenyl; m, 7.5-8.0 ppm, 8H, isoq. H₅₋₈; s, 8.38 ppm, 2H, isoq. H₃; s, 9.15 ppm, 2H, isoq. H₁. Results of elemental analysis for C₂₆H₂₀N₂, calc'd (found): %C, 86.64 (86.73); %H, 5.59 (5.55); performed by Galbraith Laboratories.

α,α' -Bis(4-isoquinolyl)-*p,p'*-ditolyl Ether, 47: To 50 ml of dry THF were added 2.45 g (0.019 mole) isoquinoline followed by 19 ml of a 1 molar solution (0.019 mole) of sodium triethylborohydride. After 30 minutes of stirring, 2.10 g (0.0093 mole) of 4,4'-diformyldiphenyl ether were added. Stirring was continued for 2.5 hours, after which the reaction was cooled to 0 °C. Then, 38 ml of 0.5 N NaOH were added followed by 19 ml 30% H₂O₂. Allowed to stir for three hours, the mixture was precipitated into 5-fold excess water. The product was extracted 3x with CHCl₃, washed 2x with water, and dried over Na₂SO₄ for a day. The solvent was removed and the yellow product dried on vacuum pump overnight. Crude yield: 3.71 g (88%). Column chromatography was performed on 3.45 g of crude solid using silica and ethyl acetate. Isolated yield after

column was 1.24 g (36%). The product was recrystallized 3x from ethanol/water. The sample, mp 117.5-118.5 °C was dried for 1 day at 80 °C under vacuum prior to sending for elemental analysis. The PNMR spectrum of the chromatographed product showed: s, 4.30 ppm, 4H, benzylic methylene; d, 6.85 ppm (J= 8 Hz), 4H, phenyl H₂; d, 7.15 ppm (J= 8 Hz), 4H, phenyl H₃; m, 7.5-7.7 ppm, 4H, isoquin. H₆, H₇; m, 7.85-8.00 ppm, 4H, isoquin. H₅, H₈; s, 8.40 ppm, 2H, isoquin. H₃; s, 9.15 ppm, 2H, isoquin. H₁. Results of elemental analysis for C₃₂H₂₄N₂O, calc'd (found): %C, 84.93 (84.84); %H, 5.35 (5.40); performed by Atlantic Microlab.

α,α'-Bis(4-isoquinolyl)-1,4-Bis(p-methylphenoxy)butane, 48: Chromatography was performed on 1.00 g crude **48** obtained from Dr. Christine K. F. Hermann (ref.: notebook of Dr. Christine K. F. Hermann, Book I, p. 147) using flash silica gel and ethyl acetate. Isolated yield of **48** from the column was 0.93 g (93%). Recrystallization from ethyl acetate yielded the product as a yellow solid, mp 167-168 °C. The PNMR spectrum of the pure sample which had been dried for 1 day under vacuum at 138 °C showed: m, 1.90 ppm, 4H, C₂ and C₃ protons of butyl; m, 3.95 ppm, 4H, C₁ and C₄ protons of butyl; s, 4.32 ppm, 4H, diaryl methylenes; d, 6.78 ppm (J= 8 Hz), 4H, aryl protons ortho to oxygen; d, 7.10 ppm (J= 8 Hz), 4H, aryl protons ortho to methylene; m, 7.55-7.70 ppm, 4H, isoquinolyl H₆ and H₇; m, 7.85-8.00 ppm, 4H, isoquinolyl H₅ and H₈; s, 8.38 ppm, 2H, isoquinolyl H₃; s, 9.15 ppm, 2H, isoquinolyl H₁. Results of elemental analysis for C₃₆H₃₂N₂O₂, calculated (found): %C, 82.41 (82.34); %H, 6.15 (6.33); %N, 5.34 (5.20); performed by Atlantic Microlab.

α,α' -Bis(4-isoquinolyl)-1,6-Bis(*p*-methylphenoxy)hexane, 49: To 120 ml of dry THF were added 7.75 g (0.060 mole) isoquinoline, followed by 60 ml of a 1 molar solution (0.060 mole) of sodium triethylborohydride. After 30 minutes, 9.47 g (0.029 mole) of 1,6-bis(*p*-formylphenoxy)hexane, **40**, were added. The reaction turned opaque and orange colored within a few minutes. The reaction was continued for three hours, after which it was cooled to 0 °C. To the mixture were added 120 ml 0.5 N NaOH, followed by 60 ml 30% H₂O₂. After stirring overnight at room temperature, the product was extracted with CH₂Cl₂, washed with water, and dried over Na₂SO₄ for a day. Solvent was removed, crude yield: 13.98 g (87%). Chromatography was performed using silica and ethyl acetate. The desired product was obtained as a yellow solid, mp 161-163 °C (49% isolated yield). After two recrystallizations from ethyl acetate, a white solid melting at 162-163 °C was obtained, which was dried in a vacuum pistol for 2 days at 138 °C. The NMR spectrum of the dried product showed: m, 1.45 ppm, 4H, C₃& C₄ protons of hexyl group; m, 1.75 ppm, 4H, C₂& C₅ protons of hexyl group; t, 3.87 ppm (J= 5 Hz), 4H, C₁& C₆ protons of hexyl group; s, 4.30 ppm, 4H, benzylic methylenes; d, 6.75 ppm (J= 8 Hz), 4H, phenyl H₂; d, 7.08 ppm (J= 8 Hz), 4H, phenyl H₃; m, 7.5-7.7 ppm, 4H, isoquinolyl H₆& H₇; m, 7.85-8.0 ppm, 4H, isoquinolyl H₅& H₈; s, 8.38 ppm, 2H, isoquinolyl H₃; s, 9.15 ppm, 2H, isoquin. H₁. Elemental analysis for C₃₈H₃₆N₂O₂, calc'd (found): %C, 82.58 (82.36), %H, 6.57 (6.62); performed by Atlantic Microlab.

α,α' -Bis(4-isoquinolyl)-1,10-Bis(*p*-methylphenoxy)decane, 50: To 120 ml of dry THF

were added 6.46 g (0.050 mole) isoquinoline followed by 50 ml of 1 molar solution of sodium triethylborohydride (0.050 mole). After 30 minutes, 9.18 g (0.024 mole) of 1,10-bis(4-formylphenoxy)decane, **44**, were added. Stirring was continued for 2.75 hours, after which the reaction was cooled to 0 °C and 100 ml 0.5 N NaOH were added, followed by 50 ml 30% H₂O₂. The mixture was stirred for 6 hours and precipitated into 6-fold excess water. The product was isolated by filtration and dried on vacuum pump overnight. Crude yield: 11.12 g (76%). Column chromatography was performed on 3.00 grams of the crude using silica and ethyl acetate. The product was collected from the column and dried, weighing 1.53 g (51% isolated yield). After four recrystallizations from ethyl acetate, a white crystalline solid was obtained, mp 110.0-112.5 °C. After drying in a drying pistol at 80 °C for 3 days, the sample was sent for analysis. The ¹H NMR spectrum of the analytical sample showed: m, 1.2-1.5 ppm, 12H, C₃-C₈ protons of the decyl group; m, 1.65-1.80 ppm, 4H, C₂& C₉ protons of decyl; t, 3.88 ppm (J= 5 Hz), 4H, C₁& C₁₀ protons of the decyl; s, 4.30 ppm, 4H, benzylic methylenes; d, 6.78 ppm (J= 8 Hz), 4H, phenyl H₂; d, 7.08 ppm (J= 8 Hz), 4H, phenyl H₃; m, 7.5-7.7 ppm, 4H, isoquin. H₆, H₇; m, 7.9-8.0 ppm, 4H, isoquin. H₅, H₈; s, 8.38 ppm, 2H, isoquin. H₃; s, 9.15 ppm, 2H, isoquin. H₁. Elemental analysis for C₄₂H₄₄N₂O₂, calc'd (found): %C, 82.86 (82.71); %H, 7.28 (7.33); performed by Atlantic Microlab.

The reaction was repeated on a larger scale, using 40.25 g (0.312 mole) of isoquinoline, 57.33 g (0.150 mole) of **44**, and 312 ml (0.312 mole) of 1.0 M NaB(Et)₃H. The crude yield was 89.27 g (98%), from which 50.00 g (56%) of product could be isolated via recrystallization from ethyl acetate.

α,α' -Bis[4(N-benzoyl-1-cyano-1,2-dihydroisoquinoly)]-1,10-Bis(*p*-methylphenoxy)decane (C₁₀-bis-Reissert Compound), 51: To 5.00 g (0.0082 mole) of the C₁₀-bis-isoquinoline, 50, in 60 ml CH₂Cl₂ were added 2.43 g (0.0173 mole) of benzoyl chloride. After 20 min. of stirring, 1.72 g (0.0173 mole) of TMSCN were added, followed by a catalytic amount of AlCl₃. Stirring was continued for 50 hours, at the end of which time no bis-heterocycle was detected by TLC (silica/ethyl acetate). The reaction was quenched with water and allowed to stir for 24 hours. The organic layer was separated and washed with 10% HCl 2x, water 2x, saturated NaHCO₃ 2x, and water 2x. The orange solution was dried over sodium sulfate for 1 day. Solvent was removed and the product dried on vacuum pump. Crude yield: 7.32 g (>100%). TLC of the crude using silica gel and 60:40 ethyl acetate:hexane showed a dark spot at R_f = 0.5 and another faint spot R_f = 0.1. Melting point of the crude product: shrank 70-78 °C, melted 81-86 °C. Column chromatography on 5.00 g of crude product (silica gel/60:40 ethyl acetate:hexane) afforded 2.87 g (57%) of the product. After two recrystallizations from ethanol, an analytically pure sample melting at 100-105 °C was obtained. The ¹H NMR spectrum of the analytical sample (NMR #6, Appendix A) showed: m, 1.2-1.4 ppm, 12 H, C₃-C₈ methylene protons; q (quintet), 1.8 ppm (J = 5 Hz), 4 H, C₂ and C₉ methylenes; AB-pattern, 3.75 ppm (J_{ab} = 15 Hz), 4 H, diaryl methylenes; triplet, 3.85 ppm (J = 5 Hz), 4 H, C₁ and C₁₀ methylenes; s, s, 6.35 ppm, 6.55 ppm, 2 H, 2 H, isoquinolyl H₁ and H₃; d, 6.80 ppm (J = 8 Hz), 4 H, protons ortho to oxy group; d, 7.15 ppm (J = 8 Hz), 4 H, protons meta to oxy group; m, 7.30-7.65 ppm, 18 H, isoquinolyl and benzoyl protons. Results of

elemental analysis for $C_{58}H_{54}N_4O_4$, cal'd (found): %C, 79.97 (79.85); %H, 6.25 (6.30); %N, 6.43 (6.35); performed by Atlantic Microlab.

The above reaction was repeated on a larger scale using 33.15 g (54.4 mmol) of **50**, 16.02 g (114 mmol) of benzoyl chloride, and 11.31 g (114 mmol) of TMSCN. The reaction time was extended to 95 hours. After identical work-up, 46.07 g (97%) of crude product were obtained. Column chromatography afforded **46** in 71% isolated yield. Instead of ethanol, the product was recrystallized from ethyl acetate/hexane. The melting point of the pure product was found to be 175-177 °C, not 100-105 °C. The ¹H NMR spectrum of the higher melting product was identical to that of the lower melting product.

Polymerization of C₁₀-Bis-Reissert, 51, with C₁₀-Dialdehyde, 44: 0.9599 g (1.1019 mmol) of the bis-Reissert compound was dissolved in 5 ml of DMF and cooled to -15 °C under nitrogen. Then, 0.0928 g of 60% NaH (2.32 mmol) was added, causing the solution to become intensely red. After 10 minutes, 0.4215 g (1.1019 mmol) of the bis-aldehyde was added in one portion. After 25 minutes of reaction, the color of the solution was green. The reaction was allowed to warm to 0 °C and kept there for 12 hours, followed by 12 hours of stirring at room temperature. The reaction was quenched directly into water, resulting in precipitation of polymer as beads. After drying under vacuum, the crude yield was 1.22 g (92%). After two further precipitations from DMF into 60:40 water/ethanol, the yield of polymer was 0.80 g (61%). The FTIR spectrum of the dried polymer (IR #1, Appendix B) showed: alkyl C-H stretch at 2928 cm⁻¹ and 2854 cm⁻¹, ester carbonyl at 1718 cm⁻¹, aromatic C-H at 1510 cm⁻¹, CH₂-O-aryl at 1246 cm⁻¹, and

methylene at 711 cm^{-1} . Intrinsic viscosity of the polymer was performed in DMF at $25\text{ }^{\circ}\text{C}$ and was found to be 0.31 dl/g . GPC (viscosity detector, absolute mw) of the polymer in CHCl_3 at $30\text{ }^{\circ}\text{C}$ showed $M_n=4,100$ and $M_w=35,400$, which corresponds to a polydispersity of 8.56. DSC of the polymer (DSC #1, Appendix C) revealed T_g at $79\text{ }^{\circ}\text{C}$ and no T_m . The polymer is stable up to $260\text{ }^{\circ}\text{C}$ in air (TGA #1, Appendix D).

4-Benzylisoquinoline, 53:⁵² To 9.95 g (0.077 mole) isoquinoline in 100 ml of THF freshly distilled from Na/benzophenone were added 85 ml of 1.0 M sol'n (0.085 mole) of $\text{NaB}(\text{Et})_3\text{H}$. The solution turned deep red almost immediately. After 25 minutes of stirring at room temperature, 9.02 g (0.085 mole) benzaldehyde were added in one portion. The color turned black almost immediately. After 5.5 hours of stirring, the chalky yellow solution was cooled to $0\text{ }^{\circ}\text{C}$ and 170 ml 0.5 N NaOH solution were added followed by the careful addition of 85 ml 30% H_2O_2 . The mixture was allowed to stir overnight, after which time it was diluted 4-fold with water. The white precipitate was collected by filtration and dried in vacuum oven. The crude yield was 14.66 g (87%), melting at $115\text{-}118\text{ }^{\circ}\text{C}$ (lit.⁵² mp: $117.5\text{-}118.5\text{ }^{\circ}\text{C}$). The ^1H NMR spectrum of the crude showed: s, 4.40 ppm, 1 H, methylene; m, 7.2-7.4 ppm, 5 H, aryl; m, 7.50-7.75 ppm, 2 H, isoquinolyl H_6 and H_7 ; d ($J=8\text{ Hz}$), 7.93 ppm, 1 H, isoquin. H_5 ; d ($J=8\text{ Hz}$), 8.00 ppm, 1 H, isoquin. H_8 ; s, 8.45 ppm, 1 H, isoquin. H_3 ; s, 9.20 ppm, 1 H, isoquin. H_1 .

N-Benzoyl-4-benzyl-1,2-dihydroisoquinaldonitrile, 54: 13.83 g (0.063 mole) 4-benzylisoquinoline were dissolved in 100 ml of CH_2Cl_2 . Then, 12.31 g (0.189 mole)

KCN in 30 ml water were added, followed by the gradual addition over two hours of 17.71 g (0.126 mole) benzoyl chloride. The mixture was allowed to stir for a total of hours. The layers were separated and the organic layer washed with water 3x, 10% HCl 3x, water 3x, sat'd NaHCO₃ 3x, water 3x, and dried over MgSO₄. Solvent was removed to afford a crude yield of 18.87 g (85%). Recrystallization from ethanol afforded an isolated yield of 71% (2 crops). Two further recrystallizations from ethanol yielded an analytically pure sample melting at 186.2-187.2 °C. The ¹H NMR spectrum of the pure sample showed: AB-pattern, 3.81 ppm (*J*_{ab} = 16 Hz), 2 H, methylene; s, s, 6.45, 6.60 ppm, 1 H each; m, 7.00-7.60 ppm, 14 H. Integration ratio of methylene to aromatics: calc'd: 2.00:16.0, found: 2.07:16.0. Results of elemental analysis for C₂₄H₁₈N₂O, calc'd(found): %C, 82.26 (82.34); %H, 5.18 (5.19); performed by Atlantic Microlab.

Phenyl-1-(4-benzylisoquinolyl)methyl Benzoate, 55: 7.01 g (0.020 mole) of the Reissert compound **54** were dissolved in 40 ml of DMF and cooled to -15 °C via ethylene glycol/dry ice. Then, 0.88 g of 60% NaH dispersion in mineral oil (0.022 mole) was added in one portion. After 10 minutes of stirring, 2.12 g (0.020 mole) benzaldehyde were added in one portion. The solution turned grayish-green immediately. Stirring was continued for 17.25 hours, at the end of which time the solution was yellow in color. The reaction was quenched by precipitation into water. The product was collected by filtration. Crude yield of light yellow solid was 8.10 g (94%). TLC of the crude product (silica/50:50 EtOAc:hexane) showed one spot, *R*_f = 0.5. Recrystallization from ethanol afforded 6.95 g (86%) of product (2 crops). Two further recrystallizations from ethanol

yielded analytically pure sample melting at 137.5-138.2 °C. The FTIR spectrum of the product showed ester carbonyl at 1702 cm^{-1} . The ^1H NMR spectrum of the product showed: s, 4.38 ppm, 2 H, methylene; m, 7.0-8.5 ppm, 21 H. Elemental analysis for $\text{C}_{30}\text{H}_{23}\text{NO}_2$, calc'd (found): %C, 83.89 (83.68); %H, 5.40 (5.47). TGA of the product in air (TGA #2, Appendix D) showed 90% weight loss occurring between 250-400 °C.

Polymerization of C_{10} -bis-Reissert Compound, **51, with**

1,6-Bis(4-formylphenoxy)hexane, **40:** 1.2192 g (1.3996 mmol) of **51** and 0.4568 g (1.3996 mmol) of **40** were dissolved in 11 ml DMF and cooled to 0 °C under nitrogen. Then, 0.118 g (2.94 mmol) of 60% NaH was added in one portion. The reaction was continued for 18 hours at 0 °C, followed by gradual warming to room temperature. Total reaction time was 75.5 hours. At the end of the reaction, the solution was deep violet and relatively viscous. The reaction was quenched by precipitation into water, followed by one precipitation of the crude product from chloroform into methanol. The yield of off-white fibrous polymer was 1.23 g (77%). FTIR of the dried product showed ester carbonyl at 1721 cm^{-1} ; no amide or aldehyde carbonyl absorptions could be observed. The DSC of the polymer showed T_g at 93 °C; no T_m was observed. The TGA of the polymer revealed stability up to 200 °C in air, losing approximately 18% by weight between 200 and 325 °C. The GPC of the polymer (GPC #1, Appendix E, absolute mw) showed $M_w = 40,000$ and $M_n = 1,200$, i.e., polydispersity of 33.8! The polymer was fractionated using chloroform/methanol by first dissolving the polymer in chloroform and adding methanol until phase separation was observed. The dilute phase was withdrawn, and the procedure

repeated. The final concentrated layer was precipitated into methanol and dried. The GPC of the dried fractionated polymer (GPC #2, Appendix E, absolute) showed $M_n=31,000$ and $M_w=69,000$. The polydispersity had improved to 2.21.

A film of the unfractionated polymer, which had been cast from chloroform was dried for 1 day at 60 °C under vacuum and submitted for mechanical testing. The tensile strength was found to be 13 MPa for a maximum strain of 3%. The tests were performed by C. A. Williams of Dr. T. C. Ward's group.

The ester groups were hydrolyzed according to procedure reported by Gibson and Bailey.⁵⁴ To a solution of 0.3110 g (0.544 mmole ester) of the above polyester in 6 ml THF were added 0.070 g (1.09 mmole) of 87% KOH, 0.2 ml water, and 0.40 ml 2-ethoxyethanol. The solution was refluxed for 18 hours and precipitated into water at the end of the reaction. The crude product was dissolved in chloroform, filtered, and precipitated into methanol to afford a yield of 0.22 g (86%) of yellow fibrous polymer. The FTIR spectrum of polyalcohol **58** (IR #2, Appendix B) showed complete loss of ester carbonyl and appearance of alcohol stretch at 3400 cm^{-1} . DSC of the polyalcohol showed T_g at 86 °C. TGA of the polyalcohol revealed stability up to 300 °C in air. A film of the polyalcohol cast from CHCl_3 had tensile strength of 38 MPa for a maximum strain of 6%.

α,α' -Bis{4[N(*o*-Toluoyl)-1-cyano-1,2-dihydroisoquinolyl]}1,10-Bis(*p*-methylphenoxy)decane (*o*-Toluoyl C_{10} -bis-Reisert Compound), **59:** To 80 ml CH_2Cl_2 were added 5.47 g (8.98 mmoles) of C_{10} -bis-isoquinoline, **50**, and 2.94 g (19.0 mmoles) of *o*-toluoyl chloride. The mixture was allowed to stir for 30 minutes, after which 2.54 ml (19.0

mmoles) of TMSCN were added, along with a small amount of AlCl_3 . The reaction was stoppered and stirred for 22.5 hours. The mixture was quenched with water and washed with 10% HCl 3x, water 3x, sat'd NaHCO_3 3x, water 3x, sat'd NaCl 1x, and dried over sodium sulfate. Removal of solvent afforded 7.61 g (96%) of a brown solid. Column chromatography was performed on 6.90 g of crude using silica gel and 65:35 hexane:ethyl acetate. The isolated yield of product after chromatography was 4.71 g (68%). An analytically pure sample was obtained after two recrystallizations from ethyl acetate/hexane. The ^1H NMR spectrum of the pure sample, mp 159-161 °C, showed: m, 1.3-1.6 ppm, 12H, C_3 - C_8 protons of decyl; m, 1.7-1.9 ppm, 4H, C_2 and C_9 protons of decyl; d, 2.25 ppm ($J = <1$ Hz), 6H, o-toluoyl methyl protons; AB-pattern, 3.68 ppm ($J_{\text{ab}} = 15$ Hz), 4H, diaryl methylenes; t, 3.88 ppm ($J = 5$ Hz), 4H, C_1 , C_{10} protons of decyl; s, 6.07 ppm, 2H, isoq. H_1 ; m, 6.7-6.8 ppm, 6H, isoq. H_3 and aryl protons ortho to oxygen; d, 7.10 ppm ($J = 8$ Hz), 4H, aryl protons ortho to methylene; m, 7.2-7.5 ppm, 14H. Elemental analysis for $\text{C}_{60}\text{H}_{58}\text{N}_4\text{O}_4$, cal'd (found): %C, 80.15 (79.93); %H, 6.50 (6.45); %N, 6.23 (6.25); performed by Atlantic Microlab.

Polymerization of o-Toluoyl-bis-Reissert Compound, 59, with

1,6-Bis(4-formylphenoxy)hexane, 40: 1.0053 g (1.118 mmoles) of the bis-Reissert compound **59** were dissolved in 4 ml of DMF and cooled to 0 °C under nitrogen. Sodium hydride was added, 0.100 g (2.50 mmoles of 60% dispersion). After five minutes, 0.3707 g (1.136 mmoles) of the dialdehyde **40** was added in one portion. The reaction was continued for 48 hours at 0 °C and quenched by precipitation into water. The polymer was

dissolved in chloroform, filtered, precipitated into 50:50 methanol:ethanol, and dried under vacuum at 67 °C for a day. The yield of light yellow, fibrous polymer was 1.00 g (75%). The FTIR spectrum of the polymer cast as a film from CH₂Cl₂ onto NaCl plate showed: aliphatic C-H at 2930, 2855 cm⁻¹; ester carbonyl at 1717 cm⁻¹; and ether at 1245 cm⁻¹. The ¹H NMR spectrum of the polymer showed: m, 1.2-1.9 ppm, aliphatic; s, 2.60 ppm, o-toluoyl methyls; m, 3.75-4.00 ppm, methylenes ortho to oxygen; s, 4.30 ppm, diaryl methylenes; m, 6.70-7.60 ppm; s, 7.75 ppm, methine protons; d, d, d, 7.88, 8.07, 8.26 ppm (J= 8 Hz each) isoquin. H₆₋₈; s, 8.38 ppm, isoquinolyl H₃. The TGA of the polymer revealed stability up to 225 °C in air, losing approximately 20% between 225-350 °C. The DSC of the polymer showed T_g at 87 °C in the first heating, and 85 °C in the second heating. The intrinsic viscosity of the polymer in chloroform at 25 °C was 0.60 dl/gram. The GPC of the polymer was performed by C. Gutberlet in THF at 30 °C using a refractive index detector. The molecular weights were determined manually by dividing the elution curve into 50 increments, measuring the peak height at each increment, and by using a master curve of polystyrene standards. All calculations were done using a MacIntosh computer. By this method, M_w = 22400, M_n = 54700 in polystyrene equivalents, the polydispersity being 2.43.

The polymerization was repeated using 0.9081 g (1.010 mmole) of **59** and 0.3349 g (1.026 mmole) of **40**. In this trial, the bis-Reissert compound and dialdehyde were dissolved in 4.5 ml of DMF, cooled to 0 °C, and stirred under nitrogen. Sodium hydride, 0.900 g (2.257 mmole of 60% dispersion) was added to the mixture in one portion. After identical reaction time and work-up, the yield of polymer was 67%. The FTIR spectrum,

TGA, and DSC were identical to the above polymer. The intrinsic viscosity of the latter polymer was 0.58 dl/g. The molecular weights of the polymer were determined same as above: $M_w = 22500$, $M_n = 57300$, polydispersity being 2.54.

Using the procedure reported by Gibson and Bailey,⁷⁰ the above polyester was quaternized with methyl iodide. 0.22 g (0.38 mmole repeat unit) of polyester **60** and 0.81 g (5.6 mmole) CH_3I were dissolved in 20 ml THF and heated to reflux. After 18 hours, an orange-brown solid precipitated. Removal of solvent via Rotavap yielded a dark brown solid which was found to be soluble in DMF and CH_2Cl_2 , slightly soluble in CHCl_3 , and insoluble in alcohols and water. Once in DMF or CH_2Cl_2 , the polymer would not precipitate from methanol. The polymer was dissolved in CH_2Cl_2 and precipitated into hexane. After drying under vacuum at 67 °C for two days, the yield of product was 0.18 g (66%). The FTIR spectrum of the polymethiodide cast as a film from CH_2Cl_2 onto NaCl showed: aliphatic C-H at 2930 cm^{-1} , quaternary nitrogen absorption between 2600-2200 cm^{-1} (broad), ester carbonyl at 1719 cm^{-1} , and ether at 1245 cm^{-1} . The TGA of the polymer in air showed weight loss beginning at 110 °C. The DSC of the polymer did not show any transitions under 110 °C. The PNMR spectrum of the polymer showed: s, 2.5 ppm, 6H, o-toluoyl methyls of quaternized segments; s, 2.6 ppm, 6H, o-toluoyl methyls of unquaternized segments; s, 4.30 ppm, 4H, diaryl methylenes of unquaternized segments; s, 4.55 ppm, 4H, diaryl methylenes of quaternized segments; s, 4.85 ppm, methyl protons of salt; and other broad aromatic protons. Elemental analysis: C, 70.04%; H, 6.21%; N, 2.31%; I, 10.57%; performed by Atlantic Microlab.

4-(p-Fluorobenzyl)isoquinoline, 61: 34.07 g (0.264 mole) of isoquinoline were dissolved in 200 ml of THF freshly distilled from Na/benzophenone. Sodium triethylborohydride was added as 1.0 M solution in three parts of total volume of 275 ml (0.275 mole). The reaction was cooled and stirred under nitrogen for 30 minutes, after which 34.40 g (0.277 mole) of p-fluorobenzaldehyde were added. The reaction was continued for 4 hours. At the end of the reaction, the solution was chalky and red. The reaction was cooled via ice bath, quenched with 550 ml 0.5 N NaOH, followed by careful addition of 275 ml 30% H₂O₂. The quenched reaction was allowed to stir for 12 hours prior to extraction with chloroform. The extract was then washed with water 4x and dried over sodium sulfate for 1 day. Solvent was removed, crude yield: 60.98 grams (97%). The ¹H NMR spectrum of the crude showed the methylene in the product at 4.34 ppm. Using the integration ratios of methylene to aromatic region, the actual yield of the reaction was found to be 80%. TLC of the crude product (silica gel/80:20 hexane:ethyl acetate) showed 2 spots, one of which was isoquinoline. Chromatography was performed on 3.5 g of crude product using silica gel and 80:20 hexane:ethyl acetate. 2.23 g (64%) of product was collected, which after two recrystallizations from petroleum ether yielded analytically pure sample, melting at 66-67 °C. The ¹H NMR spectrum of the analytical sample showed: s, 4.34 ppm, 2H, diaryl methylene; t, 6.94 ppm (J= 8 Hz), 2H, protons ortho to fluorine; m, 7.1-7.2 ppm, 2H, protons ortho to methylene; m, 7.5-7.7 ppm, 2H, isoquinolyl H₆ and H₇; d, 7.85 ppm (J= 8 Hz), 1H, isoquinolyl H₅; d, 7.97 ppm (J= 8 Hz), 1H, isoquinolyl H₈; s, 8.39 ppm, 1H, isoquinolyl H₃; s, 9.18 ppm, 1H, isoquinolyl H₁. Elemental analysis for C₁₆H₁₂NF, calc'd (found): %C, 80.99 (81.09); %H, 5.11 (5.10); performed by Atlantic Microlab.

N-Benzoyl-4-(p-fluorobenzyl)-1,2-dihydroisoquinaldonitrile, 62: 23.73 g (0.08 mole) of crude 4-fluorobenzylisoquinoline were dissolved in 120 ml of CH₂Cl₂. Then, 15.63 g (0.24 mole) KCN dissolved in 40 ml of water were added to the CH₂Cl₂ solution. The resulting mixture was stirred for 15 minutes prior to the dropwise addition of 22.49 g (0.16 mole) of benzoyl chloride over 2 hours. The reaction was stirred for 7 hours, after which 100 ml water were added. The layers were separated. The organic layer was washed with water 3x, 5% NaOH 2x, 10% NaHCO₃ 1x, 10% HCl 3x, and water 3x. The final solution was dried over sodium sulfate for a day. Solvent was removed, crude yield 32.48 g (>100%). After four recrystallizations, the isolated yield was 20.62 g (70%). Further recrystallizations from ethanol yielded the pure product melting at 163-164 °C. The NMR spectrum of the analytical sample showed: AB-pattern, 3.80 ppm (J_{AB} = 15 Hz), 2H, methylene protons; s, s, 6.40, 6.60 ppm, 1H each, isoquinolyl H₁, H₃; t, 6.95 ppm (J = 8 Hz), 2H, protons ortho to fluorine; m, 7.2-7.7 ppm, 11 H. Elemental analysis for C₂₄H₁₇N₂OF, calc'd (found): %C, 78.25 (78.29); %H, 4.65 (4.66); performed by Atlantic Microlab.

1-p-Fluorophenyl-1-[4-(p-fluorobenzyl)isoquinolyl]methanol, 63: 12.49 g (0.0339 mole) 4-fluorobenzylisoquinoline Reissert compound, **62**, 4.68 g (0.0373 mole) 4-fluorobenzaldehyde, and 0.12 g triethylbenzylammonium chloride (TEBA) were dissolved in 125 ml of acetonitrile. After 15 minutes of stirring, 15 ml 50% NaOH were added. The reaction was allowed to stir for one hour with gradual heating on an oil bath to

reflux the acetonitrile. After 1.5 hours of reflux, the reaction was diluted with one liter of water. The product was extracted with CHCl_3 and washed 2x with water. The crude yield after drying was 14.51 g (>100%). The IR spectrum of the crude product showed hydroxyl at 3400 cm^{-1} , and ester at 1720 cm^{-1} signifying incomplete reaction. The crude product was dissolved in 200 ml ethanol, 100 ml water, and 40 g (0.71 mole) of KOH were added. After refluxing for 4 hours, the product was isolated by precipitation into water. The crude yield of dried orange product was 10.71 g (87% overall), mp $120\text{-}2\text{ }^\circ\text{C}$. The FTIR spectrum of the crude product showed no ester or amide carbonyl absorptions. After two recrystallizations from ethanol, the pure product was obtained, mp $127\text{-}8\text{ }^\circ\text{C}$. The $^1\text{H NMR}$ spectrum of the analytical sample showed: s, 4.39 ppm, 2 H, methylene; s, 6.20 ppm, 1 H, hydroxyl proton; s, 6.35 ppm, 1 H, methine; m, 6.97 ppm, 4 H, protons ortho to fluorine; m, 7.1-7.35 ppm, 4 H, protons meta to fluorine; t, t, 7.48, 7.60 ppm ($J=8\text{ Hz}$ each), 1 H each, isoquinolyl H_6 and H_7 ; m, 7.9-8.0 ppm, 2 H, isoquinolyl H_5 and H_8 ; s, 8.38 ppm, 1 H, isoquinolyl H_3 . Elemental analysis for $\text{C}_{23}\text{H}_{17}\text{NOF}_2$, calc'd (found): %C, 76.44 (76.25); %H, 4.74 (4.80).

General Procedure for Oxidations Using Manganese Dioxide:⁵⁶ For 1.0 g alcohol, 30 ml benzene and 10.0 g manganese dioxide (activated, from Aldrich Chemicals) were used. The benzene/water azeotrope was collected via a Dean-Stark trap. The reaction was allowed to reflux for 12 hours. At the end of reaction, the oxides were filtered through Celite, and the Celite was washed with chloroform. Extraction of the used MnO_2 with chloroform improved the reaction yield. The collected filtrate was dried over MgSO_4 .

Solvent was then removed to obtain the crude product.

1,4-Bis(4-fluorobenzoyl)isoquinoline, 64: 8.08 g (0.0224 mole) of the alcohol afforded 4.50 g (54%) of the diketone **60** via MnO_2 oxidation procedure. A second trial of the same reaction afforded 70% crude yield when the MnO_2 at the end of reaction was extracted with CHCl_3 . After two recrystallizations from ethanol, the analytically pure compound mp 130.5-131.5 °C was obtained. The PNMR spectrum of the crude showed no methylene protons. The PNMR spectrum of the pure compound (NMR #7, Appendix A) showed: m, 7.1-7.3 ppm, 4 H, protons ortho to fluorine; t, t, 7.70, 7.8 ppm ($J = 8$ Hz each), 1 H each, isoquinolyl H_6 and H_7 ; m, 7.9-8.1 ppm, 4 H, protons ortho to ketones; d, d, 8.10, 8.25 ppm ($J = 8$ Hz each), 1 H each, isoquinolyl H_5 and H_8 ; s, 8.65 ppm, 1 H, isoquinolyl H_3 . Elemental analysis for $\text{C}_{23}\text{H}_{13}\text{NO}_2\text{F}_2$, calc'd (found): %C, 73.99 (73.74); %H, 3.51 (3.55); performed by Atlantic Microlab.

Polymerization of 64 with Bis-Phenol-A: 1.2763 g (3.418 mmole) of the diketone **64** and 0.7783 g (3.409 mmole) Gold label bisphenol-A were dissolved in 15 ml of NMP freshly distilled from CaH_2 . The slight excess of diketone was necessary to compensate for water (observed in PNMR) which could not be completely removed. Then, 1.0633 g (7.693 mmole) of anhydrous K_2CO_3 and 15 ml of toluene were added. The mixture was heated on oil bath under nitrogen. Toluene/water azeotrope began to distil at 150 °C. The temperature was kept at 155-165 °C for 9 hours. At the end of the reaction, the mixture was dark brown and moderately viscous. The reaction was cooled, diluted with CH_2Cl_2 ,

filtered, acidified with acetic acid, and precipitated into methanol to yield 1.89 g (99%) crude polymer. Two further precipitations from THF into methanol yielded 1.20 g (63%) of dried polymer. The FTIR spectrum of the polymer showed: aromatic C-H stretch at 3100 and 3000 cm^{-1} ; carbonyl at 1662 cm^{-1} ; C=C ring stretch at 1591 and 1498 cm^{-1} ; and C-O-C at 1247 cm^{-1} . Intrinsic viscosity of the polymer in chloroform at 25 °C was determined to be 0.39 dl/gr. DSC of the polymer showed Tg at 181 °C and no Tm. TGA of the polymer in air showed no weight loss up to 450 °C. The ¹H NMR spectrum of the polymer showed: s, 1.70 ppm, 6H, methyl; m, 6.95-7.05 ppm, 8H, aryl protons ortho to oxygen; m, 7.20-7.30 ppm, 4H, aryl protons ortho to isopropylidene; m, 7.60-7.80 ppm, 2H, isoquinolyl H₅ and H₈; m, 7.85-8.00 ppm, 4H, aryl protons ortho to carbonyl; d, d, 8.05, 8.20 ppm (J= 8, 8 Hz), 1H each, isoquinolyl H₅ and H₈; s, 8.65 ppm, 1H, isoquinolyl H₃.

Copolymerization of 64 with Hydroquinone and Biphenol: 1.0849 g (2.9058 mmole) of the difluoroketone **64**, 0.1608 g (1.4604 mmole) of hydroquinone, and 0.2691 g (1.4454 mmole) of biphenol were dissolved in 10 ml of NMP in a resin flask. Then, 10 ml of toluene and 0.917 g (6.6 mmoles) of K₂CO₃ were added to the stirring solution. The mixture was heated to 140 °C under nitrogen and kept there for three hours. After all of the toluene had distilled, the temperature was raised to 160-170 °C for 10.5 hours. More NMP was added and the reaction continued at 160 °C for five additional hours. The mixture was then diluted with NMP, filtered while hot, acidified with glacial acetic acid, and precipitated into water. The polymer was dissolved in CHCl₃ and precipitated into

50:50 acetone: methanol to yield 0.70 gr (50%) of a tan-colored fibrous product. Intrinsic viscosity of the polymer in chloroform at 25 °C was 0.28 dl/g. GPC (viscosity detector, absolute mw) of the polymer in chloroform showed $M_n = 4,300$, $M_w = 17,000$, the polydispersity being 3.94. DSC of the polymer showed Tg at 199 °C after 2 heats; no Tm was observed. TGA of the polymer in air revealed stability upto 400 °C, losing approximately 18% of its weight between 400-500 °C. The PNMR spectrum of the copolymer (NMR #8, Appendix A) showed: m, 6.90-7.30 ppm, 16H, aryl protons ortho to oxygen; m, 7.50-7.85 ppm, 8H, biphenyl protons and isoquinolyl H₆ and H₇; m, 7.90-8.10 ppm, 8H, aryl protons ortho to carbonyl; d, d, 8.10, 8.25 ppm (J= 8, 8 Hz), 2H each, isoquinolyl H₅ and H₈; s, 8.70 ppm, 2H, isoquinolyl H₃.

Polymerization of 64 with Biphenol: 1.1071 g (2.9652 mmole) of the difluoroketone, 0.5522 g (2.9652 mmole) of biphenol, and 0.902 g (6.523 mmole) of K₂CO₃ were dissolved in 7 ml CHP and 4 ml toluene. The mixture was heated under nitrogen to 140-160 °C and kept there for 2 hours. The temperature was then raised and kept at 220 °C for 9 hours. The mixture was diluted with NMP, acidified with glacial acetic acid and precipitated into 80:20 water:methanol. After two further precipitations from THF into 50:50 acetone:methanol, the yield of dried polymer was 0.80 gram (52%). Intrinsic viscosity of the polymer in chloroform was 0.34 dl/g. DSC of the polymer (DSC #2, Appendix C) showed Tg at 209 °C after 2 heats; no Tm was observed. TGA of the polymer in air revealed stability up to 500 °C. The PNMR spectrum of the polymer showed: m, 6.95-7.22 ppm, 6H, aryl protons ortho to oxygen; m, 7.45-7.70 ppm, 6H,

biphenyl protons and isoquinolyl H₆ and H₇; m, 7.85-8.00 ppm, 4H, aryl protons ortho to carbonyl; d, d, 8.10, 8.20 ppm (J= 8, 8 Hz), 1H each, isoquinolyl H₅ and H₈ protons; s, 8.65 ppm, 1H, isoquinolyl H₃.

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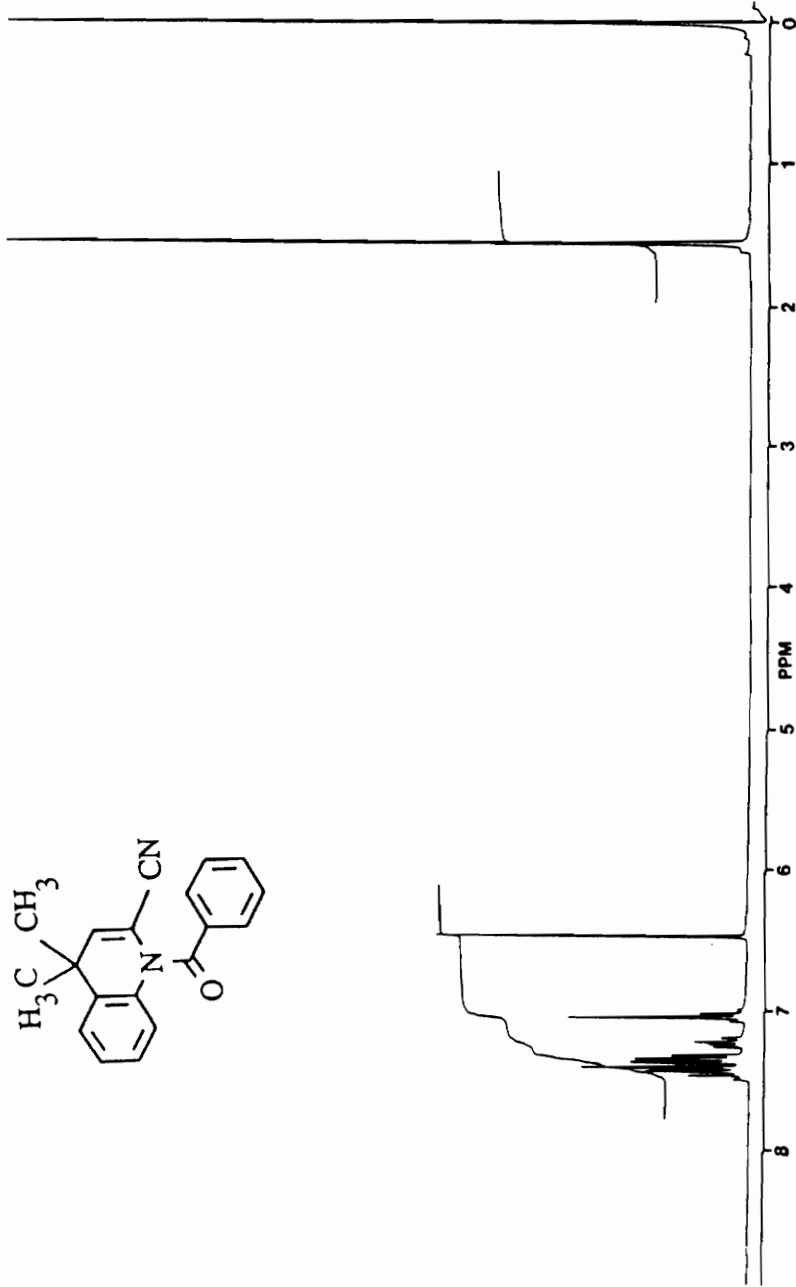
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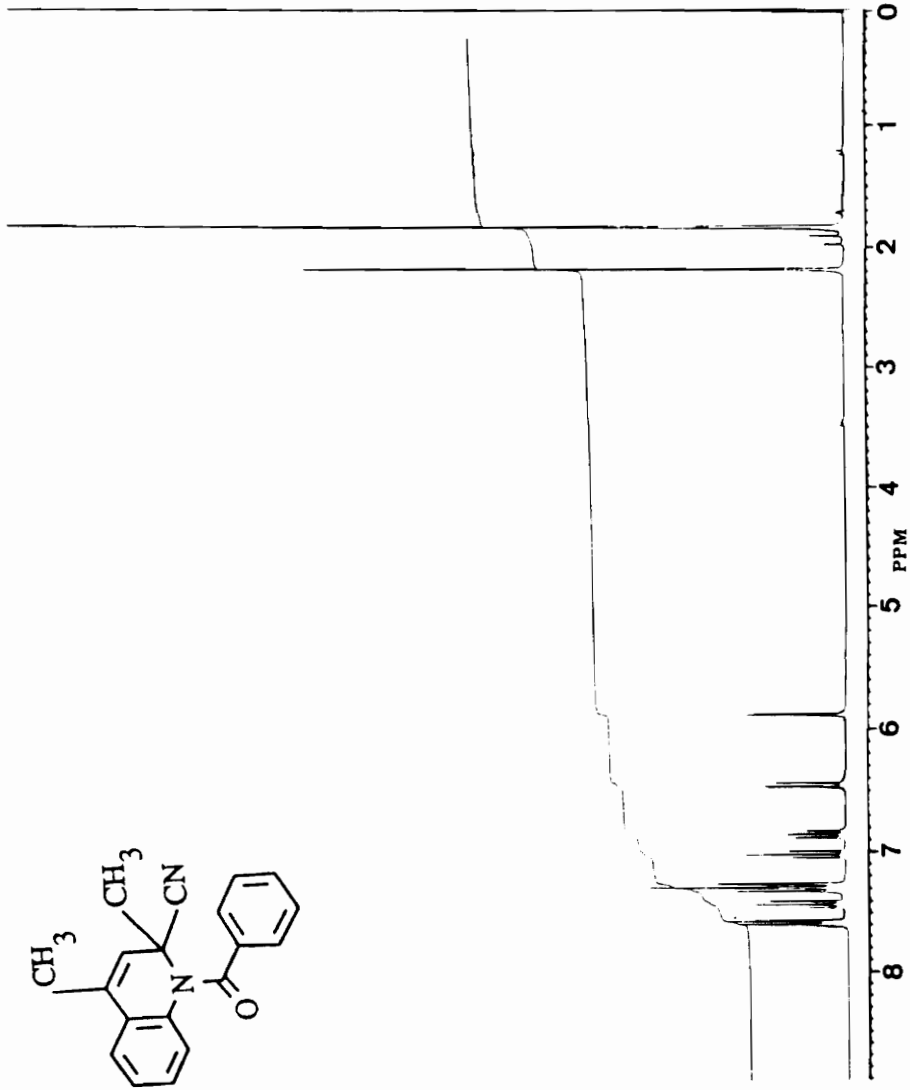
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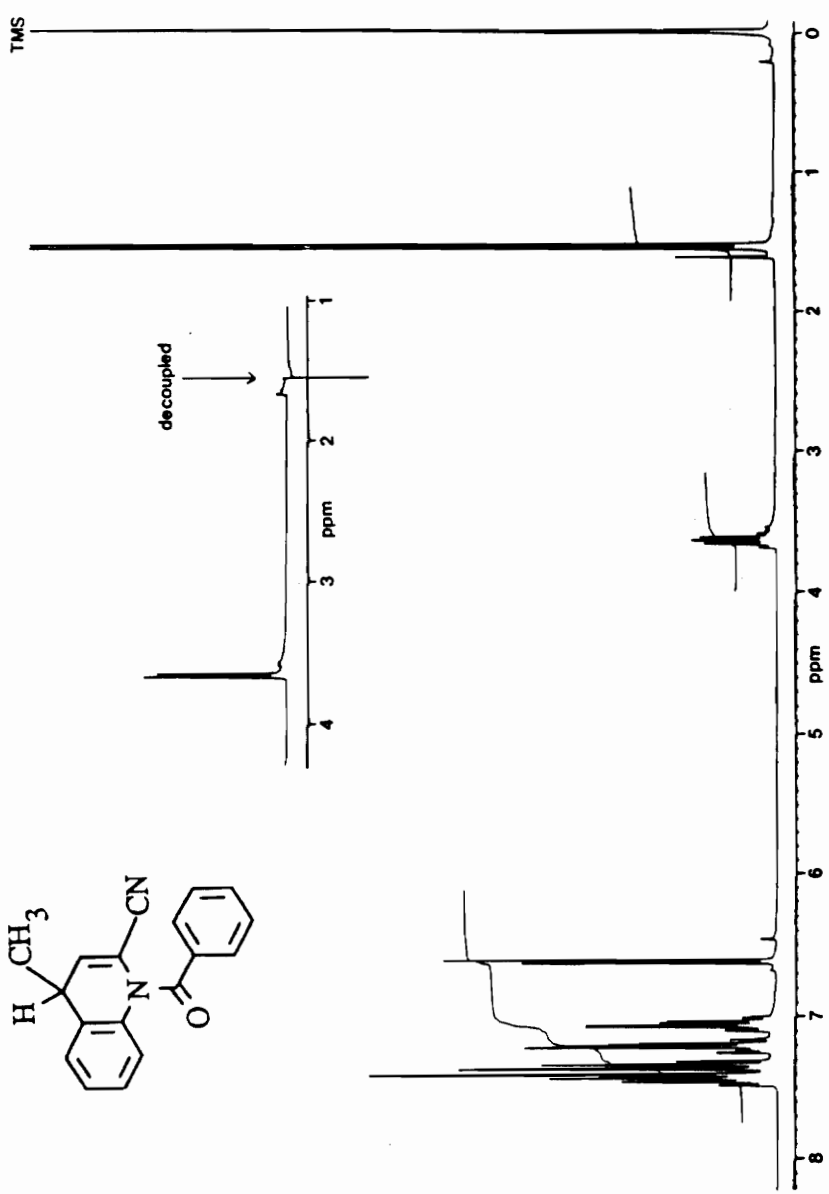
APPENDIX A: PNMR SPECTRA



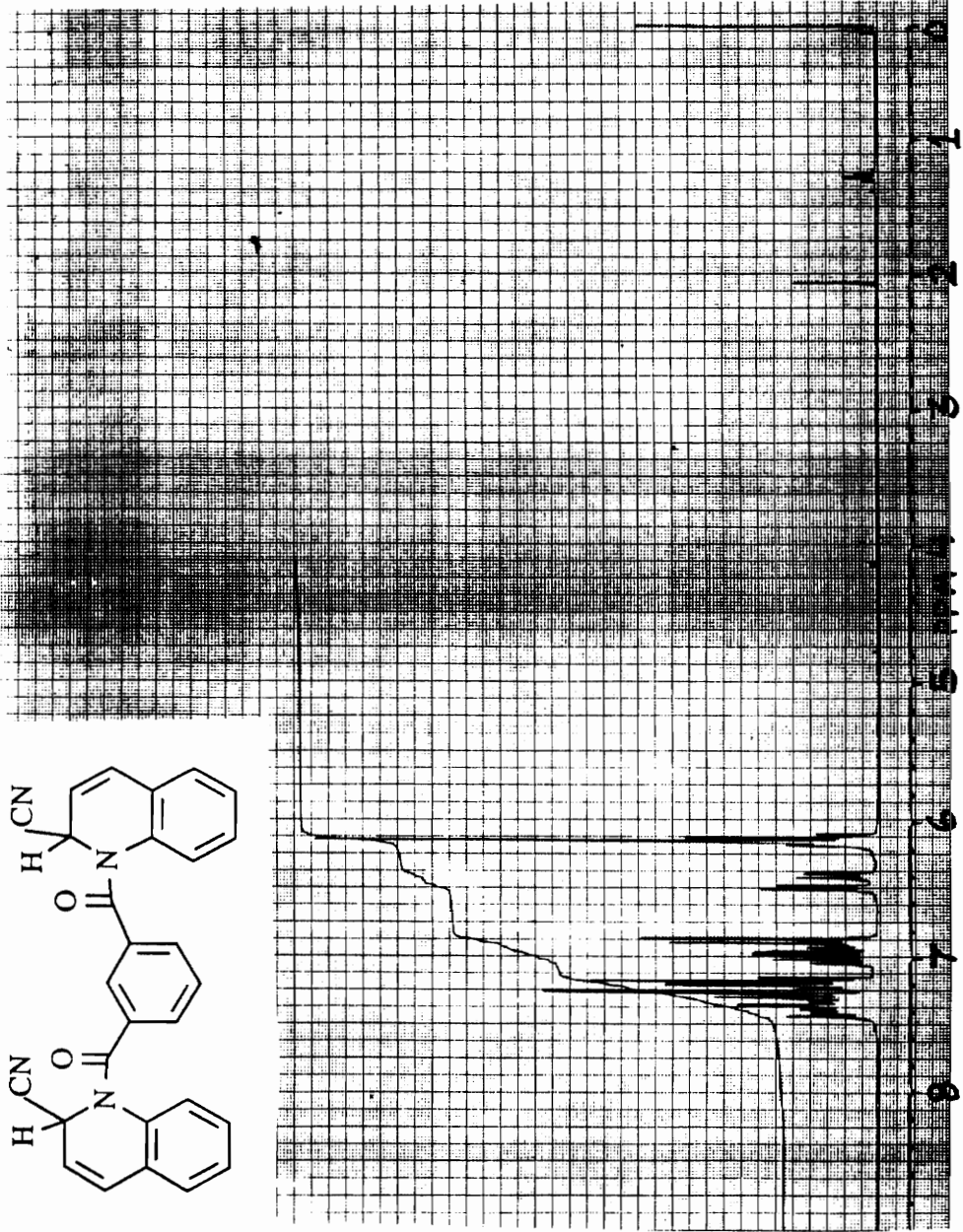
PNMR #1: N-Benzoyl-4,4-dimethyl-1,4-dihydroquinolindonitrile, 34



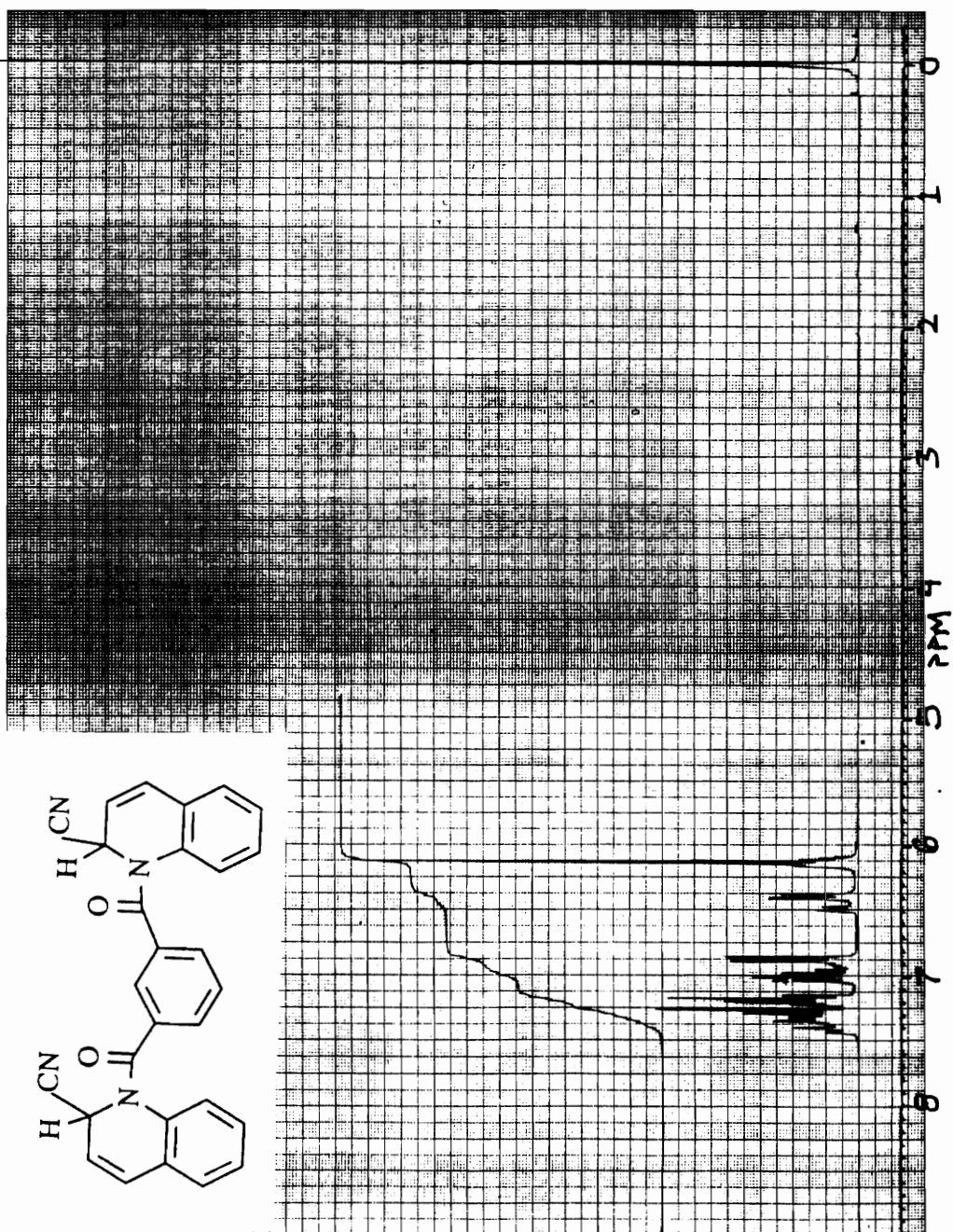
PNMR #2: N-Benzoyl-2,4-dimethyl-1,2-dihydroquinoline nitrile, 19



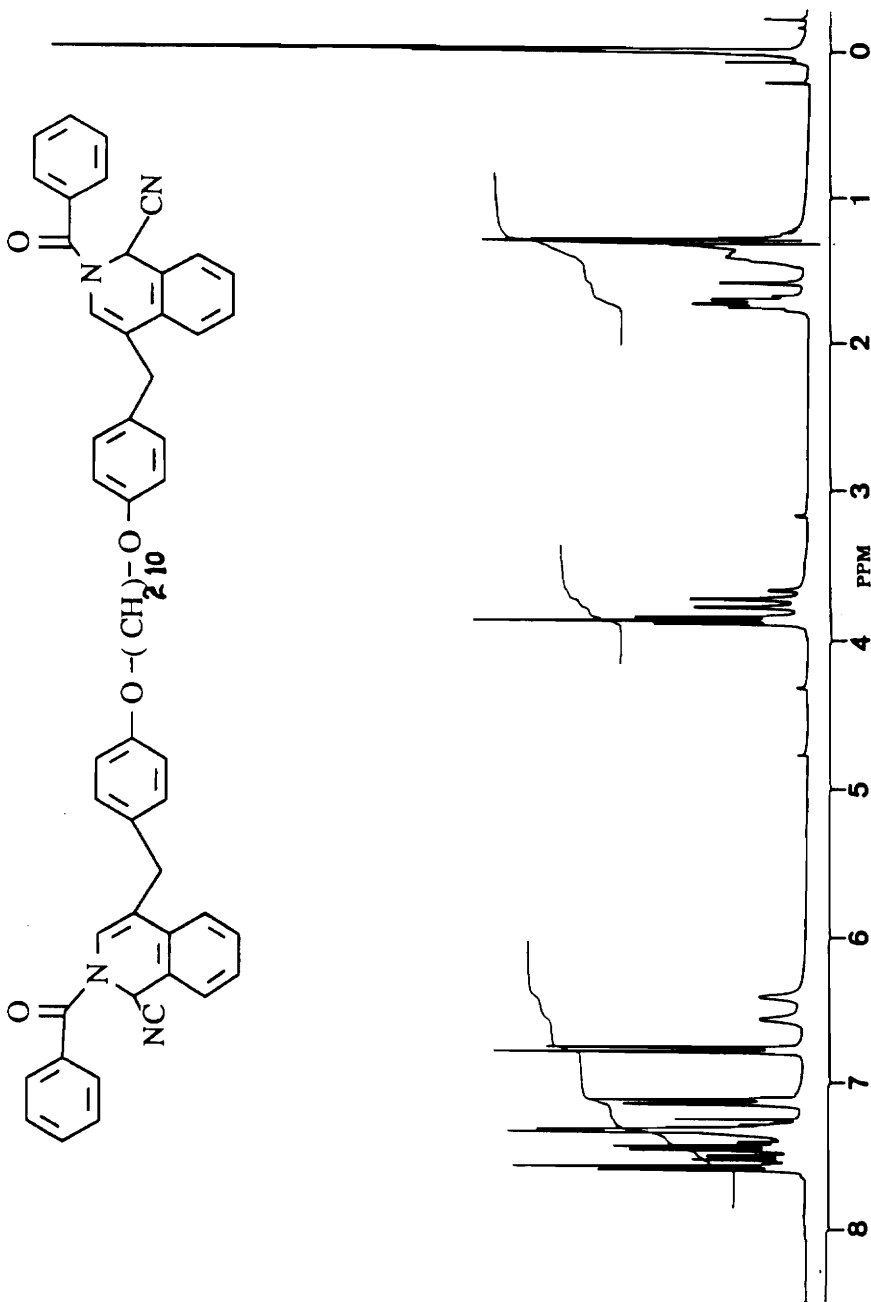
PNMR #3: N-Benzoyl-4-methyl-1,4-dihydroquinolindone, 30

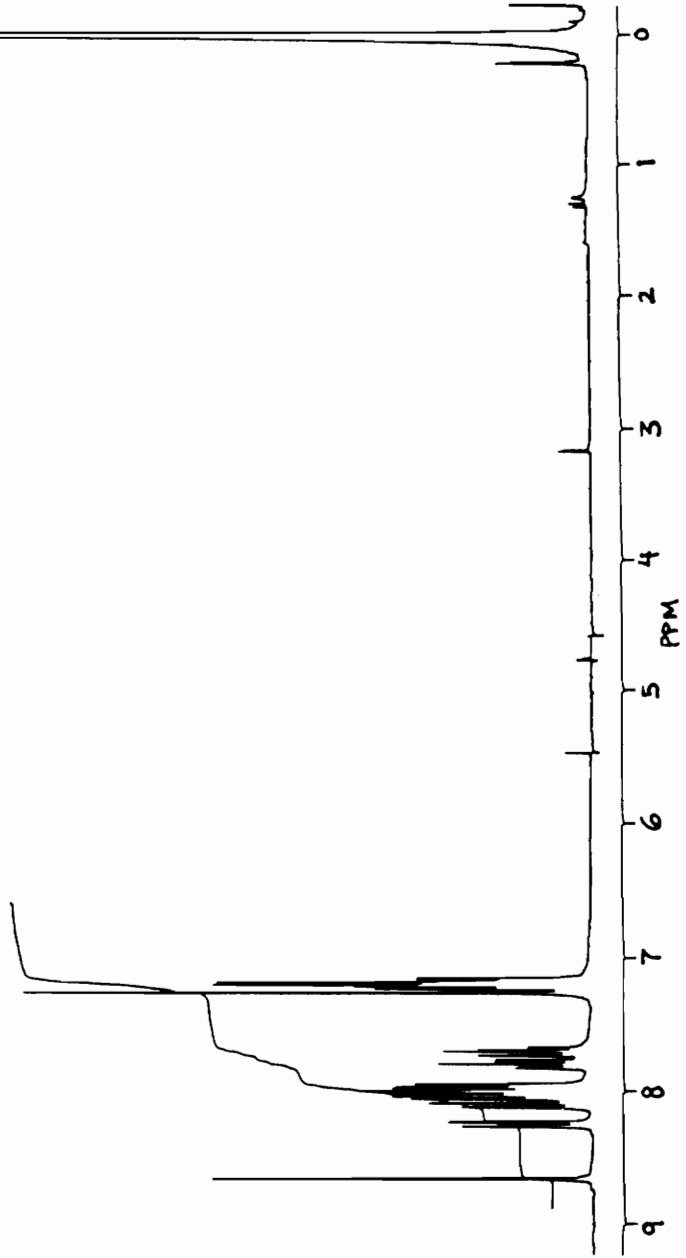
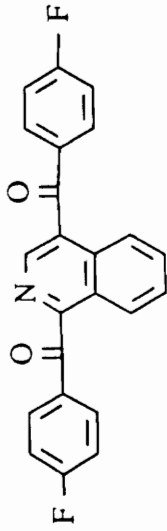


PNMR #4: Bis-Reissert Compound 38, Lower Melting Sample

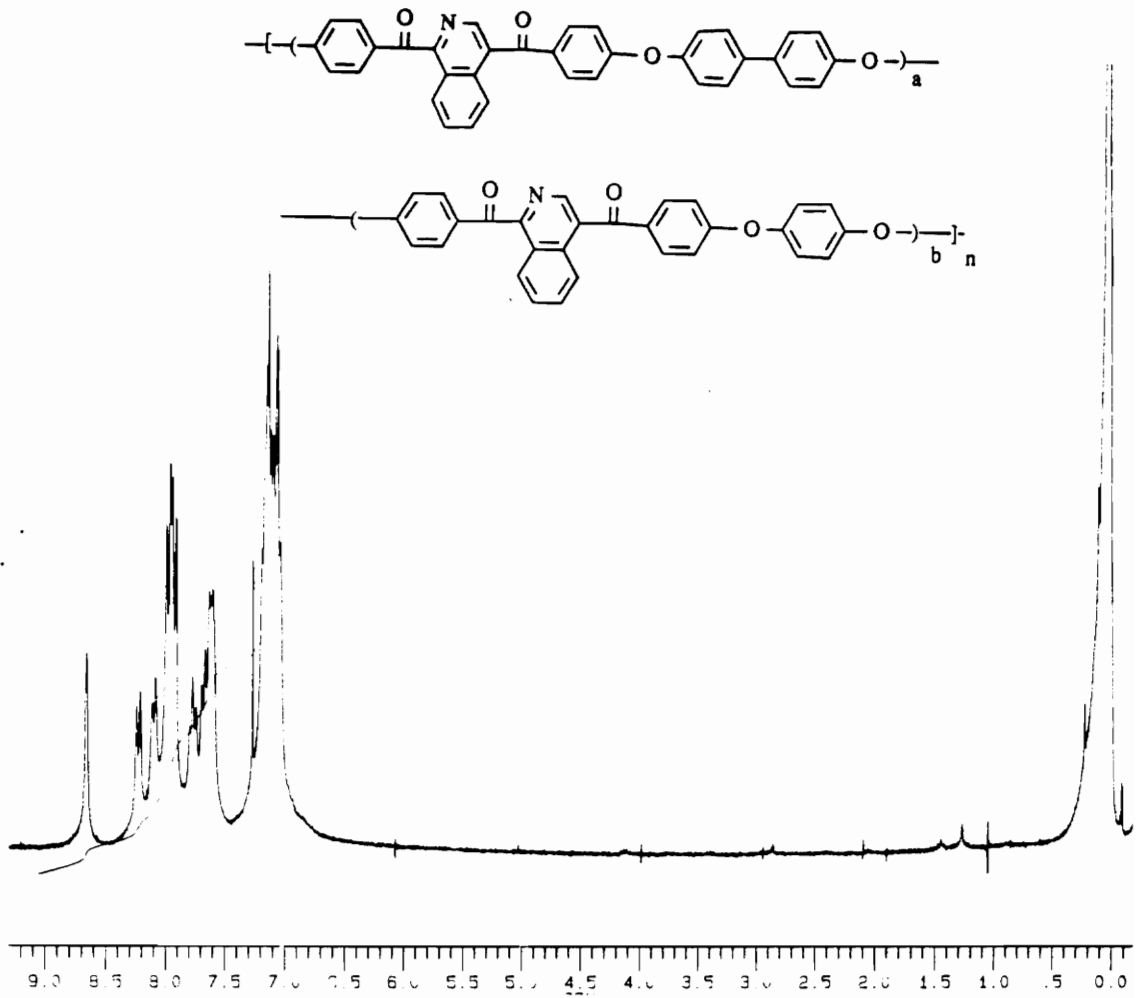


PNMR #5: Bis-Reissert Compound 38, Higher Melting Sample

PNMR #6: C₁₀-bis-Reisert Compound, 51

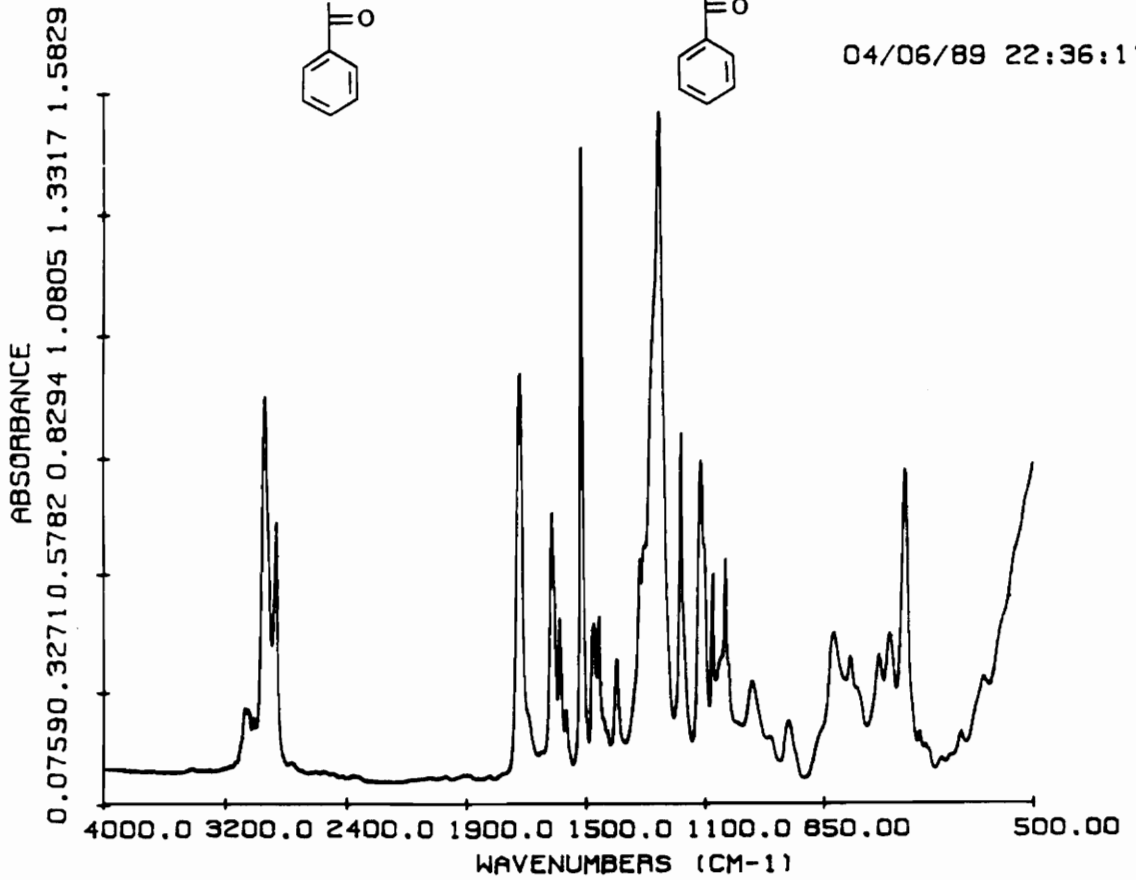
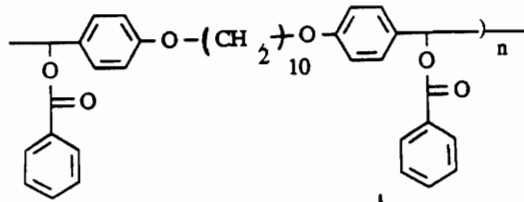
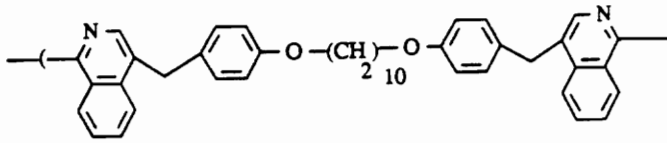


PNMIR #7: 1,4-Bis(4-fluorobenzoyl)isoquinoline, 64

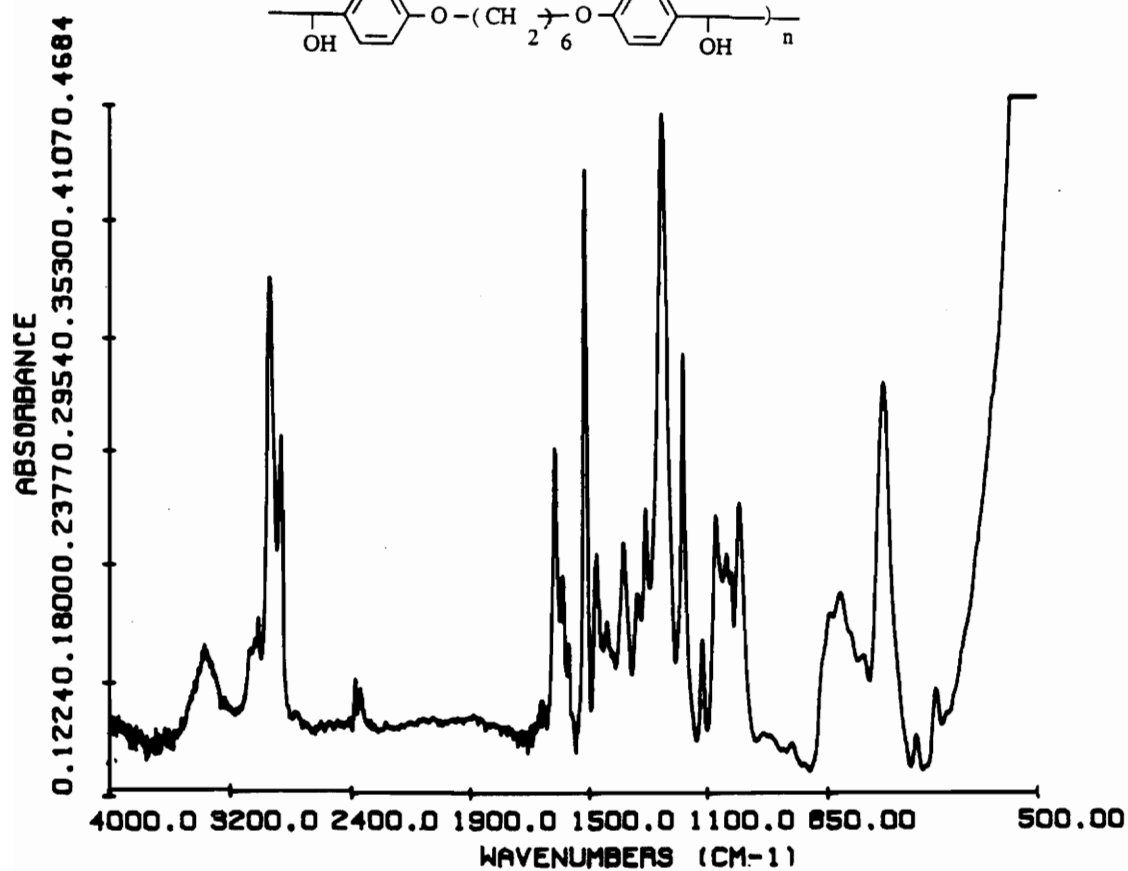
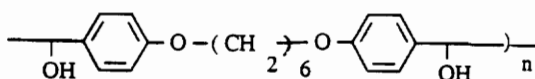
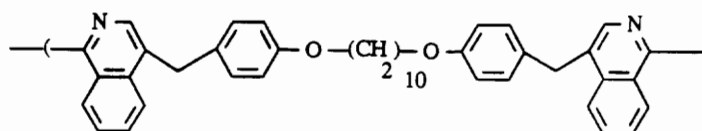


PNMR #8: Copolymer 66

APPENDIX B: FTIR SPECTRA



FTIR #1: Polyester 52



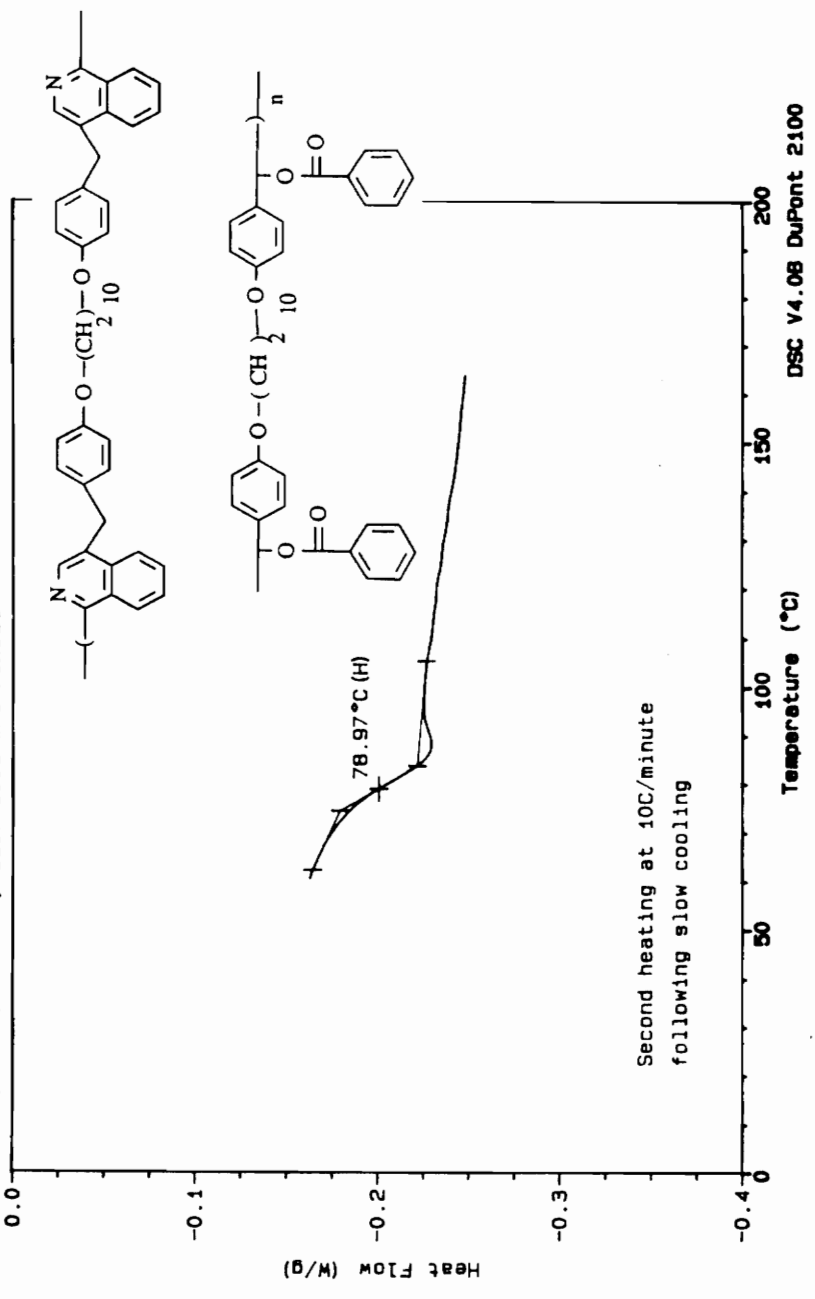
FTIR #2: Polyalcohol 58

APPENDIX C: DSC DATA

Sample: 89-I-229-12
Size: 14.7200 mg
Method: Brad Guilan's DSC
Comment: 10C/minute to 240C, slow cool and reheat

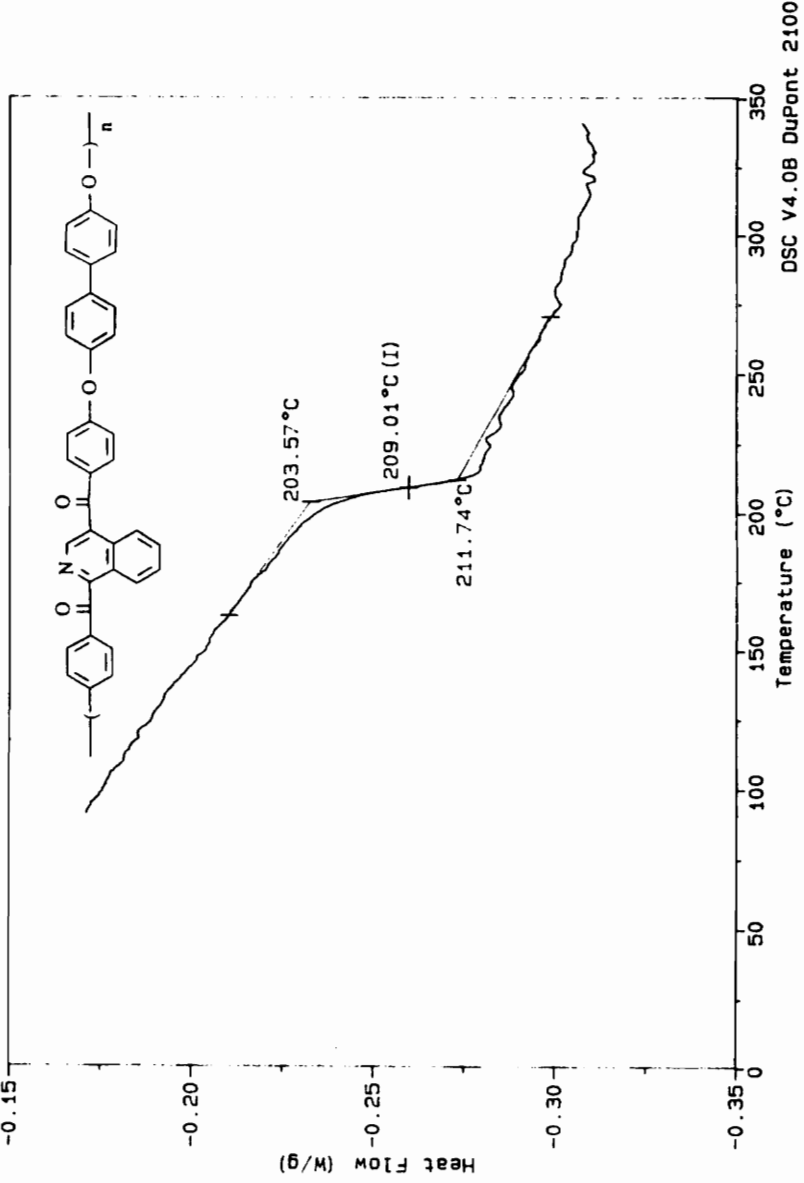
DSC

File: GUILANIB.04
Operator: Paul S. Veil
Run Date: 7-Apr-89 14:08



DSC #1: Polyester 52

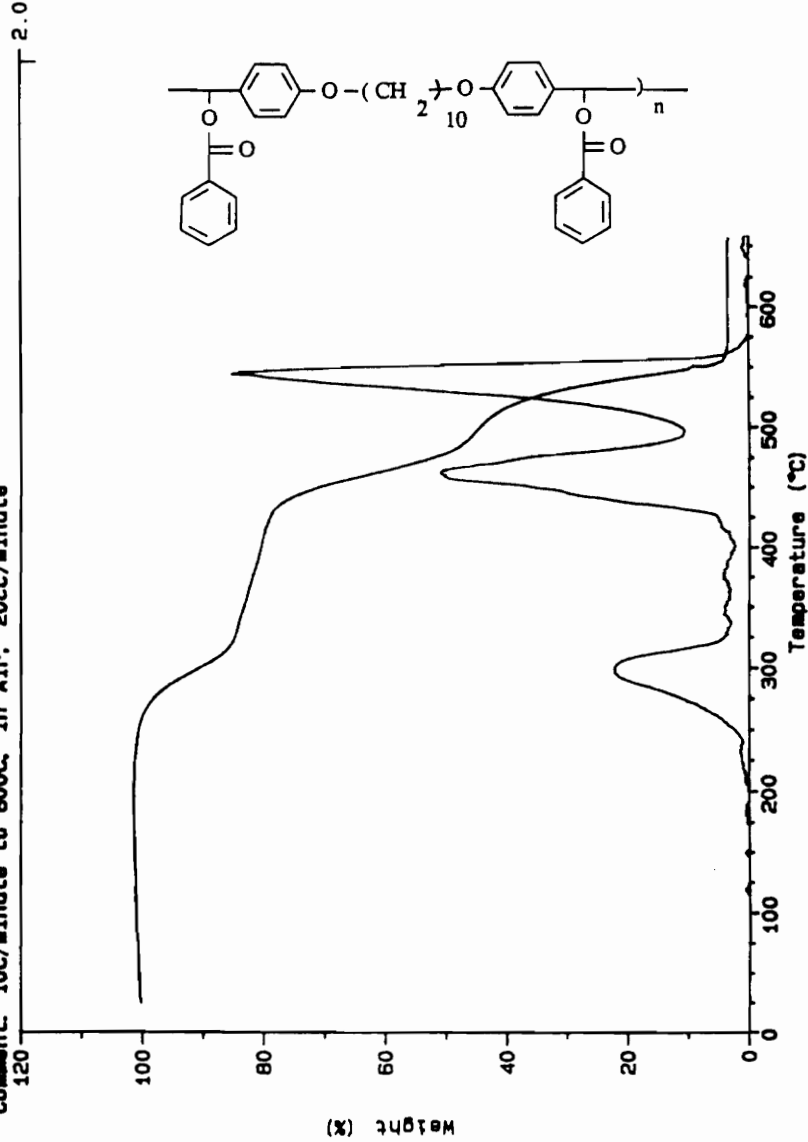
Sample: BG-I-239-10
Size: 9.8900 mg
Method: 30-340 @ 10C/min, 2 heats
Comment: 2 HEATS, 50 TO 350 C, 10 C/MIN
DSC
File: GUILANIB.13
Operator: NIRANJAN PATEL
Run Date: 20-Jun-89 17:03



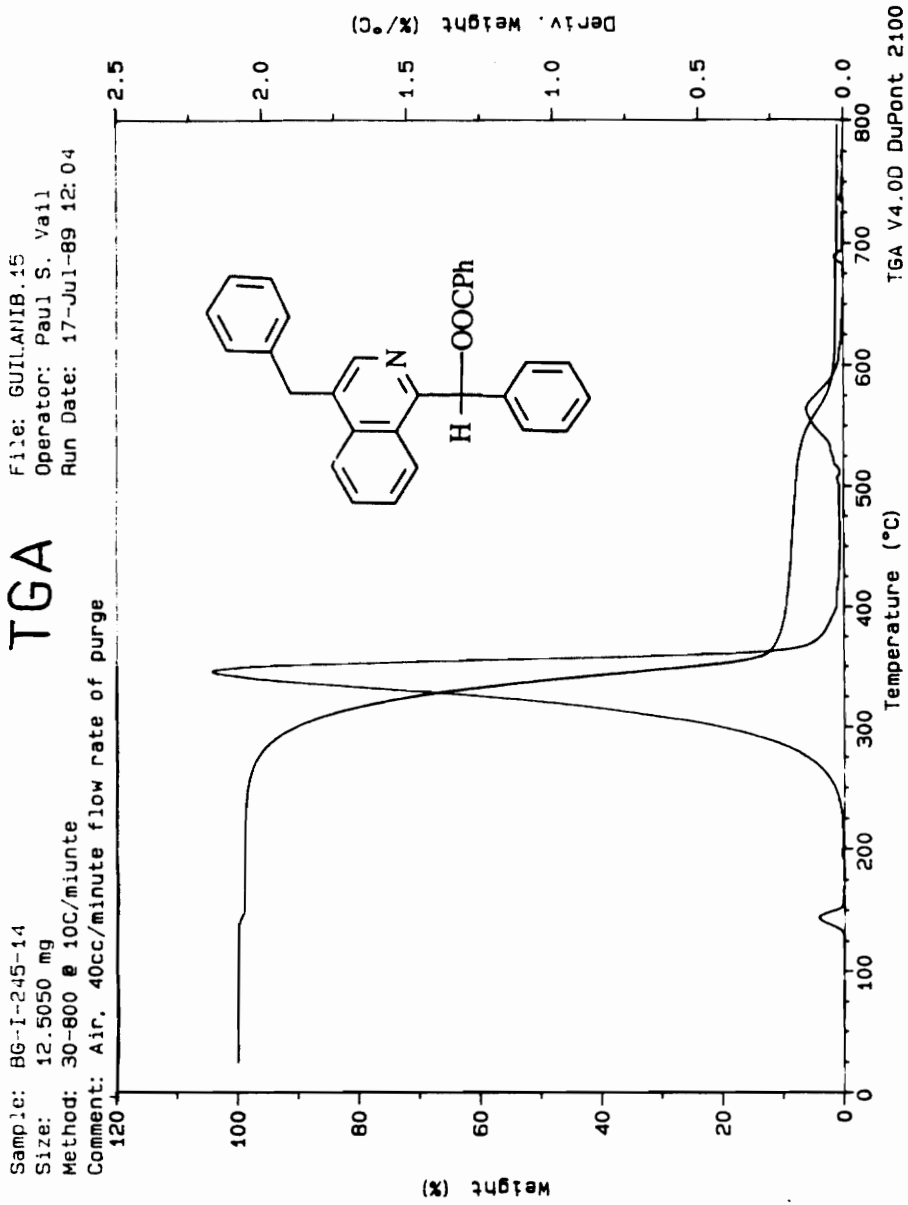
DSC #2: Poly(N-aryl-ether-ketone) 67

APPENDIX D: TGA DATA

Sample: 86-I-229-12
Size: 1.9750 mg
Method: Brad Guilan's TGA
Comment: 10C/minute to 800C, in Air, 20cc/minute
TGA
File: GUILANIB.03
Operator: Paul S. Vail
Run Date: 20-Mar-89 13:02



TGA #1: Polyester 52



TGA #2: Phenyl-1-(4-benzylisoquinolyl)methyl Benzoate, 55

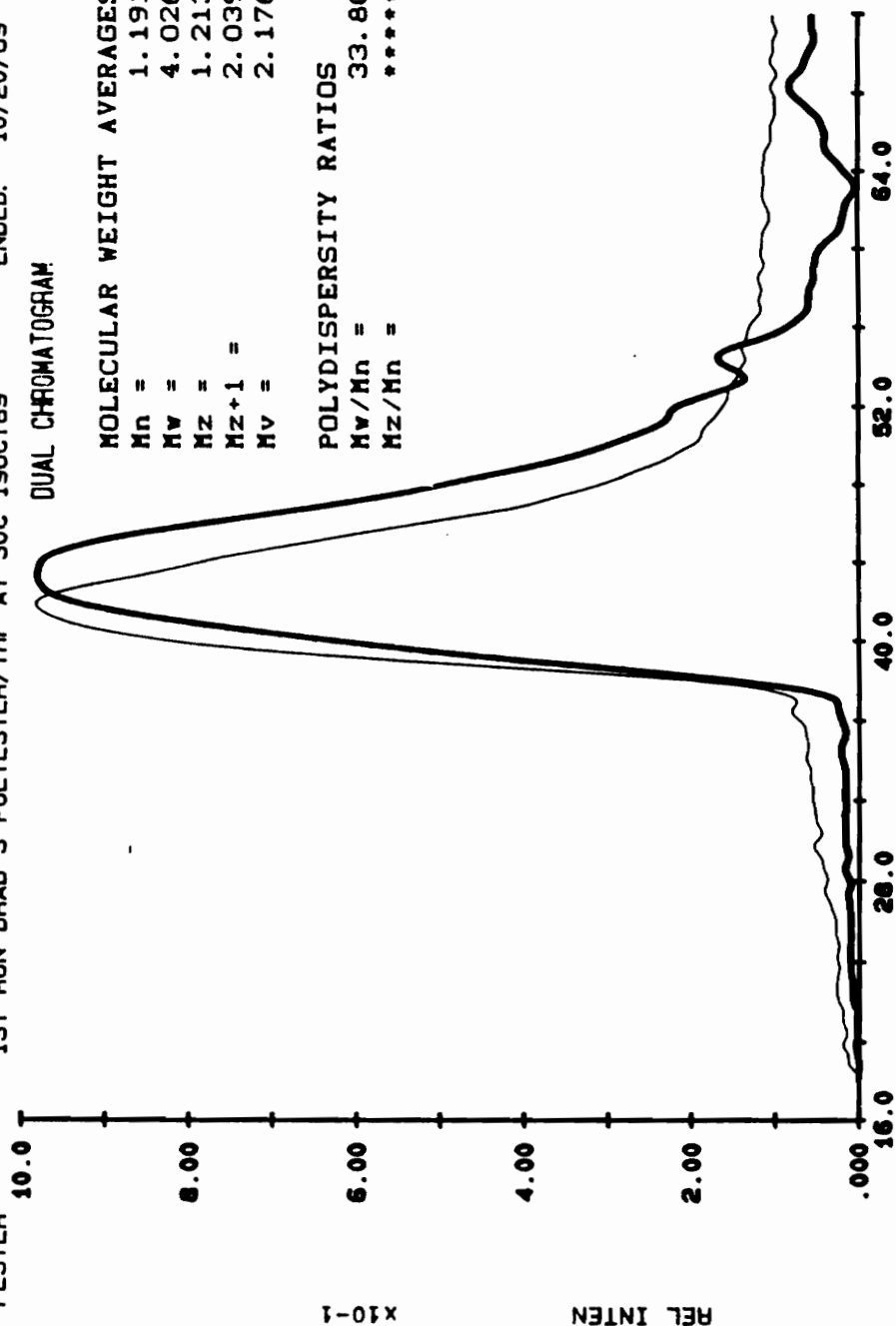
APPENDIX E: GPC DATA

PESTER 10.0 1ST RUN BRAD'S POLYESTER/THF AT 30C 19OCT89 ENDED: 10/20/89 14

DUAL CHROMATOGRAM

MOLECULAR WEIGHT AVERAGES
 Mn = 1.191E 3
 Mw = 4.026E 4
 Mz = 1.213E 5
 Mz+1 = 2.039E 5
 Mv = 2.176E 4

POLYDISPERSITY RATIOS
 Mw/Mn = 33.807
 Mz/Mn = *****

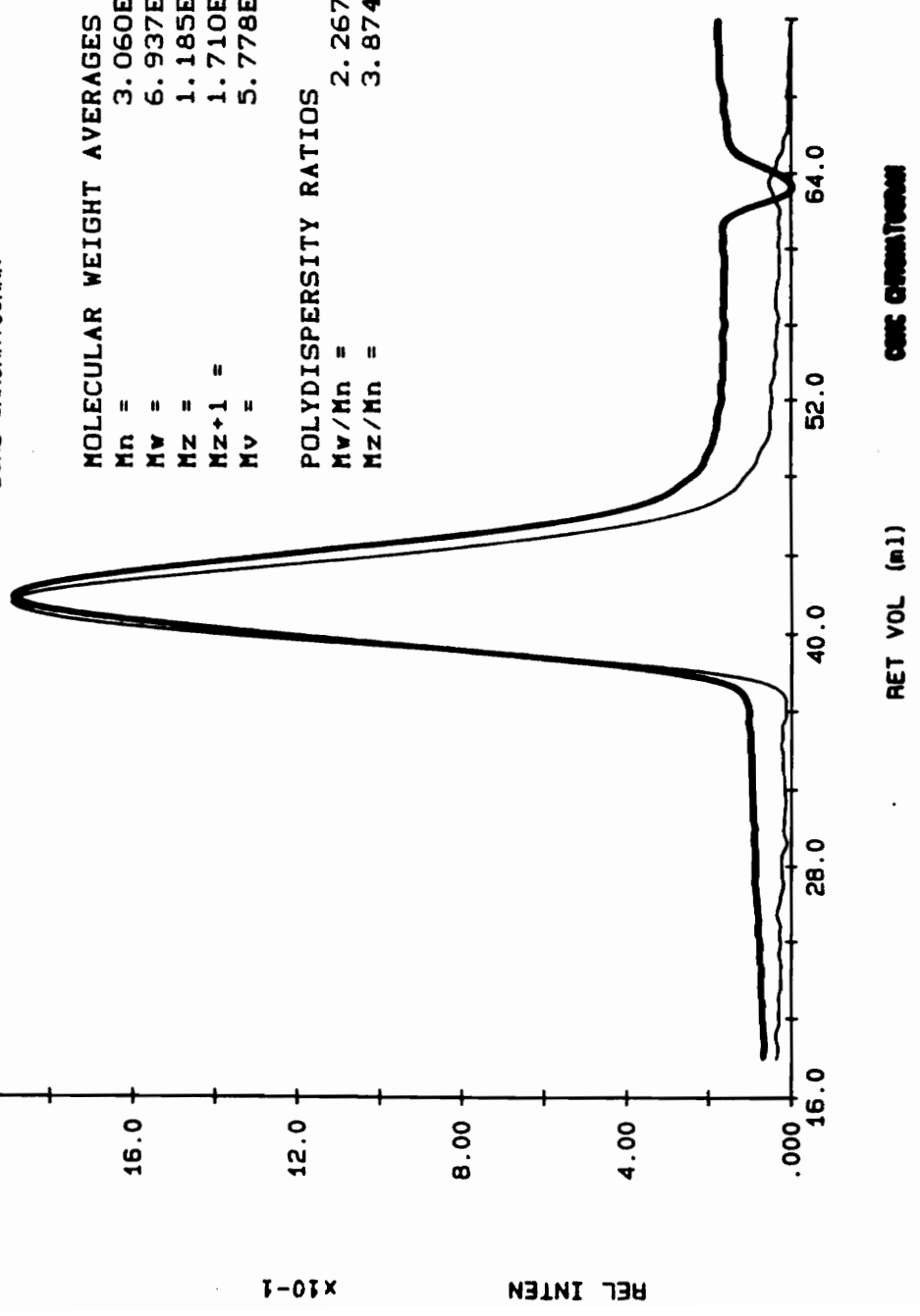


RET VOL (ml) GPC CHROMATOGRAM

GPC #1: Polyester 57, Unfractionated

PESTER4 20.0 2ND RUN BRAD'S FRACTIONATED POLYESTER/THF AT 30C 25(0)MIN: 10/26/89 12

DUAL CHROMATOGRAM



MOLECULAR WEIGHT AVERAGES
Mn = 3.060E 4
Mw = 6.937E 4
Mz = 1.185E 5
Mz+1 = 1.710E 5
Mv = 5.778E 4

POLYDISPERSITY RATIOS
Mw/Mn = 2.267
Mz/Mn = 3.874

RET VOL (ml) GPC CHROMATOGRAM

GPC #2: Polyester 57, After 2 Fractionations

IX. Vita

Bardia Guilani ("Brad") was born on August 14, 1963, to Hamideh Malek and Reza Guilani. He received a Bachelor of Arts in Chemistry from George Mason University in May 1984. After a two year interruption, he chose to pursue a graduate degree in chemistry under the direction of Dr. Harry W. Gibson. While at Virginia Tech, he became a member of the American Chemical Society and of Phi Lambda Upsilon Honorary Chemical Society. The author is currently a candidate for the degree of Master of Science in Chemistry at Virginia Tech.



Bardia Guilani