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Design, Synthesis and Characterization of Novel Heterocyclic Polymers

by

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A thesis submitted to the Faculty of Graduate Studies and research in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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Abstract

Design, Synthesis and Characterization of Novel Heterocyclic Polymers

New classes of monomers containing heterocyclic groups have been prepared in good yield from readily available compounds. The heterocyclic groups were phthalazinone, quinazolinone, benzopyrenequinone and acridone.

Bisphthalazinones, such as oxy-7-bis(1,2-dihydro-4-phenylphthalazinone) were reacted with a series of activated aryl halides to give high molecular weight novel poly(phthalazinone)s in a one-step reaction involving the formation of a N-C bond.

A series of novel quinazolinone containing monomers synthesized for nucleophilic aromatic displacement polymerization reactions, bisphenols and activated difluorides, were unstable under the polymerization conditions. Only low molecular weight oligomers were formed.

Two new quinazolinone diamines, oxy-bis(1,4-phenylene)-bis[3-(4-aminophenyl)-1-oxo-quinazolin-2-yl] and 2-(4-aminophenyl)-3-amino-4-quinazolinone were synthesized. They did not form high molecular weight polyimides because of low reactivity or instability of the monomers. A series of high molecular weight polyimides were synthesized from 2-(4-aminophenyl)-6-amino-4-quinazolinone either by one-step solution polymerization or two-step low temperature solution polymerization followed by thermal cyclodehydration.

The new monomer, 1,5-bis(4-fluorobenzoyl)naphthalene, was polymerized with a series of bisphenols to form high molecular weight poly(arylene ether)s containing the 1,5-dibenzoyl unit.

1,5-bis(4-fluorobenzoyl)naphthalene was converted to 2,3;7,8-bis(4-fluorobenzo)pyrene-1,6-quinone by a Scholl reaction using antimony pentafluoride. It was reacted with bisphenols, however because of side reactions only crosslinked insoluble material formed.

A series of novel acridone containing monomers, such as N-benzyl-3-chloro-6-fluoroacridone were synthesized for nucleophilic aromatic displacement polymerization reactions.

High molecular weight poly(arylene ether)s containing the acridone moiety could not be obtained because of instability or low reactivity of the monomers. Model reactions on acridone derivatives were carried out. The fluorine at the 3-position on acridone can be displaced by phenolate anion quantitatively. New acridone monomers which can be synthesized using this reaction were proposed.

All the high molecular weight novel polymers synthesized have very high glass transition temperatures and excellent thermal stabilities. Films made from the polymers had high moduli and maintained the high moduli to high temperatures.

Sommaire

Desein, Synthèse et Caractérisation Nouveau Polymére Hétérocyclic

Des nouvelles classes de monomères hétérocycliques comme la phthalazinone, quinazolinone, benzopyrenequinone et acridone ont été preparées avec de bons rendements utilisant des produits commerciaux.

Des polymères de hauts poids moléculaires avec des liaison N-C ont été obtenus par les réactions de bisphthalazinones (oxy-7-bis-(1,2-dihydro-4-phenylphthalazinone) avec une série de aryl halide activé.

Deux nouvelles quinazolinones diamines, oxy-bis[1,4-phenylene]-bis-[3-(4-aminophenyl)-1-oxy-quinazoline-2-yl et 2-(4-aminophenyl)-3-amino-4-quinazolinone ont été synthétisées; mais seulement des polyimides avec de bas poids moléculaires ont été obtenus à cause de leur instabilité ou de leur mauvaise réactivité. Une série de produits de haut poids moléculairé a été preparée soit par une polymérisation en une seule étape en solution, ou par deux étapes à basse température suivie par une déshydration cyclique.

Les réactions entre une série de biphénol et 1,5-bis-(4-fluorobenzoyl)naphthalène ont produit des polymères de haut poids moléculaire.

Le 1,5-Bis-(4-fluorobenzoyl)naphthalène a été converti an 2,3;7,8-di-(4-fluorobenzo)pyrene-1,6-quinone par la réaction Scholl utilisant le pentafluorine d'antimoine. Seulement des produits insolubles ont été obtenus par la réaction de 2,3;7,8-di(4-fluorobenzo)pyrene-1,6-quinone avec une série de biphénols.

Une série de monomères de type acridone, comme le N-benzyl-3-chloro-6-fluoroacridone, ont été preparés pour la polymérisation par déplacement nucléophilique aromatique. Mais des polymères avec des monomères de type acridone n'ont pu être obtenus à cause de l'instabilité ou de la mauvaise réactivité des monomeres.

Tous les polymères de haut poids moléculaire ont de hautes températures de transition de verre et une excellente stabilité thérmique. Les films de ces polymères ont de hauts modules et ces propriété sont conservées en hautes températures.

Design, Synthesis and Characterization of Novel Heterocyclic Polymers

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Glossary of Abbreviations and Symbols

Å	Angstrom (1x10^{-8}cm)
BPA	Bisphenol A (4,4’-isopropylidenediphenol)
CHP	1-Cyclohexyl-2-pyrrolidinone
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
dL	Deciliter (10^{-1}liter)
DMAc	N, N-Dimethylacetamide
DMF	N, N-Dimethylformamide
DMSO	Dimethyl sulfoxide
DMPU	1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone
DPS	Diphenyl sulfone
DSC	Differential scanning calorimetry
E’	Young’s modulus
E’’	Maximum values of loss moduli
HPLC	High pressure liquid chromatography
ΔG	Change in free energy
Gpa	Giga pascal (10^9pascal)
GPC	Gel permeation chromatography
ΔH	Change in enthalpy
HMO	Huckel molecular orbital calculation
ITO	Indium tin oxide electrode
FT-IR	Fourier transformed infrared spectroscopic analysis
LED	Light emitting diode
MALDI-TOF	Matrix assisted laser desorption ionization-time of flight mass spectrometry
mol	Mole

mmol	Millimole
M_n	Number average molecular weight
m.p.	Melting point
MS	Mass spectrum
M_w	Weight average molecular weight
NLO	Non linear optical material
nm	Nanometer
NMP	N-Methylpyrrolidinone
NMR	Nuclear magnetic resonance
PAK	Poly(arylene ether ketone)s
PD	Polydispersity
PEEK	Poly(ether ether ketone)
PPP	Poly(*p*-phenylene)
PPS	Poly(*p*-phenylene sulfide)
PPV	Poly(*p*-phenylene vinylene)
ppm	Parts per million
ΔS	Change in entropy
S_NAr	Nucleophilic aromatic substitution
T	Temperature
tan δ	E'/E''
TEC	Thermal expansion coefficient
T_g	Glass transition temperature
TGA/DTA	Thermal glavimetric analysis/ differencial thermal analysis
T_m	Crystalline melting temperature
TMS	Tetramethylsilane
THF	Tetrahydrofuran

UV	Ultraviolet
δ	Chemical shift
uL	Microliter (10^{-6} liter)

Chapter 1

Introduction

1-1 High Performance Polymers[1-7]

High performance polymers have been defined as materials with excellent mechanical strength per unit weight, high thermal stability (continuous use temperatures above 150°C, combined with low flammability), chemical resistance, as well as good electrical properties[1,5].

The quest for the development of high performance polymers began in the late 1950s to meet the demand of the aerospace industries. Since then, many different high-temperature polymer systems have been reported. Dupont patented the aramides "Nomex®" in 1960 and aromatic polyimides "Kapton®" in 1961. Marvel reported the synthesis of polybenzimidazole in 1961[9,10]. These polymers were commercialized and used not only for structural materials but also solution-processed high-modulus fibers and films. Poly(ether sulfone) (Union Carbide and ICI), polyarylate (Unichika Japan), poly(phenylene sulfide) (Phillips Petroleum), poly(phenylene oxide) (General Electric) were commercialized from the late 1960s to early 1970s. In the 1980s poly(ether ketone) "Victrex" (ICI), poly(ether imide)s (General Electric) were commercialized.

Dupont introduced "Kevlar®", which is poly(*p*-phenylene terephthalamide) in 1972. This material shows lyotropic liquid crystallinity in concentrated sulfuric acid solution. Since then, liquid crystallinity of rigid-rod polymers, which gives high strength, high modulus fibers, has received great attention.

In 1994, global demand for high performance polymers increased by over 10% from 1993 levels. In total, 130,000t of high temperature polymers valued at $3.2bn, were consumed in 1994. Since 1984, real growth in demand for high-temperature polymers has averaged almost 10% per year. This growth in volume is expected to continue over the next decade at 8.5% per year. The global market is expected to exceed 300,000t, valued at over $6bn in 2004[7]. Electrical, transportation and industrial applications have been a significant factor driving the growth of high performance polymers. It is important for these polymers to have not only thermal stability but also other attractive properties including resistance to corrosion, wear and moisture, processabilty, dimensional stability, low flammability and insulating properties. In fact, only about half of current demand is for high-temperature needs.

These engineering plastics all have aromatic structures. They contain few flexible single bonds so the main chain is rigid and the molecular rotation is restricted. As a result, they have high melting points, high modulus, and are thermally stable. However, a problem which is inherent in aromatic polymers, is that they are difficult to proccess. The challenge is to develop new high performance polymers which are processable with good properties[2,3].

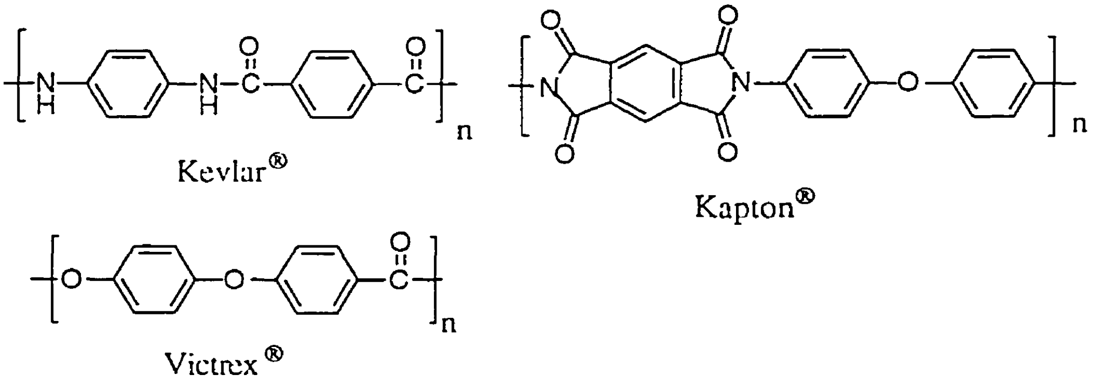

Kevlar®
Kapton®
Victrex®

Figure 1-1 Major Commercialized High Performance Polymers

1-2 Design of Thermally Stable Polymers

1-2-1 Thermal Stability of Polymers[11]

A thermally stable polymer maintains its properties to high temperatures. Most polymers are used in the solid state. Properties such as toughness or break strength decrease drastically above the melting point (T_m) or the glass transition temperature (T_g). This is due to the change in aggregation or molecular motion. These changes are reversible and a function of temperature; if the temperature is lowered, the properties are regained. These physical properties are evaluated by a measurement of T_g and T_m. When polymers are used for a long time at high temperature, chemical reactions occur along with a degradation of properties due to thermal reactions or oxidation. These chemical reactions are irreversible and a function of temperature as well as time. A qualitative estimation of thermal stability is evaluated by thermal gravimetric analysis (TGA). The requirements for use of a polymer at high temperatures are high T_g or T_m for retention of mechanical properties, and high resistance to thermal breakdown and to chemical attack, such as oxidation and hydrolysis.

1-2-2 Design of Thermally Stable Polymers[4]

The melting process involves the destruction of the ordered crystal structure that leads to the disordered liquid state when the temperature reaches the point where the crystal lattice vibration is large enough and the crystal lattice falls apart.

$\Delta G=G_l$(free energy of melt liquid) $-G_s$(free energy of solid crystal) equals 0 at melting point. ΔG is also expressed by the next equation.

$\Delta G=\Delta H-T\Delta S$, where ΔH is enthalpy difference between solid and liquid, ΔS is the entropy difference.

$$0=\Delta H_m-T\Delta S_m \quad \therefore T_m=\Delta H_m/\Delta S_m$$

According to this equation, a high heat for melting or small entropy change in melting is required to obtain a high melting point polymer. And in many cases, entropy factor is more important influence on the melting point of a polymer.

The factors affecting T_m are chain symmetry, intermolecular bonding, tacticity, branching etc. T_g or T_m can be raised by increasing the intermolecular forces between chains. This can be done by incorporating polar side groups, by increasing the opportunities for hydrogen bonding, and by cross-linking of the chains. Other methods are to increase the regularity of the chain to increase the degree of crystallinity by making the chain more rigid by the incorporation of bulky cyclic groups, especially para-linkage in the main chain.

At the glass transition temperature, the polymer changes from a hard, brittle solid below the T_g to a viscous or flexible material above. The T_g is associated with the onset of segmental motion in the amorphous phase of an amorphous or semicrystalline polymer. There are some specific properties which undergo discontinuous changes at the glass transition, such as volumetric, thermodynamic, mechanical and electromagnetic properties.

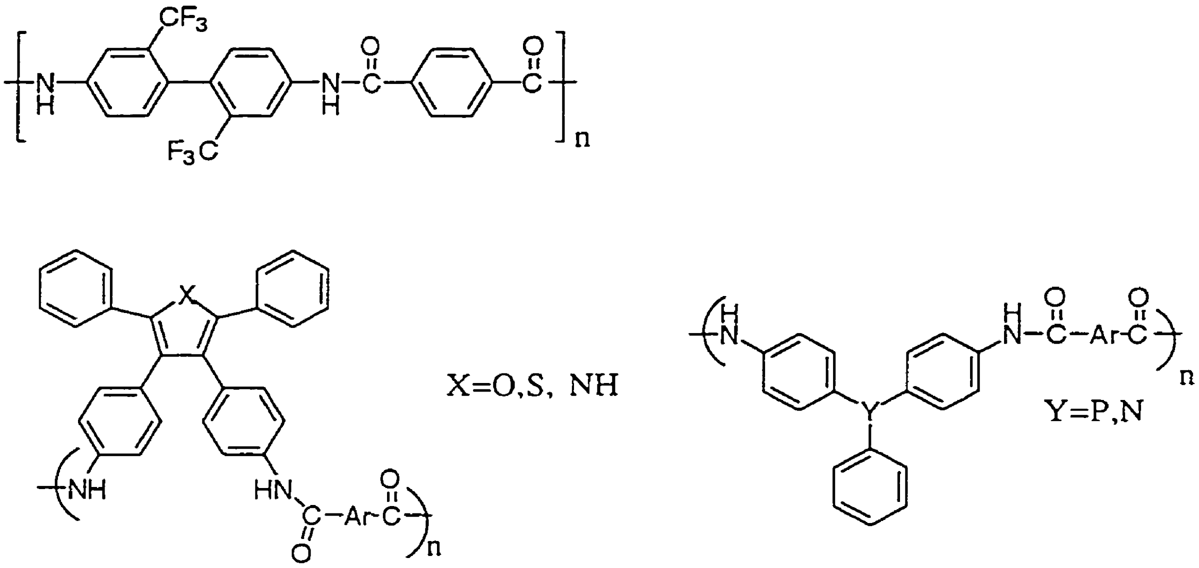
In general, intermolecular forces, flexibility and chain geometry are the three principal parameters that govern the T_g. They also affect the T_m in the same way, so a correlation between the T_g and T_m can often be found in semicristalline polymers. For a large number of linear homopolymers, the ratio of T_g/T_m is found to be around 0.5 for unsymmetrically substituted polymers and about 0.8 for symmetrically substituted polymers.

Chemical thermostability is influenced by the strength of chemical bonds in the polymer. To attain high chemical thermostability these items are considered; strong chemical bonds, resonance stabilization, polybonding, and absence of strain which causes rearrangement or other chemical reactions.

1-2-3 Solubility of Polymers[6,12,13,14]

Generally melt processing of polymers requires temperatures 100°C above T_g or 50°C above T_m. High T_g or T_m polymers have to be processed at very high temperature where decomposition is a problem when being processed. Consequently, many of them cannot be processed by injection molding. If a polymer is soluble, films can be made at low temperature by casting from the solution regardless of T_g. In order to synthesize soluble high T_g polymers a number of efforts have been made. These approaches involved: 1) the introduction of an angular or flexible linkage into the polymer backbone; 2) introduction of kinks to give an unsymmetrical structure; 3) bulky pendant groups such as phenyl and trifluoromethyl; 4) the disruption of regularity of the repeating unit through copolymerization. Rigid rod polyamides with 2,2'-trifluorobiphenyl units were synthesized[6]. They are completely amorphous and colorless because of noncoplanarity between the phenyl rings. The steric and electronic effects of trifluoro substituent are also important (Figure 1-2). Highly phenylated heterocyclic poyamides and polyimides, and polyimides or polyamides with triphenylamine, or triphenylphosphine groups were synthesized[13,14]. The polymers obtained were soluble and have high T_gs. The introduction of these bulky phenyl groups gives a twisted coplanar structure which destroys the regularity so that the polymers are amorphous.

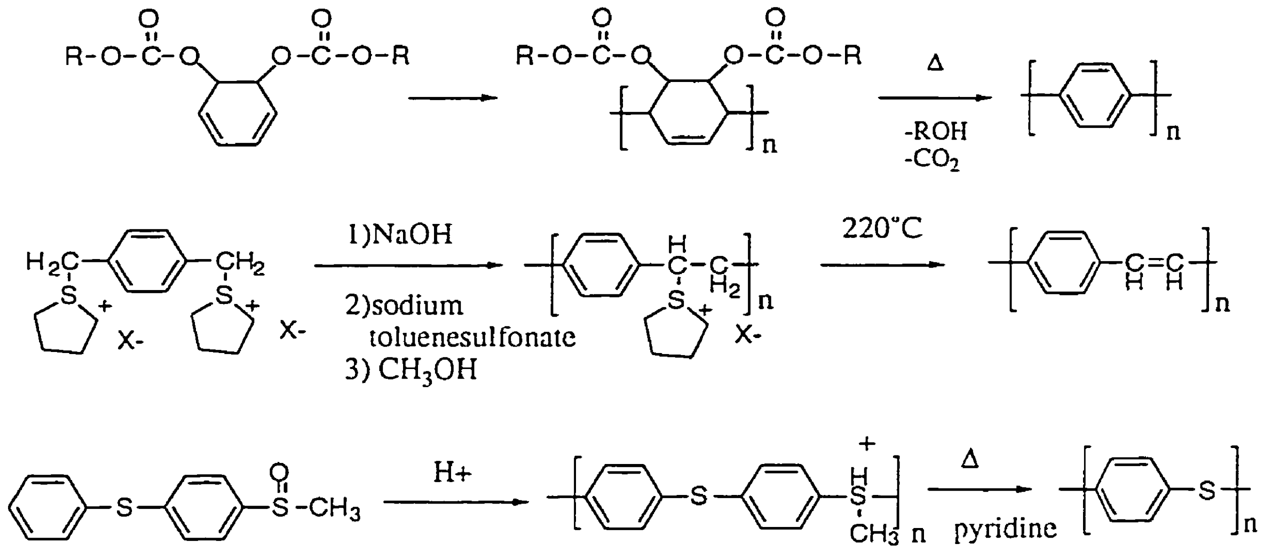
Figure 1-2



1-2-4 Polymers from Soluble Precursor

The use of soluble precursor polymers allows films of high T_g or T_m polymers to be made. Most polyimide films are made by cyclodehydration of soluble poly(amic acid) films by heating (Chapter 4). Poly(*p*-phenylene) (PPP) which is synthesized by oxidative polymerization of benzene cannot be processed. Ballard reported the preparation of PPP films by polymerization of cyclohexadiene derivatives followed by deacetylation[15]. Poly(*p*-phenylene vinylene) (PPV) films, which are fluorescent materials, can be made via soluble poly(sulfonium salt)s[16]. Poly(*p*-phenylene sulfide) (PPS) is an insoluble crystalline polymer. Yamamoto reported soluble polysulfonium salts, which can be cast into films[17,18]. This can be converted to PPS by heating in acetonitrile in the presence of pyridine (Scheme 1-2).

Scheme 1-2



1-3 Synthesis of Heterocyclic Polymers

During the past decade, significant efforts have been carried out to synthesize new heterocyclic polymers. This incorporation of heterocyclic group into a polymer chain generally enhances properties such as strength, modulus and T_g. Functional heterocyclic polymers containing functional groups are of interest. In this section we survey the synthesis of heterocyclic polymers and functional heterocyclic polymers with special functionality such as fluorescent properties.

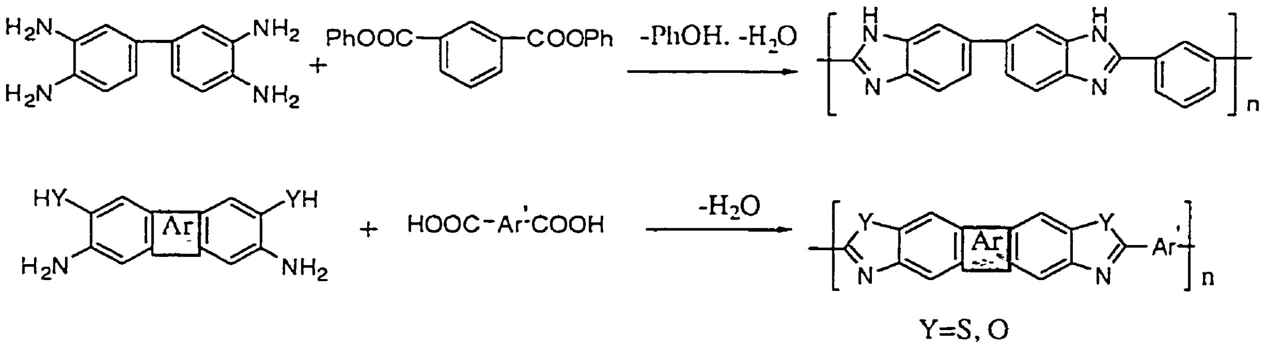
There are three synthetic strategies currently employed to introduce a heterocyclic group into polymers. One method involves the use of a heterocyclic formation reaction for a polymerization reaction. Another method involves incorporation of a heterocyclic moiety into a monomer. One of these approaches uses a heterocyclic activated nucleophilic aromatic substitution reaction, which is described in the next section. The last method involves a polymer precursor which is converted to a heterocyclic polymer by a reaction on the polymer.

1-3-1 Heterocyclic Formation Reaction

Polyimides and polybenzazoles are major heterocyclic polymers. The synthesis of polyimides is described in chapter 4. Besides polybenzazoles, polyhydantoins, polyparabanic acids, polyquinolines, and polyquinoxalines are commercial or widely studied heterocyclic polymers. Each of these polymers is synthesized from different monomers by a distinct chemical reaction.

Polybenzimidazoles are synthesized by melt condensation of aromatic tetraamines and phenyl esters of aromatic dicarboxylic acids[10]. This process consists of two steps. The mixture of tetraamine and phenyl esters of aromatic dicarboxylic acids was first heated to 200-300°C to give an oligomer, which solidified. The solid was then heated to 350-400°C in vacuo affording high molecular weight polybenzimidazole powder (Scheme 1-2). Polybenzimidazoles have also been synthesized by polyphosphoric acid solution condensation[19].

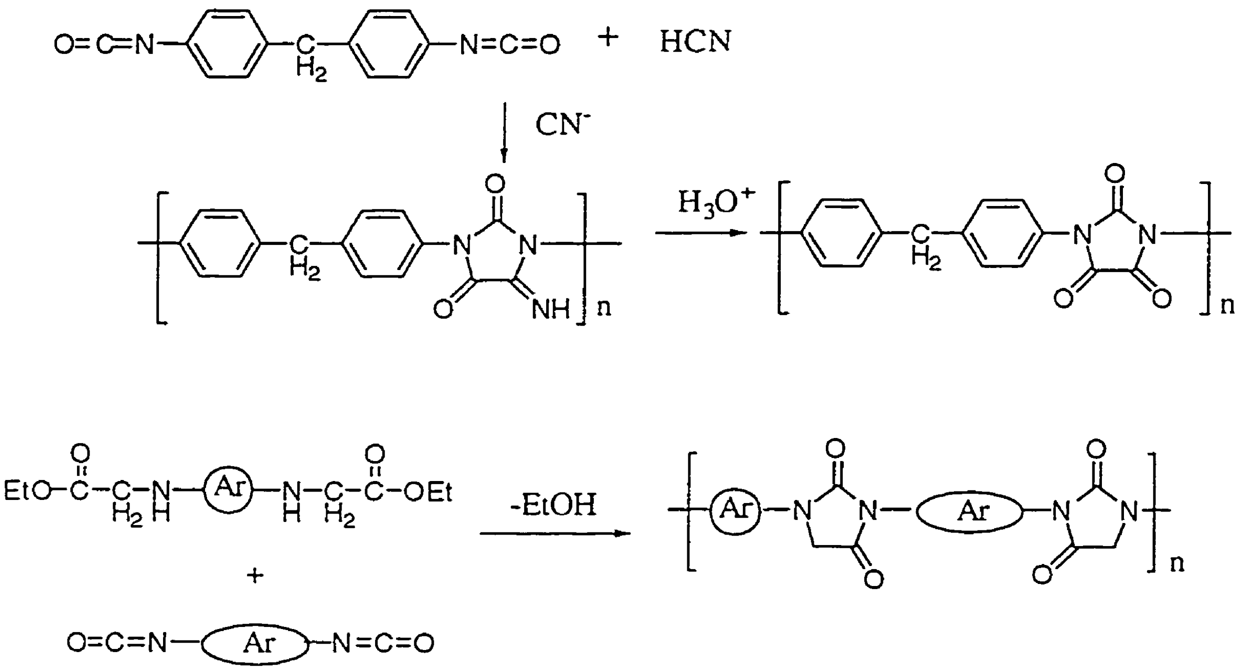
Scheme 1-2



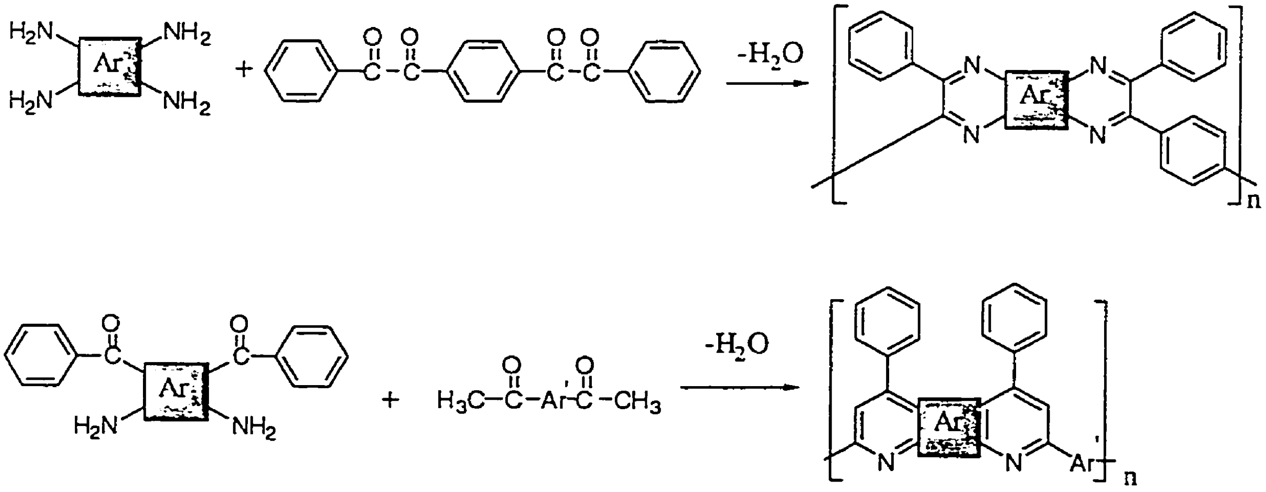
Polybenzoxazoles and polybenzthiazoles are synthesized by a similar method in polyphosphoric acid[20] (Scheme 1-2). Polybenzoxazoles can be obtained from bis(o-aminophenol) and aromatic dicarboxylic acid, and polybenzthiazoles can be obtained from bis o-aminobenzenethiol and aromatic dicarboxylic acid. Polyoxydiazoles are synthesized from aromatic hydrazides and aromatic dicarboxylic acid chlorides by a 2-step method[21].

Polyhydantoins, and poly(parabanic acid)s are used for varnishes, and coatings. Polyhydantoins are synthesized from aromatic bisamic acid esters and aromatic diisocyanates[22].

Scheme 1-3



Scheme 1-4



Poly(parabanic acid)s are synthesized by a reaction of aromatic diisocyanates and hydrogen cyanide. Diisocyanates and HCN are reacted in the presence of sodium cyanide in NMP at room temperature and the polyiminohydantoin obtained is hydrolyzed to poly(parabanic acid) in the presence of sulfuric acid catalyst by heating[23] (Scheme 1-3).

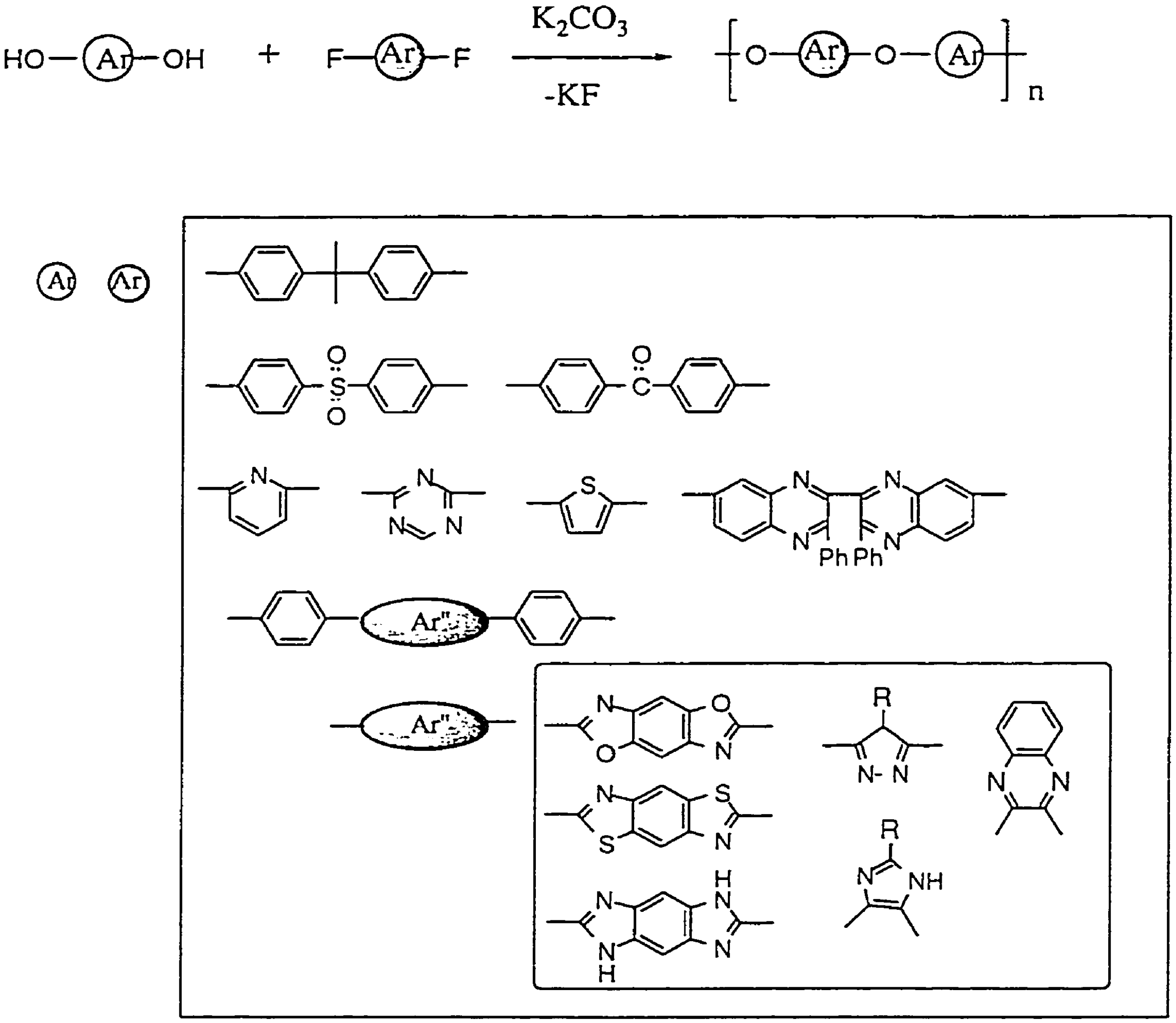
Polyquinoxalines are obtained by the reaction between aromatic tetraamines and aromatic bis(1,2-diketone)s in *m*-cresol/xylene at low temperature[24,25,26]. Polyquinolines are obtained by the reaction of aromatic bis(o-aminoketone) and aromatic diacetyl compound in *m*-cresol/ phosphorus pentoxide at 135°C[27] (Scheme 1-4).

1-3-2 Heterocyclic Polymers from Preformed Heterocyclic Monomers[28]

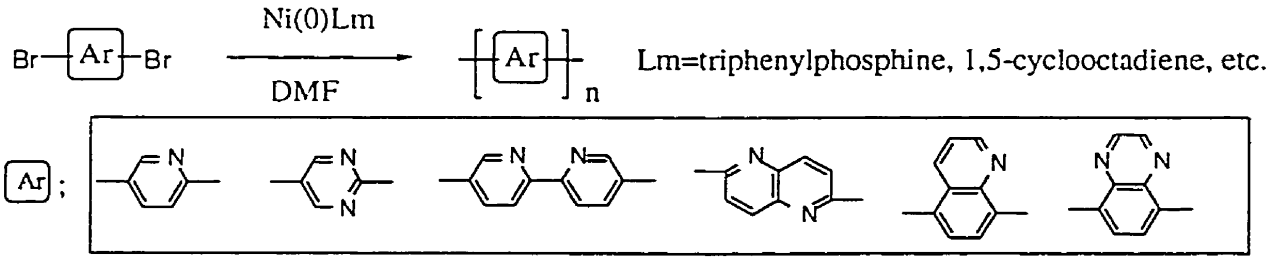
A number of heterocyclic polymers have been synthesized by polymerization of monomers which have preformed heterocyclic groups. This method does not rely on a high yield for the heterocyclic formation reaction and therefore broadens the types of structures of the monomers. Many new heterocyclic polymers have been synthesized by a nucleophilic aromatic substitution reaction (Scheme 1-5). In this polymerization reaction, a heterocyclic group is incorporated into a bisphenol or an aromatic activated dihalide. In many cases, heterocyclic group works as an activating group (see Scheme 1-9, p13). 1,3,4-Oxadiazole[29], 1,3,4-thiadiazole[30], quinoxaline[31] and benzoxazole[32] have been used successfully. Halogen atoms bound directly to the heteroaromatic ring are also strongly activated toward the nucleophilic attack. This approach has been used for a number of six-membered heteroaromatic systems such as 2,6-difluoropyridine[33], 2,6-difluoropyrazine[34], and halogenated triazines[35]. It has also been used with five-membered heteroaromatic sytems based on benzthiazole[36], thiophene[37], and oxazole[38].

Yamamoto has synthesized a series of *p*-conjugated polymers containing nitrogen containing heterocyclic polymers such as pyridine[41], pyrimidine[42], quinoline[40], and quinoxaline[39] by dehaloganation polycondensation using a nickel complex as a catalyst (Scheme 1-6).

Scheme 1-5



Scheme 1-6

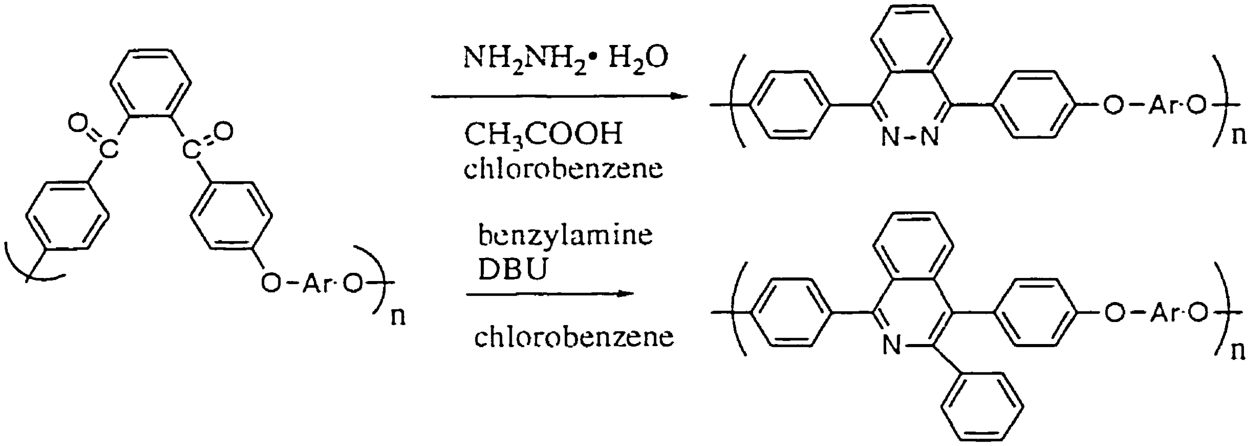


1-3-3 Heterocyclic Polymers by a Reaction on the Polymer

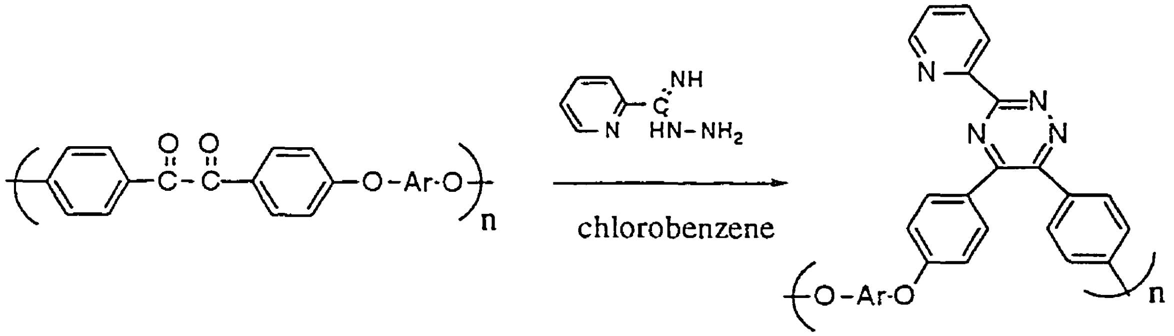
Another approach to incorporate a heterocyclic ring into a polymer is the use of a polymer precursor. Such a precursor polymer is particularly useful for the introduction of heterocyclic functionality which cannot tolerate the polymerization conditions.

Singh reported the synthesis of poly (aryl ether isoquinoline)s and poly(aryl ether phthalazine)s from high molecular weight poly(aryl ether)s containing a 1,2-dibenzoylbenzene group[43].

Scheme 1-7



Scheme 1-8



The 1,2-dibenzoylbenzene moiety is converted by treatment with hydrazine to phthalazine[44], and by treatment with benzylamine in the presence of 1,8-diazabicyclo[5.4.0]undecene (DBU) to isoquinoline[45] (Scheme 1-7). Strukelj reported the synthesis of poly(aryl ether pyridyltriazine)s from poly(aryl ether benzil)s by the reaction with (2-pyridyl)hydrazine[46] (Scheme 1-8).

1-3-4 Functional Heterocyclic Polymers

Besides high thermal stability or good mechanical properties, heterocyclic polymers with special functionality have received great attention. Functionalities that have been incorporated are conductivity, non linear optical activity, fluorescent properties, etc..

Some conjugated heterocyclic polymers, such as polypyrrole, polythiophene, exhibit conductivity when they are doped[47]. They are synthesized by chemical or electrochemical oxidative polymerization. Recently many organometalic catalyzed reactions such as the Stille reaction[48], have been applied to synthesize conjugated heterocyclic polymers.

Oxazoles, or quinoxaline derivatives display nonlinear optical behavior. Brittain synthesized polycarbonates, polyformals, and polyethers containing these NLO chromophores[49]. Benzoxazole and benzthiazole groups have a chromophoric effect on the fluorescence of conjugated systems[50]. Electro and photoactive polybenzthiazole rod-coil copolymers were synthesized and the supramolecular structure for enhanced functional and solid state photophysical properties were studied[51,52]. Oxadiazoles, oxazoles, and triazole-containing electroactive polymers were synthesized and films of these polymers were used for electron transport layers in a light emitting diode[53].

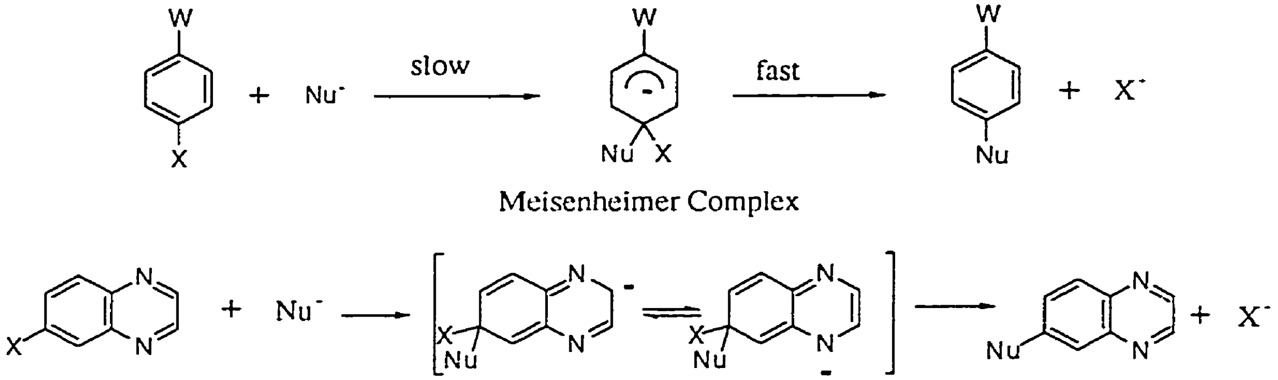
1-4 Nucleophilic Aromatic Displacement Polymerization[54,55]

Poly (aryl ether)s are an important class of commercial polymers and functional derivatives of these polymers have been of interest recently. The most commonly used synthetic route to poly(aryl ether)s involves generation of an ether linkage by a nucleophilic aromatic substitution reaction (S_NAr) as the polymer forming reaction. Many of the new polymers described in this thesis were synthesized by this S_NAr reaction. In this section, a survey of S_NAr reactions is presented. Emphasis was put on the choice of reaction conditions.

1-4-1 Mechanism[56]

Nucleophilic displacement takes place via a two-step addition-elimination mechanism (Scheme 1-9). The first step, the formation of the Meisenheimer complex, is usually the rate determining step.

Scheme 1-9



1-4-2 Reaction Conditions

Nucleophile

Generally speaking, the reactivity of the nucleophile, such as phenolate, is not as crucial as the activated halides to obtain high molecular weight polymers. The more basic the phenolate is, the more reactive it is. Bis(4-hydroxy phenyl)sulfone cannot form a high molecular weight polymer with bis(4-chlorophenyl)sulfone in DMAc; however, it forms a high molecular weight polymer in NMP at higher temperature[57]. In some cases, bisphenol A gave lower molecular weight than other bisphenols presumably because of reductive dehalogenation reactions or ether cleavages[58](section 1-4-3).

Base

In general, the order of the reactivity of the phenolate salt is Cs>K>>Na[59]. Higher polarizable cations interact more effectively with the solvent. The lithium, calcium or magnesium salts of phenols are not useful due to their insolubility in a polar solvent. The use of most reactive cesium phenolate can lower the reaction temperature and can shorten the reaction time (see chapter 3, 6, 7). In high temperature reactions, potassium salts sometimes cause side reactions so sodium carbonate was used instead[60]. Mixed metal carbonates have been used to prepare dendrimers[61]. The addition of $MgCO_3$ or $CaCO_3$ removes the fluoride ion, which cause side reactions, from the reaction system because MgF_2 or CaF_2 is insoluble in the dipolar aprotic solvent used. A combination of alkaline earth metal carbonate, such as calcium carbonate, and sodium or potassium or cesium carbonate were used to prepare poly(arylene ether)s[62]. Bisphenols were reacted with activated aryl halides in the presence of a catalytic amount of potassium carbonate and equimolar amounts of calcium carbonate in diphenyl sulfone at 300°C. The viscosities of the formed polymer were much higher than those of polymers prepared with equimolar amounts of potassium carbonate.

Reaction conditions

The optimum temperature for the displacement reaction depends on the specific system. If potassium carbonate is used, nitro or halo compounds activated by imido carbonyl groups undergo displacement reaction at 60-70°C[63]. Nitro or halo compounds activated by SO_2 or CO groups require 130-160°C. If cesium carbonate is used, displacement proceeds at 100°C.

Removal of water is crucial for the reaction. Moisture not only diminishes the nucleophilicity of the phenolate ions but also cause hydrolytic side reactions. Azeotropic distillation is usually used to remove water.

Leaving Groups

Fluoride is used commercially as a leaving group for poly(ether ether ketone) (PEEK) synthesis (4,4'-difluorobenzophenone), whereas chloride is used as a leaving group for poly(ether sulfone) synthesis (4,4'-bis(chlorophenyl sulfone)). Among halogens, the order of the reaction rate for different halogens is F > Cl > Br. Fluorine is the most reactive because of the carbon-fluorine bond polarity and low steric hindrance of fluorine atom. At high temperature fluoride ion causes ether cleavages[64,65]. Aryl chlorides are used where possible because of their reduced cost. The nitro group is also readily displaced. In the phthalimido system, the displacement of the nitro group is faster than the chloro group. Sodium nitrite which forms by displacement of the nitro group causes ring opening of the imide group in the N-substituted nitrophthalimide system[65]. Triflate has also been shown to be an effective leaving group with high reactivity. However, competitive S-O cleavage complicates the reaction[67].

Activation

The key characteristics for activating groups in the S_NAr mechanism are high electron affinity and presence of a site of unsaturation which can stabilize the Meisenheimer complex (see scheme 1-9).

The applicability of a potential activating group can often be assessed by the deshielding of the protons ortho to the group in the ^{1}H-NMR. A chemical shift of 7.5 and greater indicates probable fluorine displacement[68]. Huckel molecular orbital (HMO) calculations have also been used for the determination of the net charge densities at the C-F carbon atoms. The calculated values were qualitatively correlated with the relative reaction rate of the monomer in a nucleophilic substitution reaction[43]. Alternatively, correlation of aryl fluoride reactivity with fluorine chemical shift by ^{19}F-NMR is a useful predictive tool for the reactivity in a nucleophilic aromatic substitution reaction[69].

Solvent

Polar aprotic solvents, such as dimethyl sulfoxide (DMSO), N-methylpyrrolidinone (NMP), and dimethylacetamide (DMAc) are used in the S_NAr reaction. The reaction rate mainly depends on the polarity of the solvent and reaction temperature. Displacement takes places most rapidly in DMSO at lower temperatures because of its high polarity (Table 1-1). Cyclohexyl-pyrrolidinone (CHP)-NMP solvent mixture was used for polyquinoxaline synthesis[71]. Since CHP is not miscible with water, water generated by phenoxide formation was effectively removed with a Dean Stark trap above 100°C.

Strukelj studied the solvent effect in the preparation of poly(aryl ether benzyl)s and suggested the side reactions result from impurities in commercial NMP[70]. Decomposition products of NMP or reactions of reactive species with NMP also seem to have dramatic effect on the molecular weight. DMSO and sulfolane are very good solvents over short reaction times. However, they decompose slowly consuming base under polymerization conditions so they are not useful for long reactions. As far as solubility of polymers is concerned, NMP and DMPU[71] are excellent solvents at the reaction temperature. DMSO, DMAc and sulfolane are rather poor solvents for crystalline polymers. For poorly soluble rigid polymers, diphenyl sulfone or benzophenone is used as a solvent at about 300°C[72].

Table 1-1 Dipolar Aprotic Solvent

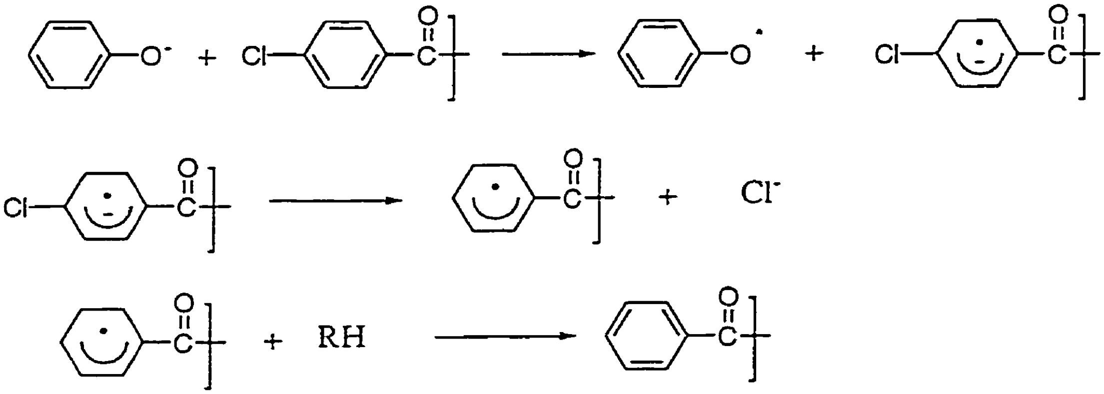
Solvent	Dielectric constant	b.p. (°C)
DMF	36.71 (25°C)	153
DMAc	37.8 (25°C)	165.5
DMSO	48.9 (20°C)	189
NMP	32.2 (25°C)	202
sulfolane	44.0 (30°C)	285
DMPU	-	146(44mHg.)
DPS	-	379

1-4-3 Side Reactions

The displacement of chlorine from bis(chloroaryl ketone)s with bisphenoxides to form high molecular weight PAKs is more difficult. A competitive reductive dehalogenation reaction via a $S_{RN}1$ (substitution, radical-nucleophilic, unimolecular) reaction mechanism has been shown to account for the formation of low molecular weight PAKs[73] (Scheme 1-9).

Factors contributing to the occurrence of the $S_{RN}1$ reaction during the synthesis of poly(arylene ether ketone)s were studied[74]. With a strong nucleophile, obtained from bisphenol A, high molecular weight polymers were formed exclusively via a nucleophilic aromatic substitution in the polymerization with 1,3-bis(4-chlorobenzoyl)benzene.

Scheme 1-9



On the other hand, oligomeric products were obtained from the weaker nucleophile from hydroquinone. In this case, both mechanisms were operative. The $S_{RN}1$ pathway, which was responsible for the formation of oligometric products, could be eliminated by the addition of a suitable radical scavenger[75] such as tetraphenylhydrazine.

The order of the radical stability in four amide solvents, 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU), 1-methyl-2-pyrrolidinone (NMP), 1,1,3,3-tetramethylurea (TMU) and N,N-dimethylacetamide (DMAc) agreed with the order of the molecular weight of the poly(arylene ether ketone)s formed in these solvents. This result supported the termination reaction by a S_{RN1} mechanism[76].

In the polymerization of 1-chloro-4-(4-fluorobenzoyl)naphthalene in NMP, BPA gave a lower molecular weight polymer than hydroquinone. The authors suggested that the isopropylidene group in BPA worked as a hydrogen source for the termination by a S_{RN1} mechanism[58].

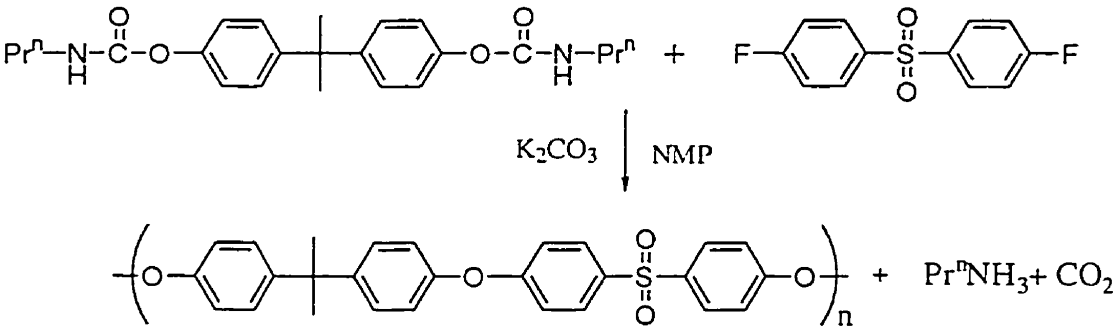
Aryl ether cleavages of poly(aryl ether ketone)s (PEKs) and poly(aryl ether sulfone)s (PESs) have been studied[65]. Aryl ethers in PESs were significantly cleaved above 280°C, while aryl ethers in PEKs were not cleaved up to 300°C in the presence of potassium fluoride in diphenyl sulfone.

High molecular weight poly(ether ketone)s were found to react with 4,4'-difluorobenzophenone in the presence of potassium carbonate in diphenylsulfone at 330°C, yielding low molecular weight poly(ether ketone) with fluorophenyl end groups. The aryl ether bonds were cleaved by the phenoxide under the reaction condition, which led to ether interchange[60].

1-4-4 Masked bisphenol

Silylated bisphenols[77], bisphenol carbamates (Scheme 1-11)[78], and polycarbonate[78] have been used as masked bisphenols for the polymerization. The use of masked bisphenols eliminates the dehydration step and thus can shorten the reaction time. In addition, it alleviates the difficulty in handling unstable monomers. Masked thiophenols are also successfully polymerized to form high molecular weight poly(arylene sulfide)s[79].

Scheme 1-11



1-5 Strategy and Goals

The aim of this thesis is the synthesis of novel heterocyclic polymers, which possess great thermal stability and processability. In addition, synthesis of novel functional heterocyclic polymers is described in Chapter 6 and 7. Based on previous structure-property relationships, the target polymer structure are designed, an effective synthetic method is then developed for the monomers, and then polymerization conditions are optimized. Finally, the new polymers synthesized are characterized and the properties are evaluated.

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Chapter 2

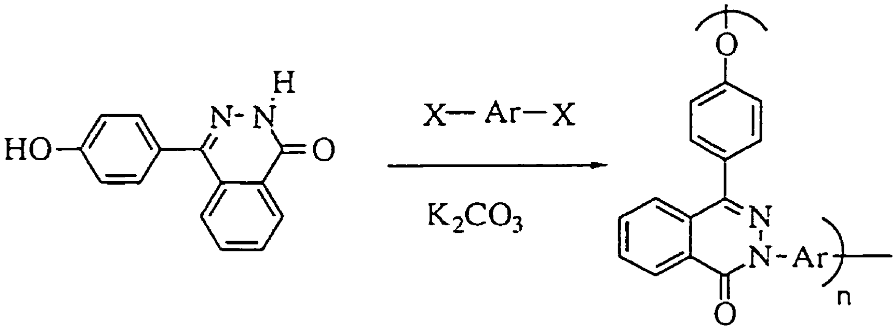
Synthesis of Phthalazinone Containing Polymers by a Novel N-C Coupling Reaction

2-1 Introduction

2-1-1 Polymer from 4-(4-Hydroxyphenyl)phthalazin-1-one

The synthesis of poly(ether sulfone)s containing the phthalazinone moiety has been described previously (Scheme 2-1)[1,2]. The monomer, 4-(4-hydroxyphenyl)-1(2H)-phthalazinone **2.1**, is made by a sequence of high yield reactions from phenolphthalein. It is polymerized with bis(4-fluorophenyl)sulfone in sulfolane in the presence of potassium carbonate to form high molecular weight polymer **2.2**. The polymer is thermooxidatively stable and has a very high T_g. In this polymerization reaction the aza-nitrogen anion, formed by reaction with potassium carbonate, undergoes a displacement reaction with activated aryl halides.

Scheme 2-1

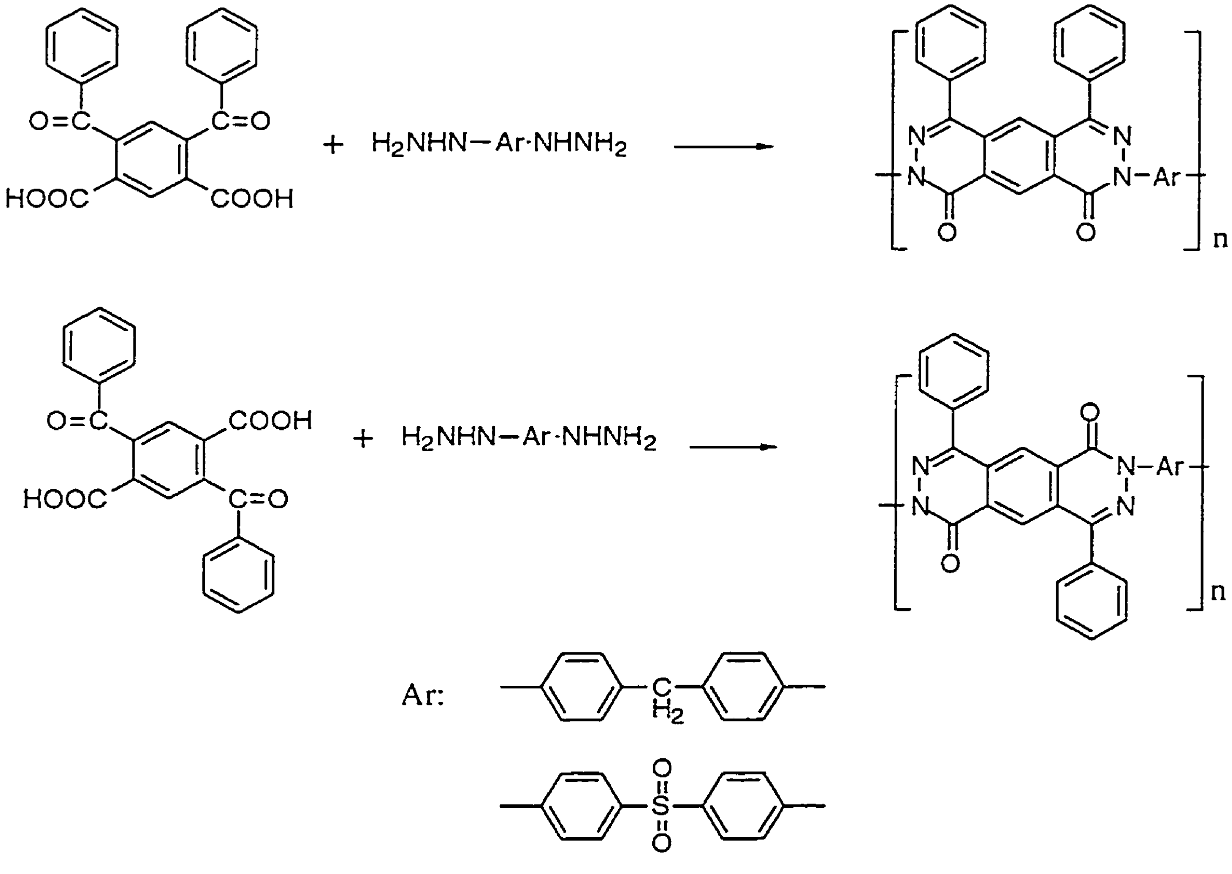


2.1 **2.2**

2-1-2 Previous Poly(phthalazinone)s

Polymers with the N-N bond in the polymer chain[3], as well as polymers whose heterocyclic ring contains the N-N linkage[4] have been previously synthesized. However, there are very few reports about the synthesis of phthalazinone containing polymers in the literature. Imai reported the synthesis of polypyridazinophthalazines from dibenzoylphthalic acids and bisarylhydrazines (Scheme 2-2)[5]. The polymers have high thermostability. However, the yields in the monomer synthesis are rather low and modification of the polymer structure is difficult.

Scheme 2-2



2-2 Strategy and goals

To the best of our knowledge, no polymerization reaction using the aza-nitrogen anionic displacement has been reported outside our laboratory. In fact, methods to form the carbon-nitrogen bond in aromatic systems are limited to rather vigorous processes which are copper mediated reactions[6,7]. If the phthalazinone NH groups behave like phenolic OH groups, then compounds with two phthalazinone groups should react similar to bisphenols in nucleophilic aromatic substitution reactions. The resulting polymers would be expected to be stable at high temperatures since similar structures have been previously synthesized by alternative routes[5]. In addition, many new polymers could be synthesized from monomers which are made from commercially available dianhydrides by this polymerization reaction.

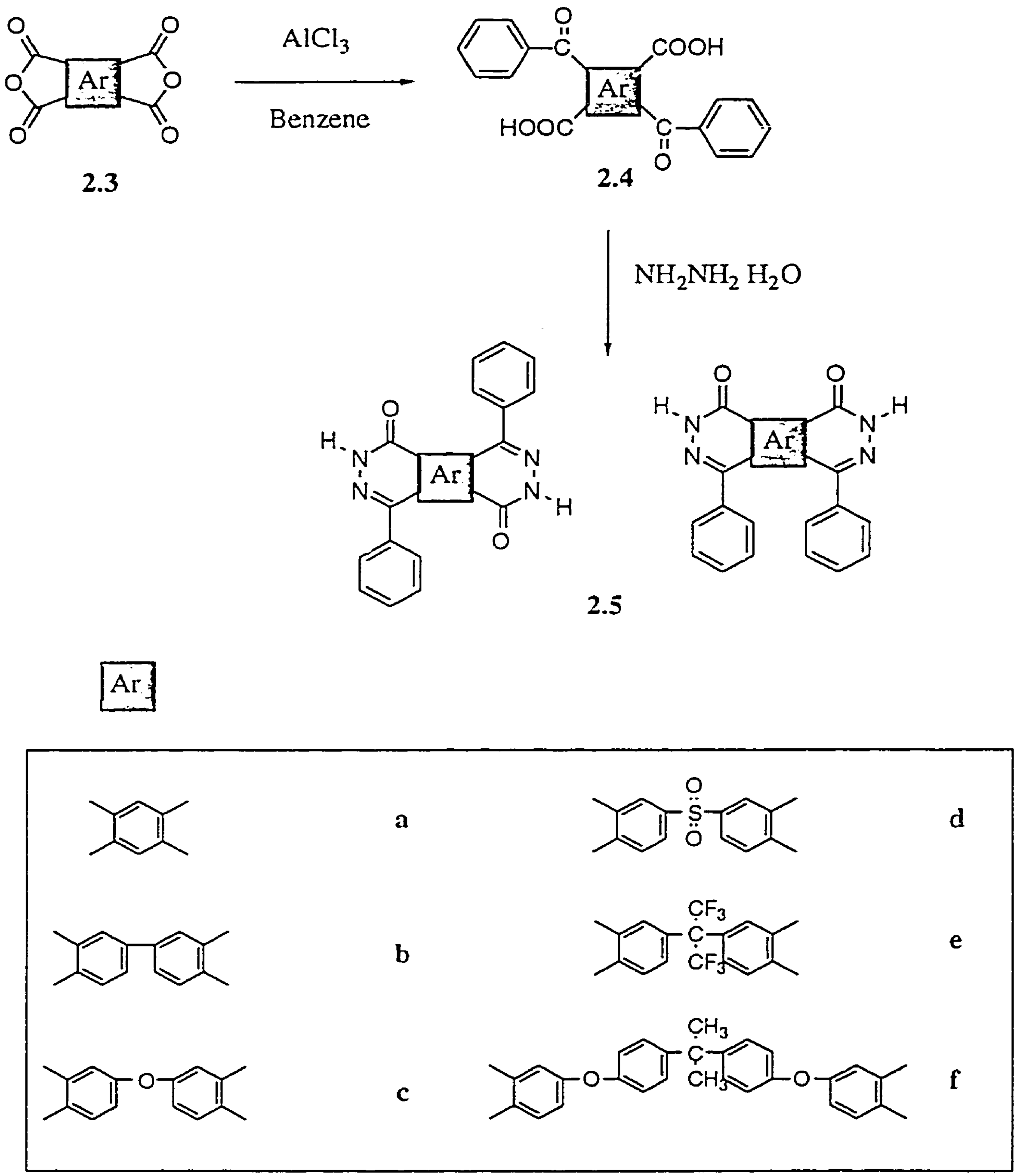
2-3 Synthesis of Phthalazinone Monomers

2-3-1 Bisphthalazinone Monomers

Three kinds of new phthalazinone monomers, bisphthalazinone monomers from diphthalic anhydrides, bisphthalazinone monomers from phthalic anhydride, and AB-type self condensation phthalazinone monomers, were synthesized from readily available compounds.

Bisphthalazinone monomers **2.5b-f** and 2,3,7,8-tetraazaanthracenediones **2.5a** were synthesized from the corresponding dianhydrides in two steps (Scheme 2-3). The first step was a Friedel-Crafts reaction between a series of dianhydrides and benzene. There were 3 possible isomers in the case of **2.5b-e**. In the case of **2.5a**, the two isomers, 4,6-dibenzoylphthalic acid and 2,5-dibenzoylphthalic acid, which formed in a ratio of 2:1, were separated by fractional recrystallization from glacial acetic acid. In the case of the anhydrides containing electron-withdrawing groups such as **2.3b**, **2.3d**, **2.3e**, the acylinium ion para to the electron-withdrawing group was destabilized in the Friedel-Crafts reaction, favoring the formation of one isomer.

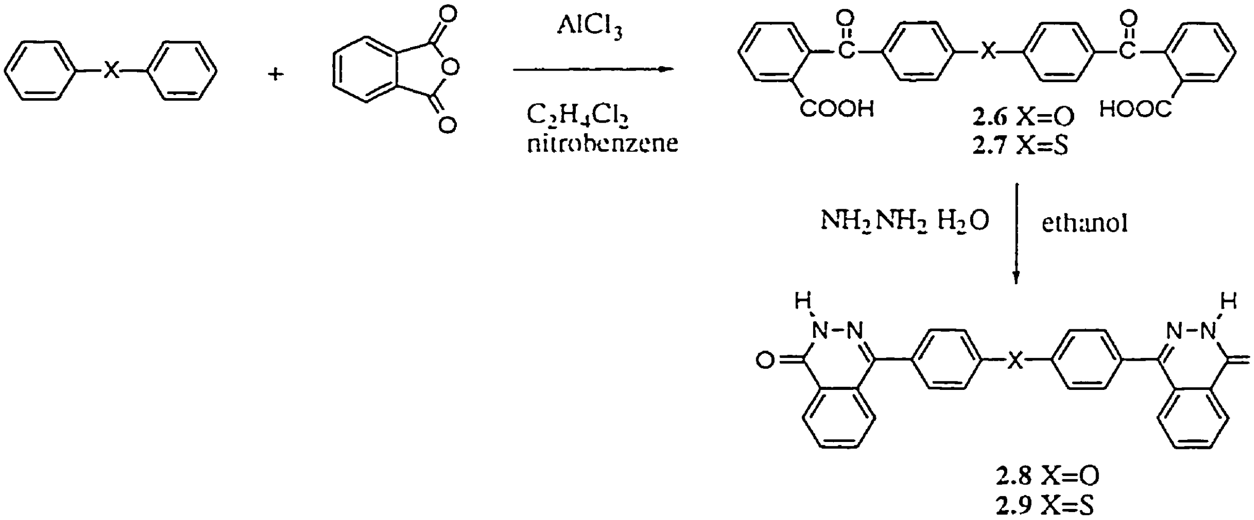
Scheme 2-3



The ketoacids **2.4c**, **2.4f**, which were formed from dianhydrides containing electron-donating groups, **2.3c**, **2.3f**, were thermally unstable and could not be purified. The crude products were directly reacted with hydrazine monohydrate. In the case of **2.3c** and **2.3f** three isomers were thought to have formed based on the ^{1}H-NMR spectra and the melting points of the final products. The isomers were not separated and the mixture was reacted directly with hydrazine monohydrate to form the mixture of phthalazinones.

The other bisphthalazinone monomers **2.8**, **2.9** were synthesized from diphenyl sulfide or diphenyl ether and phthalic anhydride in two steps (Scheme 2-4). The Friedel-Crafts reaction proceeded at room temperature and mono substitution took place selectively as described by Wolf et al[8]. The formed ketoacids were reacted with hydrazine monohydrate affording the bisphthalazinones **2.8**, **2.9** in high yield.

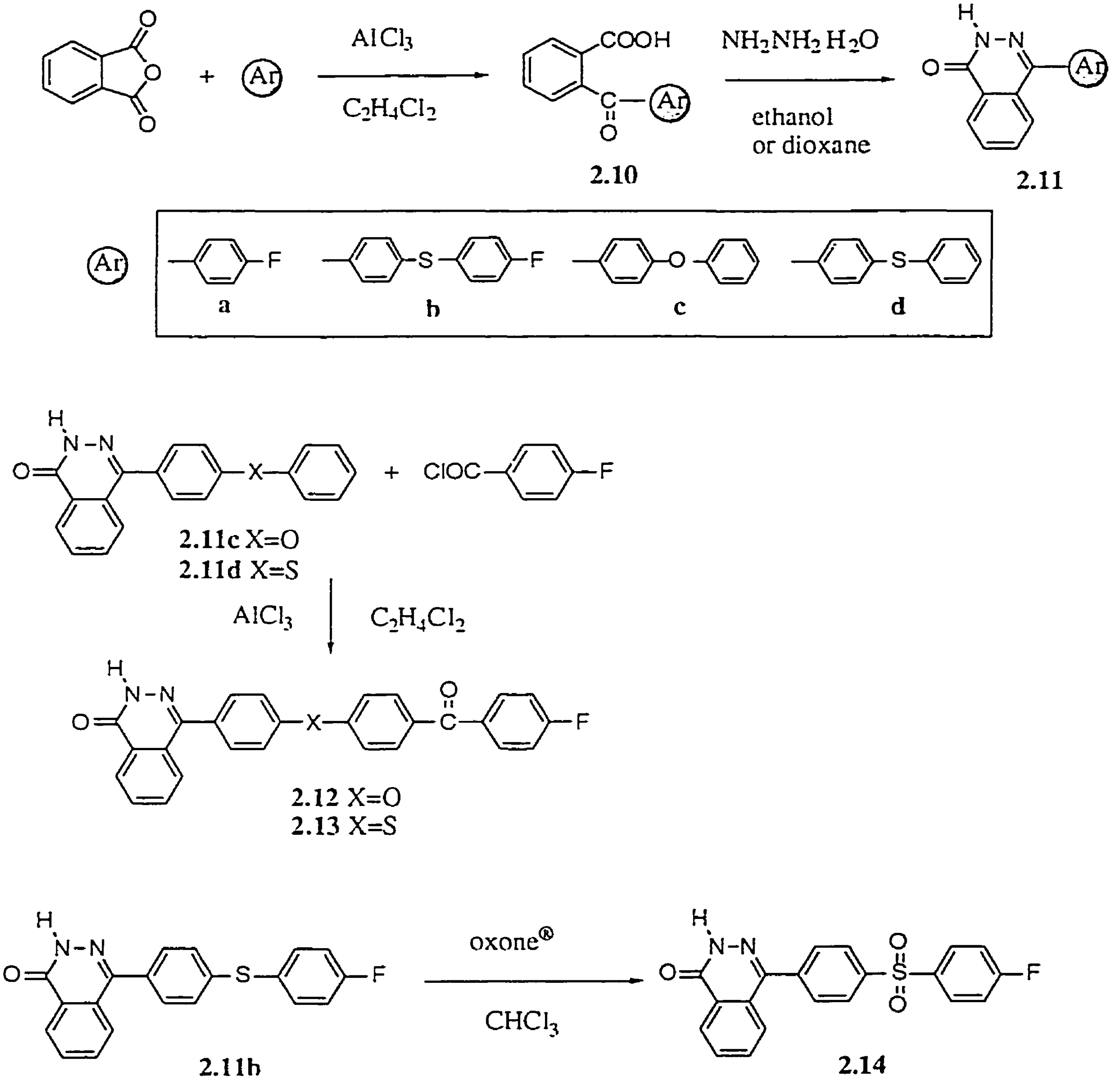
Scheme 2-4



2-3-2 AB-type Phthalazinone Monomers

AB-type self-condensation phthalazinone monomers were synthesized from phthalic anhydride as shown in Scheme 2-5. Phthalic anhydride was reacted with fluorobenzene or 4-fluorophenyl sulfide or diphenyl ether in the presence of anhydrous aluminum chloride at room temperature to form the corresponding ketoacids **2.10a-d** in good yield, which were then reacted with hydrazine monohydrate affording the phthalazinones **2.11a-d**. Phthalazinone **2.11b** was oxidized by Oxone® to form the phthalazinone **2.14** containing a fluoride which was activated by the sulfone group. Phthalazinones **2.11c**, **2.11d** were reacted with 4-fluorobenzoyl chloride in the presence of anhydrous aluminum chloride affording phthalazinones **2.12**, **2.13**, which contained a 4-fluorobenzophenone group, in high yield.

Scheme 2-5



2-4 Polymerization of Phthalazinone Monomers

2-4-1 Bisphthalazinone Monomers

The poly(phthalazinones)s were prepared by the reaction of the bisphthalazinone monomers **2.5a-f**, **2.8**, **2.9** with either bis(4-fluorophenyl)sulfone **2.22**, 4,4'-difluorobenzophenone **2.23** or 2,6-dichlorobenzonitrile **2.24** in a dipolar aprotic solvent (Scheme 2-6). **2.5f** was polymerized in N-methyl-2-pyrrolidinone (NMP) with toluene in the presence of potassium carbonate. The remaining monomers were polymerized in diphenyl sulfone (DPS) at higher temperatures. In the case of monomers **2.8** or **2.9**, longer reaction times were needed to obtain high molecular weight polymers, compared to monomers **2.5b-c**. The phthalazinone aza-nitrogen anions, which were formed via deprotonation by potassium carbonate, attack the activated aryl halides with elimination of fluoride. High molecular weight polymers with inherent viscosities of 0.3-0.4 dL/g (see Table 2-1) were obtained, except for polymers **2.15a**, **d**, **2.19** and **2.20**. Polymers containing monomer **2.5f** in the polymer backbone were soluble in chloroform. Their inherent viscosities were 0.25-0.32 dL/g with weight average molecular weights in the range of 30,000-50,000 g/mol by GPC, compared to polystyrene standards (Table 2-1). In the case of **2.5a**, the polymerization reaction was carried out for each of the separated isomers; however, neither of them formed high molecular weight polymers, presumably due to their insolubility. The mixture of the isomers obtained from **2.3a** gave higher molecular weight polymer than the polymer from the separated single isomer. However, the structure of **2.5a** is so rigid that even in the reaction with **2.22**, which forms the most soluble polymer, the insoluble oligomer precipitated out at an early stage of the polymerization reaction. When 4,4'-difluorobenzophenone, **2.23** was reacted with the bisphthalazinone monomers, insoluble oligomer also precipitated out of the reaction mixture before high molecular weight polymer formed, except for monomers **2.5c**, **2.5f**. When 2,6-dichlorobenzonitrile **2.24** was used as a monomer, only **2.5c** formed a high molecular weight polymer.

Scheme 2-6

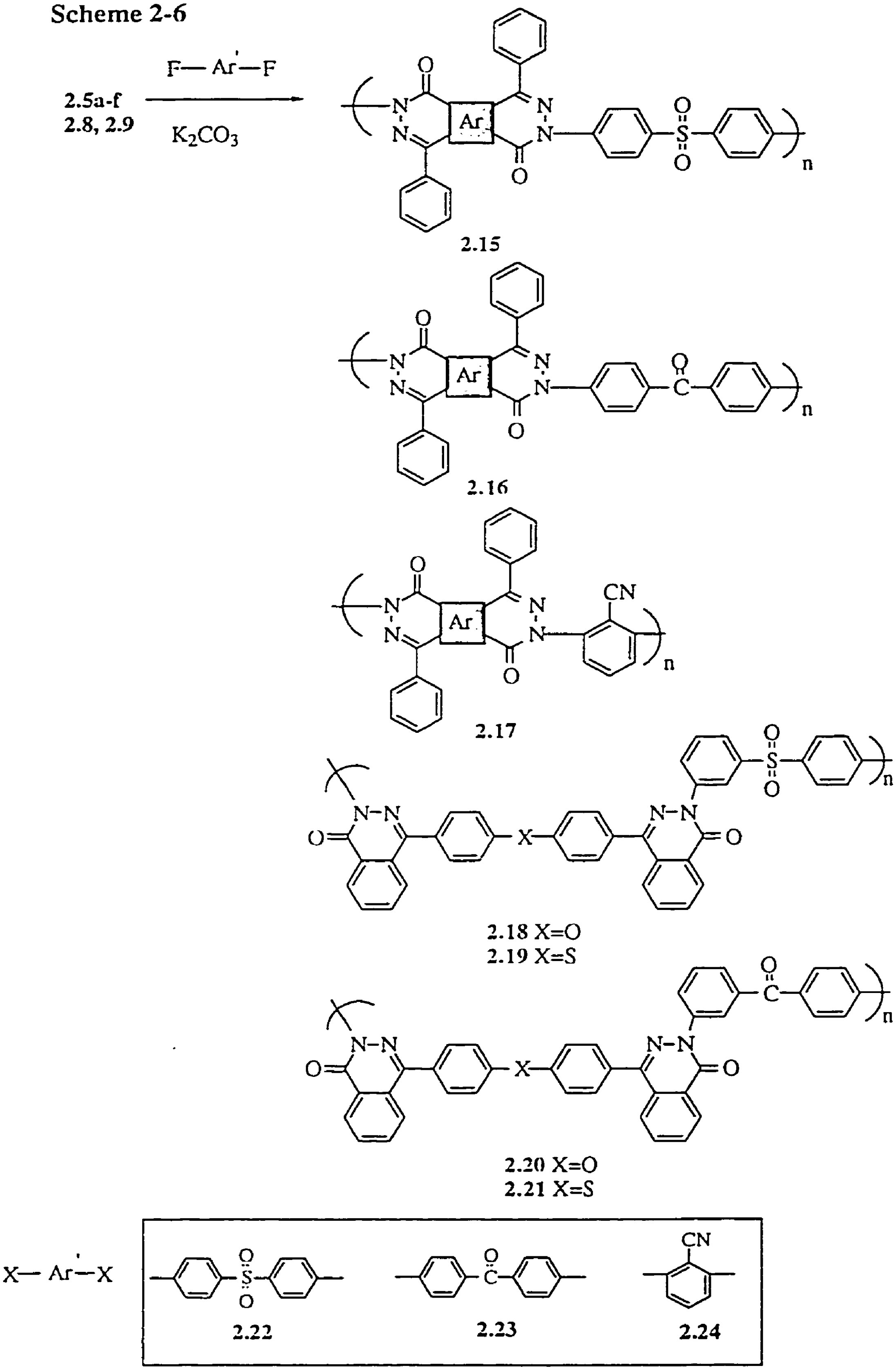

F— Ar' —F
2.5a-f
2.8, 2.9
K$_2$CO$_3$
Ar
2.15
2.16
2.17
2.18 X=O
2.19 X=S
2.20 X=O
2.21 X=S
X— Ar' —X
2.22
2.23
2.24

Table 2-1 Polymerization of Bisphthalazinone Monomers

Polymer	Solvent	Temperature (C)	Yield (%)	η_{inh}[b] (dL/g)	Mw	Mn	PD
2.15a	DPS	310	99	0.18[c]	-	-	-
2.15b	DPS	280	97	0.33	-	-	-
2.15c	DPS	280	89	0.51	-	-	-
2.15d	DPS	310	92	0.11	-	-	-
2.15e	NMP	190	0[a]	-	-	-	-
2.15f	NMP	160	86	0.29	44000	15200	2.89
2.16c	DPS	230	96	0.42	-	-	-
2.16f	NMP	190	81	0.32	51000	14900	3.42
2.17c	DPS	250	98	0.29	-	-	-
2.17f	NMP	190	78	0.25	33000	8900	3.71
2.18	DPS	310	92	0.32	-	-	-
2.19	DPS	310	91	0.21	-		-
2.20	DPS	310	94	0.33	-	-	-
2.21	DPS	310	94	0.19	-	-	-

a) Decomposition. b) Inherent viscosity was measured at a concentration of 0.5 g/dL in NMP at 25°C
c) At a concentration of 0.5 g/dL in conc. H_2SO_4 at 25°C. d) Molecular weight was determined by GPC
d) Molecular weight was determined by GPC in chloroform based on polystyrene standard.

2-4-2 Reactivity of NH Groups of Phthalazinone Monomers

The monomers containing electron-withdrawing groups, such as **2.5d** and **2.5e** did not form high molecular weight polymers. Monomer **2.5d** formed only oligomers during the polymerization reaction and monomer **2.5e** decomposed during the reaction regardless of the reaction conditions used. The electron-withdrawing group makes the NH group more acidic and consequently the resulting anion becomes less nucleophilic, thereby limitting the polymerization reaction. The H-chemical shift of the acidic NH proton of the phthalazinone monomers can be used as a measure of their reactivity (Figure 2-1). The electronic effect of heterocyclic group on a phenyl group could be evaluated by ^{1}H-NMR, as the deshielding of the protons ortho to a substituent is indicative of an electron-withdrawing group[9]. However, correlation between ^{1}H-NMR chemical shift and inductive effect of the heterocyclic often fails.

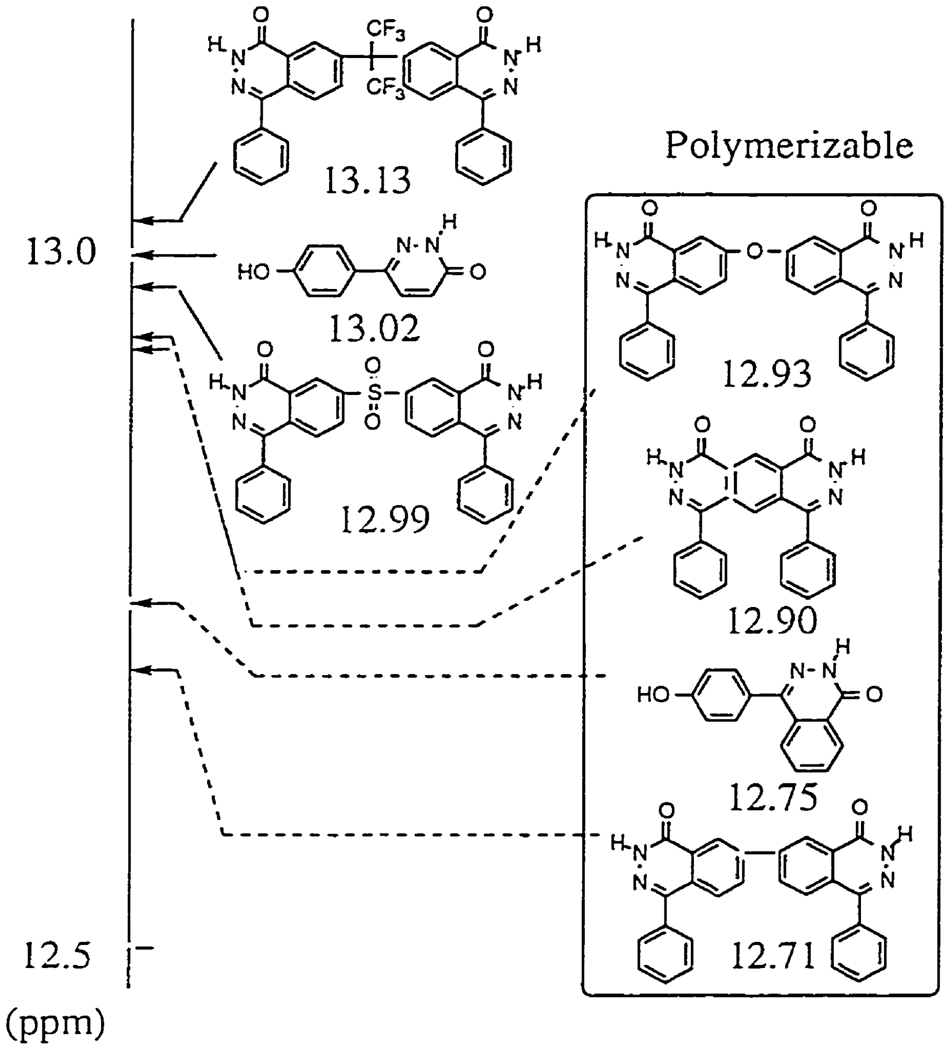


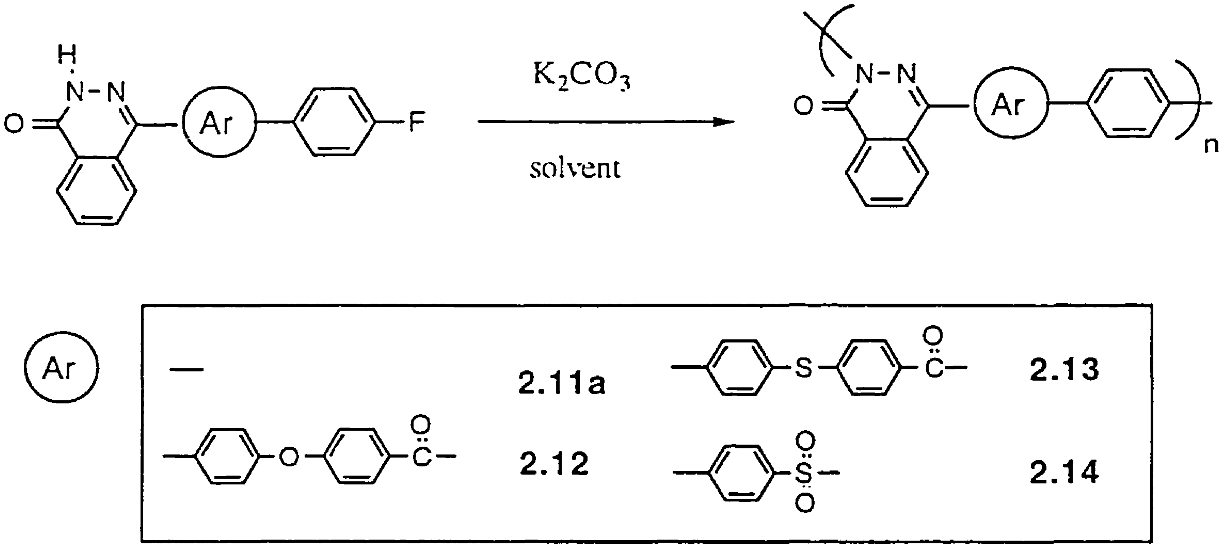
Figure 2-1 ^{1}H-NMR Chemical Shift of NH Acidic Proton of the Phthalazinone Monomers in DMSO-d_6

This is because ^{1}H-NMR chemical shift is influenced by other factors such as an anisotropic effect, and also because the reactive site is not at the protons ortho to a substituent . In the phthalazinone monomers' case, the reactive site is the aza nitrogen anion which is directely related to the NH proton acidity and it is part of heterocyclic ring. Therefore, the correlation works very well.

2-4-3 AB-type Phthalazinone Monomers

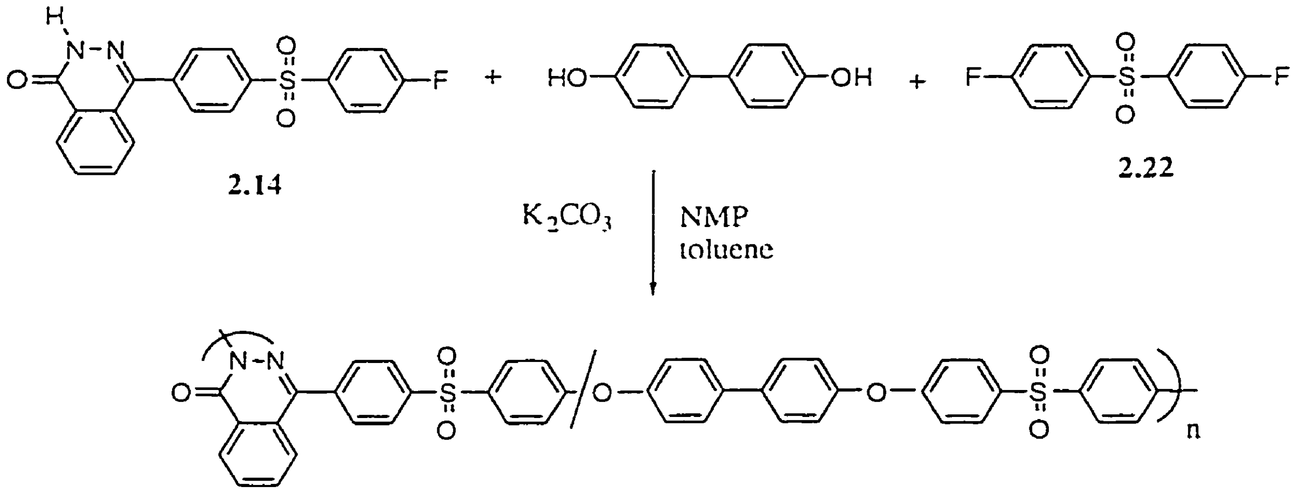
AB-type phthalazinone monomers **2.11a**, **2.12**, **2.13**, **2.14** were polymerized in diphenylsulfone (DPS), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU), and 1-cyclohexyl-2-pyrrolidinone (CHP) at 250-300°C (Scheme 2-7). Because of high crystallinities of the polymers, premature precipitation took place. None of them formed high molecular weight polymers even under stringent conditions, such as 300°C in DPS. The polymer from the AB monomer **2.12** had a lower molecular weight, and the same empirical formula as the polymer formed from **2.1** and **2.20**, which had a high molecular weight (Scheme 2-1). The latter polymer, which formed from 2 monomers, contains head to head linkages and head to tail linkages, so that the crystallinity was reduced by the random arrangement of the two monomer's linkages. The amorphous polymer was soluble in sulfolane at 220°C and formed high molecular weight polymer without premature precipitation. We attempted to copolymerize monomer **2.11a** with 4,4'-biphenol and bis(4-fluorophenyl)sulfone **2.22**, however, only low molecular weight oligomers formed.

Scheme 2-7



The fluoride group in this monomer is unreactive and high molecular weight polymer was not formed. Monomer **2.14**, however, could be successfully copolymerized with 4,4'-biphenol and **2.22** to form high molecular weight polymer (Table 2-2, Scheme 2-8). This suggests that the reactivity of the aza nitrogen anion of the phthalazinone is comparable to that of the biphenol. The copolymers have higher T_gs and lower solubilities as the amount of **2.14** increases (Figure 2-2).

Scheme 2-8



2.25

Table 2-2 Copolymerization of AB-type Phthalazinone Monomer **2.14**

Polymer	2.14 %	Yield %	η_{inh}*	M_n	M_w	PD	T_g °C
2.25a	0	90	0.48	17000	63400	3.7	240
2.25b	20	91	0.46	8900	35000	3.9	273
2.25c	50	89	0.31	-	-	-	323
2.25d	100	87	0.11	-	-	-	422

*In H_2SO_4 at 25°C

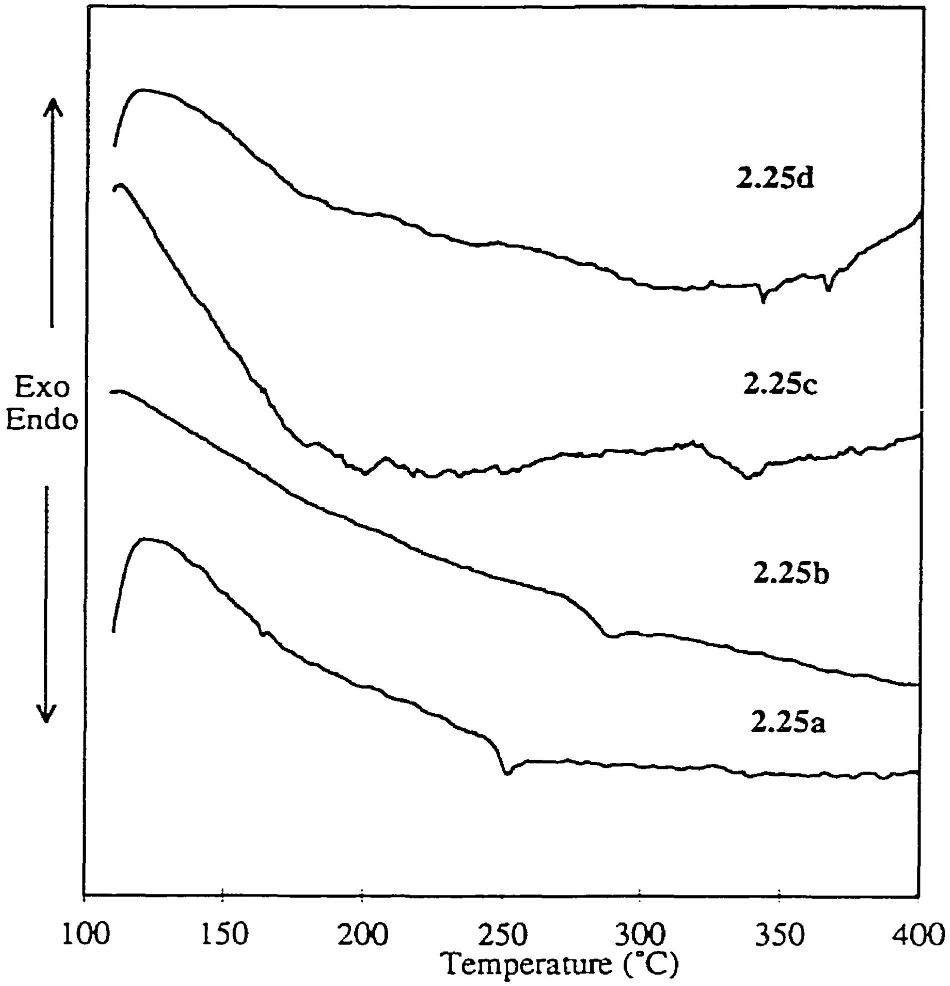


Figure 2-2 DSC Thermograms of Copolymer **2.25a-d**

2-5 Characterization and Properties of the Polymers

Polymers with BPA linkage are soluble in chlorinated solvent such as chloroform. The remaining polymers are soluble in solvents like NMP or *m*-cresol. A few are soluble only in concentrated sulfuric acid (Table 2-3). Polymers with flexible ether linkages, such as **2.15c**, **2.16c** were solution cast into flexible films from *m*-cresol while **2.15f** was cast from 1,1'2,2'-tetrachloroethane. Polymer **2.15a** is only soluble in a solvent such as concentrated sulfuric acid.

Table 2-3 Solubilities of Phthalazinone Polymers

	sulfuric acid	m-cresol	TCE	chloroform	NMP
2.15a	+	-	-	-	-
2.15b	+	+	-	-	+
2.15c	+	+	-	-	+
2.15f	+	+	+	+	+
2.16c	+	+	-	-	+-
2.16f	+	+	+	+	-
2.17c	+	+	-	-	+-
2.17f	+	+	+	+-	+
2.21	+	+-	-	-	-
2.22	+	+-	-	-	-
2.23	+	+-	-	-	-
2.24	+	+-	-	-	-

a) Solubility: +, soluble at room temperature; +-, partially soluble;
-, insoluble

All the polymers obtained showed characteristic phthalazinone CO stretching at 1650 cm^{-1} in their IR spectra. The IR spectra of **2.15a** (both of the polymers from separated isomers) were identical to the polymers which were synthesized by another route[5].

The glass transtion temperatures (T_g) listed in Table 2-4 were measured by differential scanning calorimetry (DSC). Typical DSC curves for poly(phthalazinone)s are shown in Figure 2-3. The poly(phthalazinone)s showed very high T_gs around 300°C. The T_g of polymer **2.15a** was not detectable by DSC. Thermal stabilities of the poly(phthalazinone)s were determined by thermogravimetric analysis (TGA) (Figure 2-4). All the poly(phthalazinone)s showed a similar pattern of decomposition with no weight loss below 400°C in either air or nitrogen. The temperatures for 5% weight loss were observed between 480-530°C.

Table 2-4 Thermal Properties of Phthalazinone Polymers

Polymer	T_g(°C)[a]	TGA(°C)[b]	
		air	N_2
2.15a	_[c]	478	488
2.15b	344	478	479
2.15c	310	485	499
2.15f	221	471	489
2.16c	286	512	497
2.16f	195	465	486
2.17c	301	531	526
2.17f	200	469	501
2.18	295	477	476
2.19	279	465	471
2.20	301	467	468
2.21	281	459	461

a) T_g was determined by DSC at heating rate 20°C/min under nitrogen (160 mL/min), the values were reported from the second scan. b) Reported for 5% weight loss at heating rate 20°C/min under air or nitrogen (flow rate 200mL/min). c) not detected.

Young's moduli for polymers **2.15b**, **2.15c**, **2.15f**, **2.16c** are given in Table 2-5. All polymers have Young's moduli in the range 1.75-2.21 GPa at 25°C. These values are typical for engineering thermoplastics. When films of these polymers are heated they maintain good mechanical properties in the GPa range above 200°C. The T_gs of polymers as measured from the tan δ are lower than the values measured by DSC due to the mild mechanical deformations inherent in the testing method[10].

Table 2-5 Mechanical Properties of Phthalazinone Polymers

Polymer	Young's Modulus (GPa)		Tanδ (°C)
	20°C	200°C	
2.15b	2.15	1.26	283
2.15c	1.81	1.29	279
2.15f	1.75	1.11	200
2.16c	2.21	1.44	265

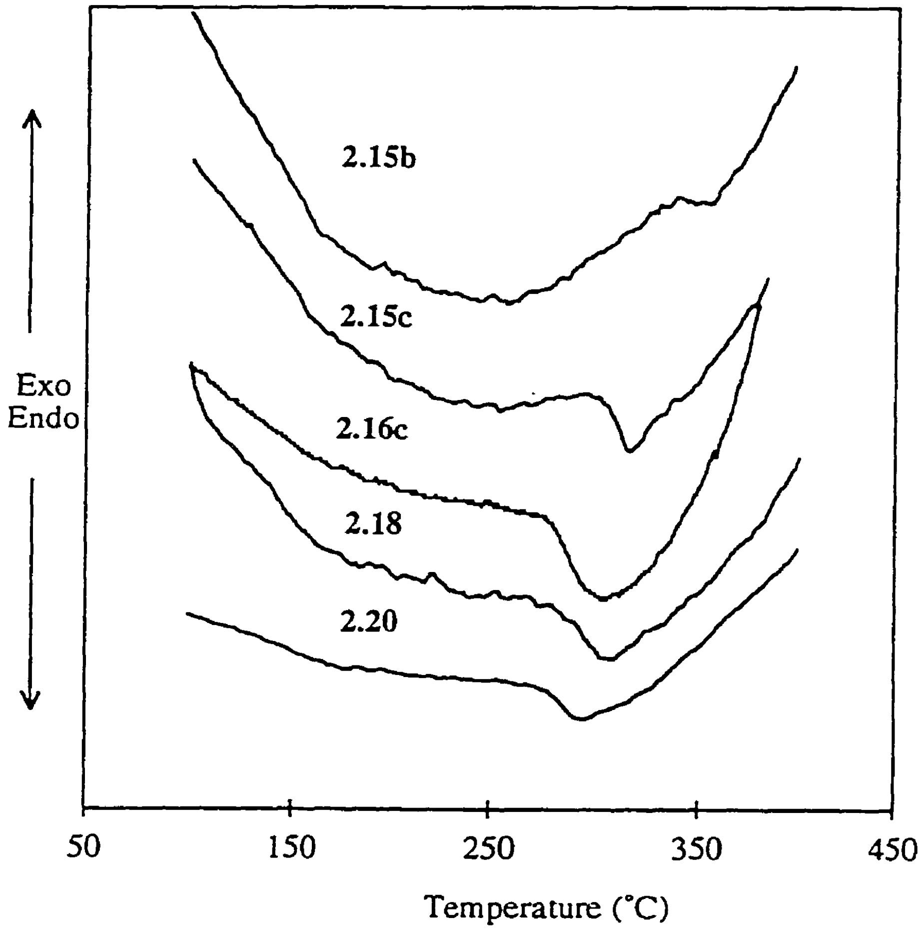


Figure 2-3 DSC Thermograms of Polymers **2.15b, 2.15c, 2.16c, 2.18, 2.20**

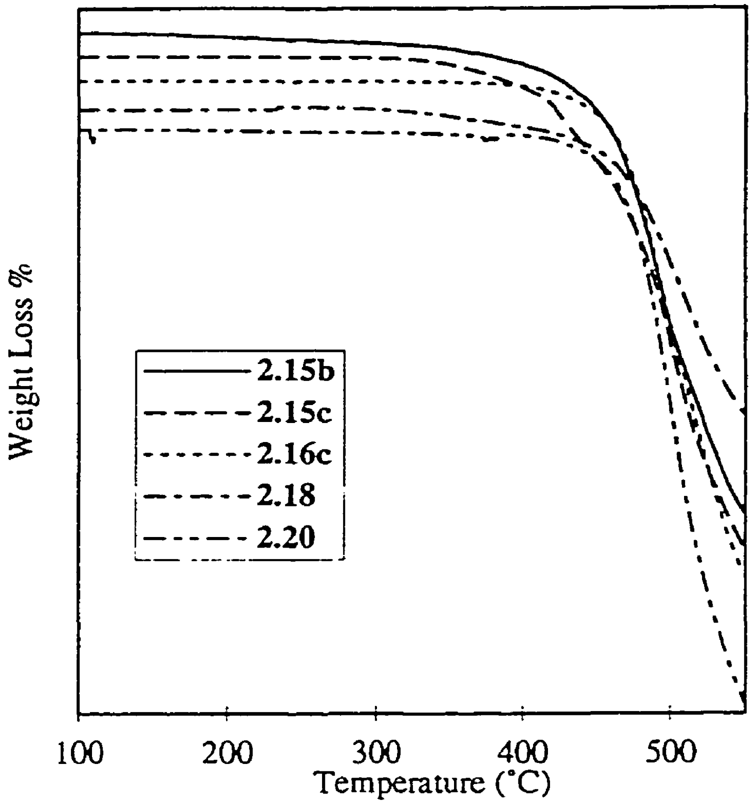


Figure 2-4 TGA Thermograms of Polymers **2.15b, 2.15c, 2.16c, 2.18, 2.20**

2-6 Conclusions

A new class of monomers, bisphthalazinones, have been prepared in two steps in good yields from readily available compounds. They were reacted with a series of activated aryl halides to give high molecular weight novel poly(phthalazinone)s in a one-step reaction involving the formation of a N-C bond. The formed polymers had high glass transition temperatures and excellent thermostabilities. AB-type phthalazinone monomers also have been prepared and successfully copolymerized with poly(ether sulfone) affording polymers with higher T_gs.

2-7 Experimental

Materials

Tetramethylene sulfone (sulfolane), 1,1,2,2-tetrachloroethane (TCE), were used as obtained from Aldrich. Diphenyl sulfone and 2,6-dichlorobenzonitrile (**2.24**) (Aldrich) were recrystallized from ethanol. 3,3'4,4'-Biphenyltetracarboxylic dianhydride (**2.3b**), 1,2,4,5-benzenetetracarboxylic dianhydride (**2.3a**), diphenyl sulfide, diphenyl ether, phthalic anhydride, 4,4'-difluorobenzophenone (**2.22**), 4,4'-bis(4-fluorophenyl)sulfone (**2.23**) were used as obtained from Aldrich. Anhydrous aluminum chloride, anhydrous potassium carbonate were obtained from Omega. 4,4'-Oxy diphthalicanhydride (**2.3c**), 4,4'-sulfonyl diphthalic anhydride (**2.3d**) were obtained from Chriskev Company INC. Hexafluoroisopropyliden-2,2'-bis(phthalic anhydride) (**2.3e**) was obtained from Hoechst Co. 4-Fluorobenzoyl chloride was obtained from Lancater. Bisphenol A dianhydride (**2.3f**) was kindly donated by General Electric Co. All common solvents were obtained from Caldelon and used as received or as otherwise noted.

Characterization

The melting points of monomers were obtained using a Fisher-Johns melting point apparatus or a Mettler FP800 DSC and are uncorrected. The ^{1}H-NMR spectra were measured with a JEOL 270 instrument using dimethyl-d_6-sulfoxide (DMSO-d_6) as a solvent. The chemical shifts were calibrated using tetramethylsilane (TMS). The chemical shift (δ) and coupling constant (J) data were quoted in ppm and Hertz, respectively. Infrared spectra were recorded using an IR Analect AQS-18 FT-IR spectrometer. Glass transition temperatures (T_gs) were obtained using a Seiko 220 DSC instrument at a heating rate of 20°C min^{-1} in N_2 (160 mL/min). The T_g values were reported from the second scan. The T_g was taken from the midpoint of the change in the slope of the baseline. The weight loss data were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 20°C/min in N_2 and air (200 mL/min) and the values reported were for 5% weight loss. Inherent viscosity (η_{inh}) data were obtained with a calibrated Ubbelohde viscometer. Measurements were made in NMP or H_2SO_4 at 25°C in a concentration of 0.5 g/dL. Thermomechanical studies were performed on a Seiko 120 thermomechanical analyzer thermal stress-strain analyzer (TMA/SS) with a heating rate of 3°C/min. Films for the thermomechanical analyzer were cast from *m*-cresol, or 1,1',2,2'-tetrachloroethane at 145°C and dried under vacuum at 150°C for 4 hours and at 200°C for 24 hours.

Monomer Synthesis

4,6-Dibenzoylisophthalic acid (DBIA) and 2,5-dibenzoylterephthalic acid (DBTA). (2.4a)

4,6-Dibenzoylisophthalic acid (DBIA) and 2,5-dibenzoylterephthalic acid (DBTA) were synthesized according to the reported procedure by the Freidel-Crafts reaction of pyromellitic dianhydride with benzene in the presence of anhydrous aluminum chloride[11]. Two isomers were separated by fractional recrystallization from aqueous methanol. DBIA; yield 42%, m.p. 328°C (DSC), (lit. m.p. 318°C[5]) DBTA; yield 18%, m.p. 285-287°C, (lit. m.p. 277-278°C[5])

1,8-Diphenyl-2,3,6,7-tetraazaanthracene-4,5-diones. (2.5a)

To a 250 mL round bottom flask, were added 3.74 g (0.01 mol) of DBTA (DBIA or a mixture of two isomers) and 100 mL of ethanol, and 0.50 g (0.01 mol) of hydrazine monohydrate. The reaction mixture was heated to reflux and stirred for 4 hours. A white powder precipitated, which was washed with water, then methanol, and dried under reduced pressure at 80°C; yield 89%, m.p. 330°C° (DSC); ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.58-7.69 (m, 10H), 8.55 (m, 2H), 12.89 (s, 2H); IR (KBr) 1670 cm^{-1}; MS (m/e, relative intensity %): 365.9 (M^+, 100); Analysis calc'd for $C_{22}H_{14}O_2N_2$: C, 72.12; H, 3.85; N, 15.29; found: C, 72.84; H, 3.85; N, 15.75.

4,8-Diphenyl-2,3,6,7-tetraazaanthracene-1,5-dione. (2.5a)

Yield 92%, m.p. >400C°; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.58-7.69 (m, 10H), 8.55 (m, 2H), 12.89 (s, 2H); IR (KBr) 1655 cm^{-1}; MS (m/e, relative intensity %): 365.9 (M$^+$, 100%); Analysis calc'd for $C_{22}H_{14}O_2N_2$: C, 72.12; H, 3.85; N, 15.29; found: C, 72.67; H, 3.80; N, 15.82.

Mixture of two isomers. (2.5a)

Yield 97%, m.p. 330°C (DSC); ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.58-7.69 (m, 10H), 8.55 (m, 2H), 12.89 (s, 2H); IR (KBr) 1670cm^{-1} ($\sqrt{}_{C=O}$); MS (m/e, relative intensity %): 365.9 (M$^+$, 100); Analysis calc'd for $C_{22}H_{14}O_2N_2$: C, 72.12; H, 3.85; N, 15.29; found: C, 72.03 ; H, 3.83 ; N, 15.30

3,3'-Dibenzoyl (1,1'-biphenyl)-4,4'-dicarboxylic acid. (2.4b)

In a 500 mL three-neck round-bottom flask equipped with a mechanical stirrer and a water-cooled condenser, were added, 3,3',4,4'-biphenylenetetracarboxylic dianhydride **(2.3b)** (8.82 g; 0.03 mol) and anhydrous aluminum chloride (19.99 g; 0.15 mol) and 200 mL of benzene freshly distilled from sodium. The reaction mixture was heated up to reflux with vigorous stirring and held at this temperature for 16 hours. The hot reaction mixture was poured onto 300 g of crushed ice containing 5 mL of concentrated hydrochloric acid. The white granular mass was filtered, washed with water, and dissolved in warm dilute potassium hydroxide solution. After filtration to remove a little insoluble matter, the keto acids were precipitated with dilute hydrochloric acid. The white powder was filtered, dried and recrystallized from glacial acetic acid; yield 81.0% (10.93 g), m.p. 255-257 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.50 (m, 4H), 7.65 (m, 6H), 7.76 (d, J_2=8.15, 2H), 8.42 (d-d, J_3=1.97, J_2=8.14, 2H), 8.54 (d, J_3=1.97, 2H)

1,2,1',2'-Tetrahydro-4,4'-diphenyl[1,1']biphthalazin-1,1'dione. (2.5b)

Bisphthalazinone monomers **2.5b** were prepared by the reaction of keto acid **2.4b** with hydrazine monohydrate in methanol using the procedure described above for compound

2.5a. The crude product was recrystallized from glacial acetic acid; yield 88% (9.46 g), white powder, m.p. 385 °C (DSC endothermoic peak); ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.51-7.89 (m, 10H), 8.35 (m, 2H), 8.50 (m, 2H), 8.70 (s, 2H), 12.71 (s, 2H), MS (m/e, relative intensity %): 442.48 (M^+,100). Analysis calc'd for $C_{28}H_{18}N_4O_2$: C, 76.01; H, 4.10; N, 12.66; found: C, 75.40; H, 4.13; N, 12.66

4,5'-Sulfonyl bis[benzoyl benzoic acid]s. (2.4d)

This compound was prepared by the Friedel-Crafts reaction of 4,4'-sulfonyl diphthalic anhydride (**2.3d**) with benzene in the presence of anhydrous aluminum chloride using the procedure described above for compound **2.4b**; yield 55.5%, light yellow powder, m.p. 289-291°C. ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.52 (m, 4H), 7.66 (m, 6H), 7.76 (d, J_2=8.15, 2H), 8.43 (d-d, J_2=8.03, J_3=1.97, 2H), 8.56 (d, J_3=1.99, 2H)

7-Sulfonyl-bis[1,2-dihydro-4-phenylphthalazinone]. (2.5d)

Bisphthalazinone monomers **2.5d** were prepared by the reaction of keto acid **2.4d** with hydrazine monohydrate in methanol using the procedure described above for compound **2.5a**. The crude product was recrystallized from glacial acetic acid; yield 91.0%, white powder. m.p. 346.4°C (DSC); ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.52-7.61 (m, 10H), 7.87 (m, 2H), 8.45 (m, 2H), 8.83 (s, 2H), 13.20 (s, 2H), MS (m/e, relative intensity %): 506 (M^+, 100). Analysis calc'd for $C_{28}H_{18}N_4O_4S$: C, 66.39; H, 3.58; N, 11.06; found: C, 65.90; H, 3.49; N, 11.31

4,5'-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]-bis[2-benzoyl benzoic acid]s. (2.4e)

This compound was prepared by the Friedel-Crafts reaction of hexafluoroisopropyliden-2,2'-bis(phthalic anhydride) (**2.3e**) with benzene in the presence of anhydrous aluminum chloride using the procedure described above for the compound **2.4b**. This compond is partially soluble in benzene. After the reaction mixture was poured into crushed ice containing concentrated hydrochloric acid, benzene was removed by distillation and white granular mass remaining in the hot liquid was filtered. It was then treated by the same procedure as for **2.4b** and **2.4d**; yield 39.8%, white powder, m.p. 224-226 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.5-7.8 (m, 14H), 8.08 (s, 2H)

7-(1,1,1,3,3,3-Hexafluoropropane-2,2-diyl)-bis[1,2-dihydro-4-phenylphthalazinone]. (2.5e)

Bisphthalazinone monomers **2.5e** were prepared by the reaction of keto acid **2.4e** with hydrazine monohydrate in methanol using the procedure described above for compound **2.5a**. The crude product was recrystallized from glacial acetic acid; yield 94%, white powder. m.p. 353°C (DSC), ^{1}H-NMR (270MHz, DMSO-d_6) 7.51-7.61 (m, 10H), 7.84 (m, 4H), 8.37 (s, 2H), 13.13 (s, 2H). MS (m/e, relative intensity %): 594.08 (M$^+$, 6.5), 593.08 (33.9), 592.08 (100). Analysis calc'd for $C_{31}H_{18}F_6N_4O_2$: C, 62.84; H, 3.06; N, 9.46; found: C, 62.29; H, 3.29; N, 9.50

Bisphenol A -4.4'-dibenzoyl benzoic acids. (2.4f)

Bisphenol A 4,4'-dianhydride (10.40 g; 0.02 mol) was suspended in 500 mL of freshly sodium-distilled benzene in a 1L-round bottom, three-neck-flask equipped with a condenser and a mechanical stirrer. To this, was added slowly 13.33 g (0.10 mol) of anhydrous aluminum chloride at room temperature. The resulting dark red suspension was heated up 65-70°C and stirred for 3 hours. The resulting black solution was poured into 500 mL of crashed ice. After the ice melted, the white powder was filtered off and washed with chloroform repeatedly. The washed chloroform and benzene layers were put together and the solvents were removed under reduced pressure at 25 °C. The resulting brown powder was dried in vacuo at 25 °C. 4.50 g of brown powder was obtained. This compound reacts at 40 C° to form an insoluble residue. All attempts to recrystallize it failed. An endothermic peak starts at 40 C° (DSC); ^{1}H-NMR (270 MHz, DMSO-d_6) δ 1.62 (s, 6H), 7.10-8.00 (24H, m)

Bisphenol A 7-bis[1,2-dihydro-4-phenyl-phthalazinone]. (2.5f)

This compound was prepared by the reaction of keto acid **2.4f** with hydrazine monohydrate in methanol using the procedure described above for compound **2.5a**. The crude product was recrystallized from toluene and methanol, alternately followed by 5 to 6 recrystallizations which were needed to obtain monomer grade purity material;.8.02-8.24 (m, 24H), 8.34 (d, J_2=8.69, 1.4H), 12.79 (s, 1.3H), 12.82 (s, 0.7H). Because there are three isomers, interpretation of the peaks was not carried out. No effort was made to separate the isomers. Overall yield 7%, MS (m/e, relative intensity %): 669 (M^+, 15), 370.99 (100). Analysis calc'd for $C_{43}H_{32}N_4O_4$: C, 77.23; H, 4.82; N, 8.38; found: C, 76.83 ; H, 4.77 ; N, 8.51

Oxy-7-bis[benzoylbenzoic acid]s. (2.4c)

In 1L-round bottom, three-neck flask equipped with a condenser and a mechanical stirrer, 6.20 g (0.02 mol) of 4,4'-oxydiphthalic anhydride (**2.3c**) was suspended in 500 mL of freshly sodium-distilled benzene. To this was added slowly 13.33 g (0.10 mol) of anhydrous aluminum chloride at room temperature. The reaction mixture was heated up to reflux and stirred for 24 hours. The reaction mixture was a white slurry at the beginning, then a sticky light yellow residue separated, and finally a viscous black half solid formed. The benzene was decanted and the black partial solid was poured into 1 L of crushed ice in water. A white powder obtained, 18.2 g, after filtration and drying at room temperature in vacuo. This compound reacts at about 40°C to form an insoluble residue. All attempts to recrystallize it failed. ^{1}H-NMR (270MHz, DMSO-d_6) δ 7.19-7.25 (m, 2H), 7.34-7.38 (m, 2H), 7.45-7.62 (m, 2H), 8.01-8.09 (m, 2H)

Oxy-7-bis[1,2-dihydro-4-phenyl-phthalazinone]s. (2.5c)

This compound was prepared by the reaction of keto acid **2.4c** with hydrazine monohydrate in methanol using the procedure described above for compound **2.5a**. The crude product was recrystallized from NMP. Overall yield 44%, m.p. 290, 310, 324 °C (DSC endothermic peaks). ^{1}H-NMR (270MHz, DMSO-d_6) 7.29 (d, J_3=2.54, 1.2H), 7.47-7.85 (m, 12H), 8.40-8.45 (d, J_2=8.67, 1H), 12.91 (s, 0.8H), 12.90 (s, 1.2H); Because of the three isomers, interpretation of the peaks was not done. No effort was made to separate the isomers. MS (m/e,relative intensity %): 457.94 (M^+,100).). Analysis calc'd for $C_{28}H_{18}N_4O_3$: C, 73.35; H, 3.96; N, 12.22; found: C, 73.52 ; H, 4.12 ; N, 11.63

4,4'-bis(2-carboxybenzoyl)diphenyl ether. (2.6)

4,4'-bis(2-carboxybenzoyl)diphenyl ether was synthesized from diphenyl ether and phthalic anhydride according to Stille[8]. Yield 68%, m.p. 261-263°C (Lit. 263-267°C) ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.16 (d, J_2=8.88, 4H), 7.42 (d, J_2=8.10, 2H), 7.68 (m, 8H), 7.99 (d, J_2=8.10, 2H)

Oxy-bis[1,2-dihydro-4-(1,4-phenylene)phthalazinone]. (2.8)

2.6 (4.68g; 0.01 mol) was reacted with 0.50 g (0.01 mol) of hydrazine monohydrate in dioxane at reflux for 24 hours. At the beginning of the reaction the reaction mixture was a white emulsion which on heating cleared up. After 2 hours a white powder started to come out. The reaction mixture was cooled down and the precipitate was collected by filtration. **2.8** was obtained after recrystallization from glacial acetic acid as a white powder; yield 4.17 g (91%), m.p. 390°C (DSC); ^{1}H-NMR (270 MHz, DMSO-d_6) 7.00-8.00 (m, 14H), 8.20-8.50 (m, 2H), 12.90 (s, 2H). MS (m/e, relative intensity %): 455.99 (M^+, 100). Analysis calc'd for $C_{28}H_{18}N_4O_3$: C, 73.35; H, 3.96; N, 12.22; found: C, 72.38 ; H, 4.23 ; N, 11.96

4,4'-bis(2-carboxybenzoyl)diphenylsulfide. (2.7)

This compound was prepared using the procedure described above for compound **2.6**. Yield 81 %, m.p. 281-283°C. ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.05-7.25 (m, 10H), 7.30-8.00 (m, 4H), 8.20-8.30 (m, 2H)

Thio-bis[1,2-dihydro-4-(1,4-phenylene)phthalazinone). (2.9)

This compound was prepared using the procedure described above for compound **2.8**. Yield 95 %, m.p. 380°C (DSC), ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.64 (m, 8H), 7.72 (m, 2H), 7.90 (m, 4H), 8.36 (m, 2H), 12.78 (s, 2H), MS (m/e, relative intensity %): 474 (M^+,0.5), 460 (1.0%), 307 (38.4%). Analysis calc'd for $C_{28}H_{18}N_4O_2S$: C, 70.87; H, 3.82; N, 11.81; found: C, 70.33 ; H, 3.85 ; N, 11.48

2-[4-Fluorophenyl(oxomethyl)]benzoic acid. (2.10a)

To a 1L- 3-neck round bottom flask equipped with a mechanical stirrer, were added 25 g (0.17 mol) of phthalic anhydride, 108 mL (1.16 mol) of fluorobenzene and 50 g (0.375 mol) of anhydrous aluminum chloride. The reaction mixture was heated to reflux over 30 minutes. The color changed from yellow to red brown, and finally dark brown. The reaction mixture was stirred for 1 hour, and then cooled to room temperature. The minimum amount of water (ca. 20 mL) was added to the dark colored solution, then the black solution turned to a light yellow slurry with generation of hydrochloric acid. The precipitates were added into 20 mL of concentrated hydrochloric acid and then washed twice with water. The yellow powder was dissolved in warm dilute potassium hydroxide solution. The small amount of insoluble material was filtered off and the filtrate was acidified with concentrated hydrochloric acid (ca.10 mL). A white powder precipitated out. The powder was filtered and recrystallized from toluene-petroleum ether; yield 40% (16.4 g), white needles, m.p. 141-143°C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.31 (m, 2H), 7.42 (d, J_2=8.64, 1H), 7.62-7.78 (m, 4H), 7.96 (d, J_2=8.64, 1H)

1,2-Dihydro-4-(4-fluorophenyl)-1-oxo(2H)phthalazine. (2.11a)

The acid **2.10a** (4.80 g; 0.015 mol) and hydrazine monohydrate (0.75 g; 0.015 mol) were heated in methanol (50 mL) at reflux for 6 hours. A white powder precipitated from solution. After cooling to room temperature it was collected by filtration and recrystallized from aqueous acetic acid; yield 90%, white needles, m.p. 279-281°C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.34-7.40 (m, 2H), 7.61-7.66 (m, 3H), 7.85-7.92 (m,2H), 8.30-8.34 (m, 1H), 12.89 (s, 1H), MS (m/e, relative intensity %): 239.85 (M^+,100), 238.85 (95.2). Analysis calc'd for $C_{14}H_9FN_2O$: C, 70.00; H, 3.78; N, 11.66; found: C, 70.00 ; H, 3.80 ; N, 11.73

(4-Fluorophenyl)phenylsulfide

This material was prepared by the reaction of copper (I) benzene thiolate with 4-bromofluorobenzene according to Peach[12]; yield 67%, b.p. 171C° (3.2kpa)

2-[4-(4-Fluorophenylthio)phenyl(oxomethyl)]benzoic acid (2.10b)

To the ice-cooled mixture of phthalic anhydride (5.92 g; 0.04 mol) and (4-fluorophenyl)sulfide (8.16 g; 0.04 mol) in 80 ml of 1,2-dichlorobenzene, was added anhydrous aluminum chloride (10.67 g; 0.08 mol). The temperature was raised gradually to room temperature. The reaction mixture, a reddish black solution, was stirred for 30 hours. The reaction mixture was poured into 400 mL of crushed ice and 20 mL of concentrated hydrochloric acid forming a white emulsion. The water layer was decanted off and the solvent was evaporated from the organic layer. The resulting white powder was recrystallized from aqueous acetic acid; yield 77% (10.92 g), white powder, m.p. 159-161 C°; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.18 (d, J_2=8.40, 2H), 7.32 (d, J_2=7.80, 2H), 7.38 (d, J_2=5.70, 2H), 7.53 (d, J_2=8.40, 2H), 7.58-7.75 (m, 3H), 7.97 (d, J_2=7.16, 1H)

1,2-Dihydro-4-[(4-fluorophenylthio)phenyl]-1-oxo(2H)phthalazine. (2.11b)

This material was prepared by the reaction of compound **2.10b** with hydrazine monohydrate in methanol using the procedure described above for compound **2.11a**. The crude product was recrystallized from aqueous acetic acid; yield 88%, colorless needles. m.p. 244-246°C ; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.13-7.17 (m, 1H, 7.21-7.39 (m, 2H). 7.42-7.71 (m, 4H), 7.85-7.94 (m, 2H)

1,2-Dihydro-4[4-(4-fluorophenylsulfonyl)phenyl]-1-oxo(2H)phthalazine. (2.14)

The phthalazinone **2.11b** was added to a vigorously stirred suspension of wet alumina (2.0 g) and Oxone® (1.23 g, 2.0 mmol) in chloroform (10 mL). The mixture was heated at reflux for 12 hours. The mixture was cooled and the solids were washed thoroughly with warm chloroform. Removal of solvent afforded crude sulfone which was recrystallized from aqueous acetic acid; Yield 82%, m.p. 268-269 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.45-7.52 (m, 2H), 7.62-7.69 (m, 1H), 7.84-7.95 (m, 4H), 8.22-8.25 (m, 4H), 8.32-8.39 (m, 1H), 12.98 (s, 1H). MS (m/e, relative intensity %): 379.88 (M^+,100). Analysis calc'd for $C_{20}H_{13}N_2O_3S$: C, 63.15; H, 3.44; N, 7.36; found: C, 62.83 ; H, 3.22 ; N, 6.99

2-[4-phenoxyphenyl(oxomethyl)]benzoic acid. (2.10c)

This material was prepared by the reaction of phthalic anhydride with diphenyl ether in 1,1,2,2-tetrachloroethane- nitrobenzene mixed solvent (volume ratio 5 to 1) according to Stille's procedure[8]. The crude product was recrystallized from aqueous acetic acid; yield 74%, white needles. m.p. 161-163 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.04 (d, J_2=8.69, 2H), 7.13 (d, J_2=7.83, 2H), 7.26 (t, J_2=7.70, 1H), 7.39-7.50 (m, 2H), 7.60-7.78 (m, 5H), 8.00 (d, J_2=7.29, 1H)

1,2-Dihydro-4-(4-phenoxyphenyl)-1-oxo(2H)phthalazine. (2.11c)

This material was prepared by the reaction of compound **2.10c** with hydrazine monohydrate in methanol using the procedure described above for compound **2.11b**. The crude product was recrystallized from aqueous acetic acid; yield 89%, white needles; m.p. 244-245°C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.15 (m, 5H), 7.45 (m, 2H), 7,59 (m, 2H), 7.71 (m, 1H), 7.92 (m, 2H), 8.31 (m, 1H), 12.83 (s, 1H)

1,2-Dihydro-4-[4-(4-[4-fluorophenyl(oxomethyl)]phenoxy)phenyl]-1-oxo(2H)phthalazine. (2.12)

To an ice-cooled mixture of *p*-fluorobenzoyl chloride (3.32 g; 0.021 mol) and anhydrous aluminum chloride (5.33 g; 0.04 mol) in 150 mL of 1,2-dichloroethane, 6.28 g (0.020 mol) of the phthalazinone **2.11c** was added. The yellow slurry turned into a red brown solution. The temperature was raised gradually to room temperature. The reddish black solution was stirred for 24 hours. The reaction mixture was poured into 200 mL of crushed ice and 10 mL of concentrated hydrochloric acid. The resulting white powder was filtered, washed with methanol, and recrystallized from aqueous acetic acid; 80 % yield (0.70 g), m.p. 277-281 °C; ^{1}H-NMR (DMSO-d_6) δ 7.20-7.40 (m, 7H), 7.63-7.90 (m, 8H), 8.33 (m, 1H), 12.88 (s, 1H). MS (m/e, relative intensity %): 436 (M^+,2.9), 314 (100%). Analysis calc'd for $C_{27}H_{17}N_2O_3$: C, 74.30; H, 3.93; N, 6.42; found: C, 73.95 ; H 3.98 ; N, 6.39

2-[4-(4-fluorophenylthio)phenyl(oxomethyl)]benzoic acid. (2.10d)

This material was prepared by the reaction of phthalic anhydride with phenyl ether in 1,1,2,2-tetrachloroethane-nitrobenzene mixed solvent (volume ratio 5 to 1) according to Stille's procedure[8]. The crude product was recrystallized from aqueous acetic acid; yield 78 % , white needles, m.p. 128-129°C; ^{1}H-NMR (DMSO-d_6) δ 7.24 (d, J_2=8.40, 2H), 7.42-7.72 (m, 10H), 7.97 (d, J_2=7.29, 1H)

1,2-Dihydro-4-[4-(4-fluorophenylthio)phenyl]-1-oxo(2H)phthalazine. (2.11d)

This material was prepared by the reaction of compound **2.10b** with hydrazine monohydrate in methanol using the procedure described above for compound **2.11a**. The crude product was recrystallized from aqueous acetic acid; yield 95%, colorless needles, m.p. 244-246°C; ^{1}H-NMR (DMSO-d_6) δ 7.43-7.56 (m, 7H), 7.58-7.63 (m, 2H), 7.68-7.73 (m, 1H), 7.87-7.92 (m, 2H), 8.32-8.35 (m, 1H), 12.86 (s, 1H)

1,2-Dihydro-4-[4-(4-[4-fluorophenyl(oxomethyl)]phenylthio)phenyl]-1-oxo(2H)phthalazine (2.13)

This material was prepared by the reaction of compound **2.11d** with *p*-fluorobenzoyl chloride in the presence of anhydrous aluminum chloride in 1,2-dichloroethane using the procedure described above for compound **2.12**. The crude product was recrystallized from aqueous acetic acid; 79% yield, white needles, m.p. 268-270 °C; ^{1}H-NMR (DMSO-d_6) δ 7.37-7.49 (m, 7H), 7.18-7.95 (m, 8H), 8.33-8.37 (m, 1H), 12.92 (s, 1H), MS (m/e, relative intensity %):452.94 (M^+, 26.5), 451.94 (85.1), 329.96 (100.00). Analysis calc'd for $C_{27}H_{17}FN_2O_4S$: C, 71.67; H, 3.79; N, 6.19; found: C, 71.38 ; H, 3.81 ; N, 6.14

General procedure for the preparation of phthalazinone polymers

Polymerizations were typically carried out in a dry 50 mL three-neck flask equipped with a stirbar, a Dean-Stark trap fitted with a condenser, and a nitrogen inlet.

1) Polymerization of Phthalazinone Monomer 2.5f

(Example; polymer **2.15f**)

To a dried flask containing 0.254 g of bis(4-fluorophenyl)sulfone **2.22** (0.0010 mol), 0.669 g (0.0010 mol) of phthalazinone monomer **2.5f**, 6 mL of toluene, and 4 mL of NMP was added 0.152 g of anhydrous potassium carbonate (0.0011 mol). The resulting mixture was heated to reflux (130°C) with stirring. A strong flow of nitrogen was maintained to remove the water formed with toluene. After 2 hours of dehydration, the temperature was increased to 190°C by bleeding toluene from the Dean-Stark trap. After 10 hours the solution was cooled to 100°C, diluted with 10 mL of TCE, and precipitated into methanol (200 mL) containing a few drops of concentrated hydrochloric acid. The resulting fibrous polymer was dissolved in chloroform (40 mL), filtered through a thin layer of celite to remove the inorganic salts, and reverse precipitated into 200 mL of methanol. After drying under reduced pressure at 80°C, 0.759 g of light yellow powder **2.16f** (yield 86%) was obtained.

2) Polymerization of Phthalazinone monomers in DPS

(Example; polymer **2.15c**)

To a three-neck 50 mL flask, were added **2.5c** (0.4586 g; 0.001mol), anhydrous potassium carbonate (0.1510 g; 0.0011 mol) and bis(4-fluorophenyl)sulfone **2.22** (0.2542 g; 0.001 mol) and DPS (4.32 g). The reaction mixture was stirred at 150°C for 6 hours. The water that formed was removed by purging with nitrogen. The reaction mixture temperature was raised to 200°C for 6 hours and finally at 280°C for 24 hours. The mixture, a dark colored viscous liquid, was added to acetone (100 mL) and acetic acid (2 mL), and the tan-colored fibrous polymer seperated out. It was dissolved in 7 mL of hot NMP, filtered through a thin layer of celite, precipitated into methanol, filtered and dried to give 0.569 g of polymer **2.16c** (yield 89%).

2-8 References and Notes

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Chapter 3

Attempted Synthesis of Poly(arylene ether)s Containing the Quinazolinone Moiety

3-1 Introduction

3-1-1 Quinazolinone[1]

Quinazoline is a name for the compounds which have fused pyrimidine rings. 3,4-Dihydro-4-oxoquinazolines ("Quinazolinones") form the largest group of quinazolines known (Figure 3-1). This is partly because they are easily prepared and partly because the 4-oxoquinazoline moiety is found in several quinazoline alkaloids and also in a number of derivatives which possess biological activities of various types.

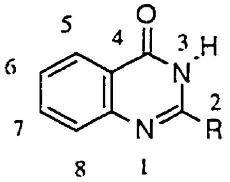
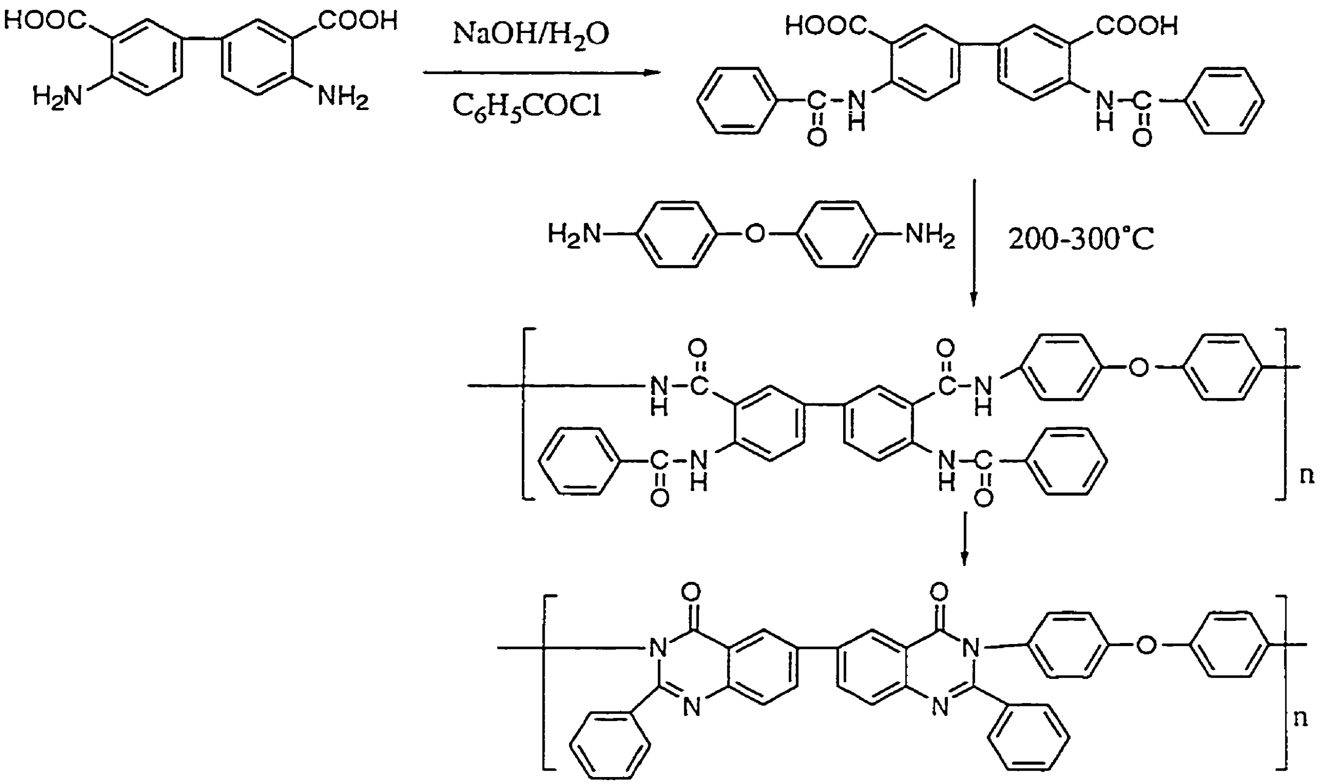


Figure 3-1 Quinazolinone

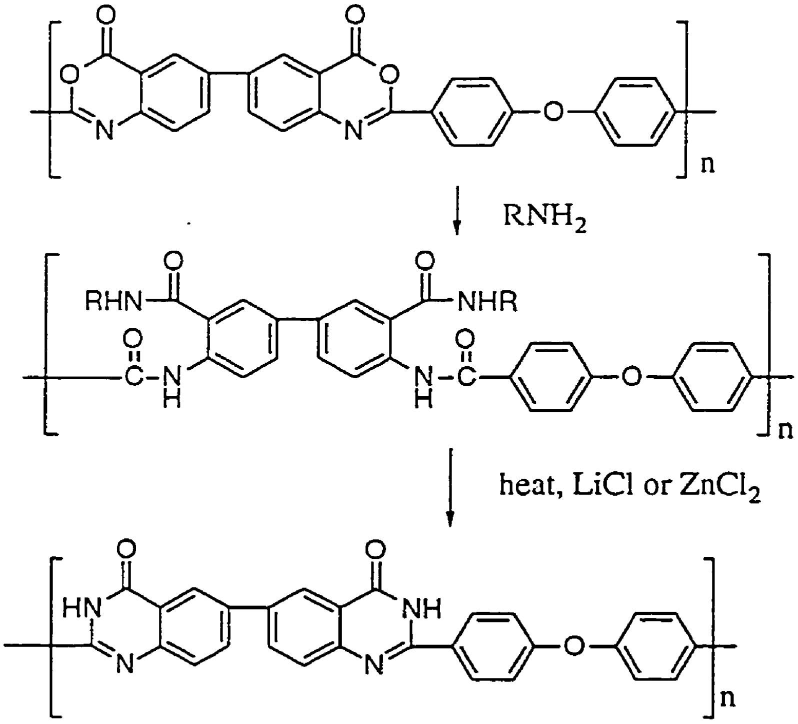
3-1-2 Previous Quinazolinone Containing Polymers

The first synthesis of a polyquinazolinone appeared in a German patent. An aromatic diamine was heated to 200-300°C with a bisamic acid, which was synthesized from a bisamino acid and benzoyl chloride (Scheme 3-1)[2]. The polymers were stable to 525°C in nitrogen and 425°C in air. Yoda reported polyquinazolinone synthesis by a reaction on the polymer chains.[3] Polybenzoxazinone[4] was reacted with a primary amine to form a poly(amic acid). When it was heated in the presence of LiCl or $ZnCl_2$, it dehydrated to give the polyquinazolinone (Scheme 3-2).

Scheme 3-1



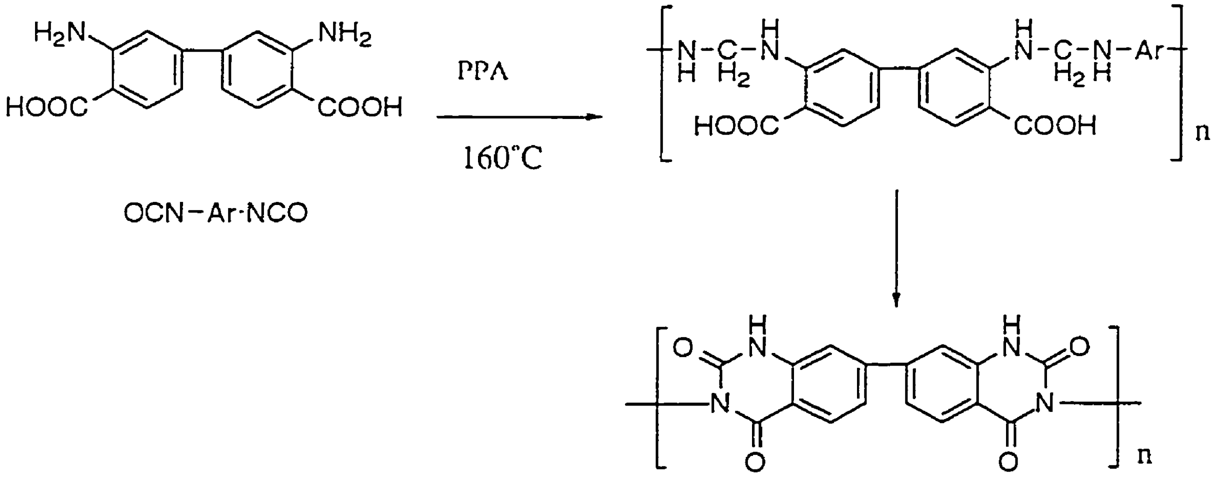
Scheme 3-2



If no salts were present, it reverted back to the polybenzoxazinone starting material. This was due to the formation of a complex of the ortho amide groups with the inorganic salt. The intermediate poly(amic acid) was soluble in a dipolar aprotic solvent such as DMF. The polyquinazolinone was soluble only in strong acid such as conc. H_2SO_4. The polymers were stable to 530°C in nitrogen and 440 °C in air.

Another heterocyclic polymer similar to the polyquinazolinone, poly(quinazolinedione)s have also been synthesized. They were synthesized by the reaction of a diisocyanate and aromatic bisaminocarboxylic acid followed by thermal cyclization (Scheme 3-3)[5]. The intermediate was soluble in dipolar aprotic solvents such as NMP and flexible films could be cast from these solvents. The final cyclized polymers were insoluble and showed excellent thermooxidative stability indicated by TGA analysis. This polymer was synthesized by another route from aniline and N-mesyloxyphthalimide[6].

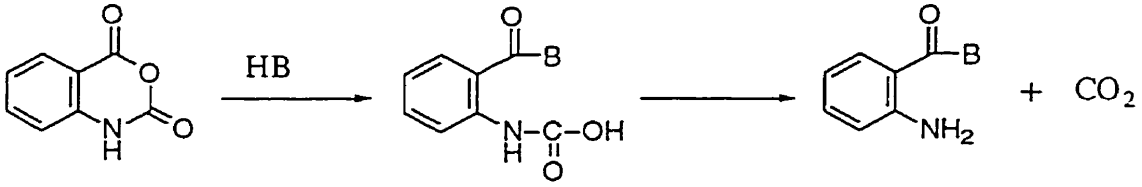
Scheme 3-3



3-1-3 Design of Quinazolinone Monomers

Isatoic anhydride is a convenient reagent for certain anthranoylations, which are precursors of substituted tetrahydroquinazoline derivatives. Anthranoylations take place if isatoic anhydride is reacted with compounds containing reactive hydrogen atoms (ammonia, primary amines, alcohols, phenols) (Scheme 3-4)[7].

Scheme 3-4



B=-NH_2, -NHR, -NHAr, -OR, -OAr

The liberation of carbon dioxide is characteristic of these reactions, which are those of a cyclic mixed anhydride of a simple carboxylic acid and carbamic acid. The formed amine is reacted with substituted benzoyl chlorides to form 2-(benzamido)benzamide derivatives, which are cyclized to quinazolinones. Various functionalities, such as phenol, may be introduced into quinazolinones on the 3- or 4- position by using various substituted benzoyl chlorides.

If a 4-fluorophenyl group is placed on the 2-position of the quinazolinone, the fluorine should be reactive in a nucleophilic aromatic substitution reaction because it is activated by the two nitrogens of the quinazolinone. In addition, the quinazolinone monomers from isatoic anhydride have ortho linkages. Recently the synthesis of thermally stable high molecular weight polymers containing ortho linkages has been of interest[8]. Ortho linkages create disorder in the regularity of polymer chains and reduce crystallinity. Consequently, the polymers become soluble and the melting points of the polymers are lowered so that the polymers can be easly processed. High T_g, soluble poly (ether ketone)s containing the ortho benzoyl moiety have been reported[9]. Melt processable poly(ether imide)s with ortho ether linkages have also been synthesized[8].

3-2 Strategy and Goals

In Chapter 2, the successful synthesis of high molecular weight poly(phthalazinone)s by a novel N-C coupling reaction was described. In this chapter, synthesis of quinazolinone monomers and their attempted polymerization are described. Quinazolinone is an isomer of phthalazinone and possesses The NHCO group. First, the possibility of an N-arylation reaction was explored. Then, quinazolinone containing bisphenols and difluoride monomers were synthesized from inexpensive isatoic anhydride. These monomers were polymerized under nucleophilic aromatic substitution reaction conditions. A previous synthesis of polyquinazolinones has been reported[2,3]. However, the molecular weights of the polymers were not high and expensive starting materials were needed.

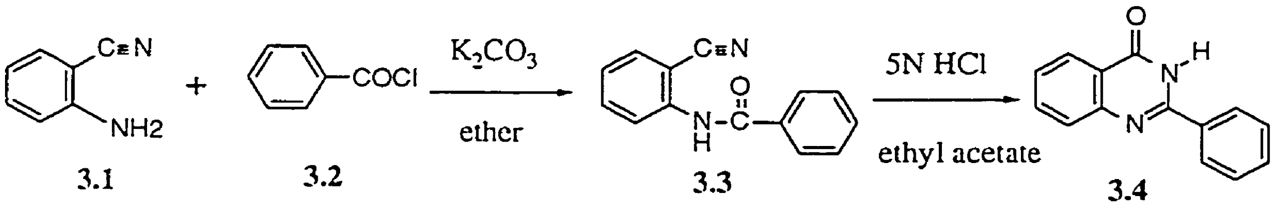
3-3 Attempted N-arylation of Quinazolinone

The possibility of N-arylation of quinazolinone was examined using model reactions. 4(3H)-2-phenylquinazolinone was synthesized and reacted with activated aromatic fluorides under nucleophilic aromatic substitution conditions.

3-3-1 Synthesis of 4(3H)-2-Phenylquinazolinone

4(3H)-2-Phenylquinazolinone 3.4 was prepared by the method reported by Showell[11].

Scheme 3-5

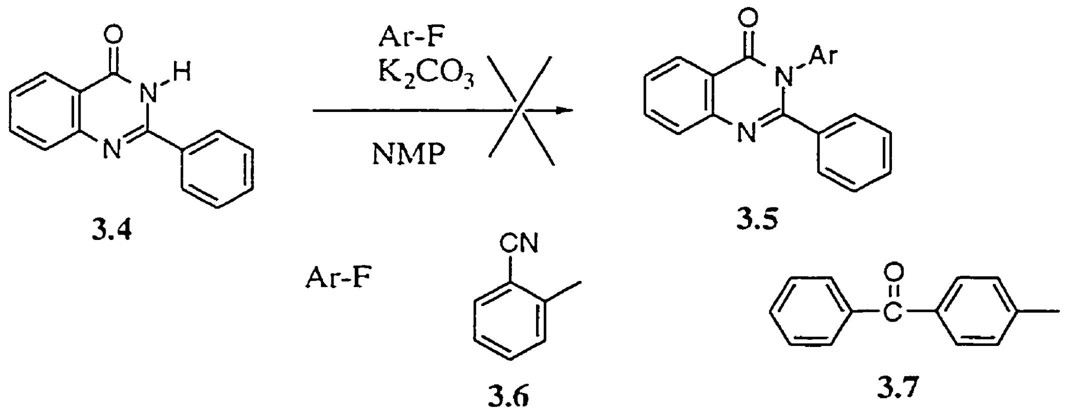


2-(Benzoamido)benzonitrile **3.3** was prepared by a reaction of anthranilonitrile **3.1** and benzoyl chloride **3.2** in the presence of excess of potassium carbonate in diethyl ether[10]. **3.3** was stirred in ethyl acetate with 5N HCl for 10 minutes at room temperature[12]. Basification with 10% NaOH solution gave **3.4** in good yield (Scheme 3-5).

3-3-2 Attempted N-Arylation of Quinazolinone

In order to determine the possibility of the use of N-arylation of quinazolinones as a polymer forming reaction, the reaction of **3.4** with activated halides under nucleophilic aromatic substitution reaction conditions were carried out. **3.4** was reacted with 2-fluorobenzocyanide **3.6** or 4-fluorobenzophenone **3.7** in dipolar aprotic solvents such as NMP in the presence of anhydrous potassium carbonate. Regardless of the conditions used, no reaction took place. The nucleophilicity of the aza nitrogen anion of the quinazolinone is low. In addition, the 3- position is sterically hindered because of the phenyl group on the 2-position.

Scheme 3-6



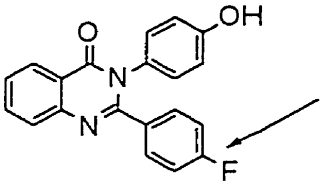
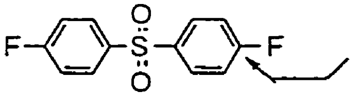
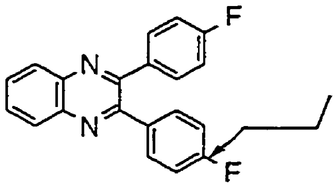
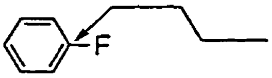
3-4 Synthesis of Quinazolinone Containing Monomers

In contrast to phthalazinone, the aza nitrogen anion of the quinazolinone turned out to be unreactive in a nucleophilic aromatic substitution reaction. We therefore synthesized, 6 novel quinazolinone monomers for the preparation of novel poly(arylene ether)s containing the quinazolinone moiety.

3-4-1 Reactivity of the Fluorine on the 2-Phenyl Group of the Quinazolinone

As described in Chapter 1, the reactivity of an aromatic fluoride in nucleophilic aromatic substitution reactions can be predicted by ^{19}F-NMR chemical shift, or charge density of a carbon which has a fluorine by HMO calculations. Fluorines in the 4-position of a quinazolinone monomers such as A in Table 3-1, would be expected to be reactive in a nucleophilic aromatic substitution reaction because the fluorine is activated by the two adjacent nitrogens in the quinazolinone.

Table 3-1 ^{19}F-Chemical Shifts (in DMSO-d_6) and HMO Charge Densities of Fluorinated Compounds

		Electron Density	^{19}F-NMR Shift
A		0.016	-111.085
B		0.041	-104.08
C		0.021	-111.99
D		-0.007	-112.77

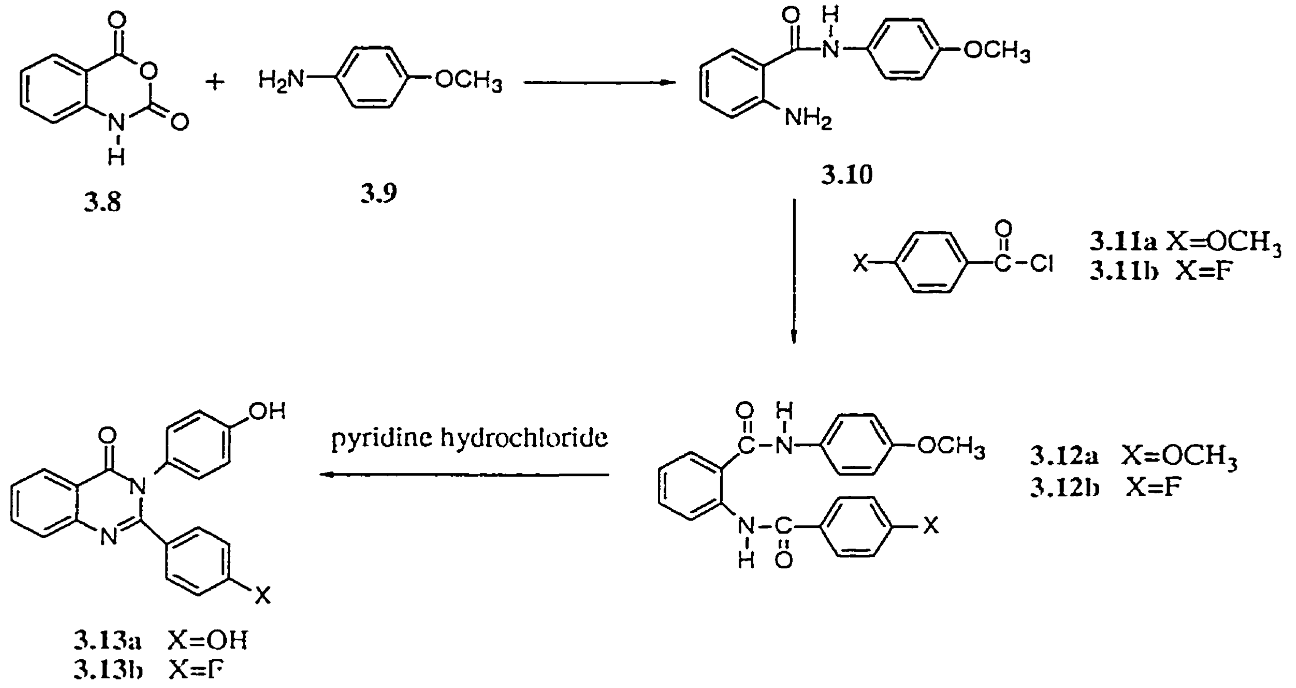
The ^{19}F-NMR chemical shift of the fluorine on quinazolinone monomer **A** and electron density of the carbon which has a fluorine as a substituent on **A** are shown in Table 3-1. Fluorobenzene **D**, bis(4-fluorophenyl)sulfone **B** are included to provide standards for an unreactive fluorinated compound and a polymerizable fluorinated monomer, respectively. We[13] and others[14] synthesized high molecular weight polymers from 2,3-bis(4-fluorophenyl)quinoxaline **C**, which is weakly activated, toward the nucleophilic displacement of fluorine by bisphenolates.

The fluorine chemical shift of **A** shifted further upfield than that of **B**. The electron density of the carbon to which fluorine is attached is much less positive than that of **B**. The fluorine is not as reactive as the fluorine on **B**. Compared with **D**, the electron density of A is much more positive and the ^{19}F-NMR chemical shift is down field from that of **D**. Compared with **C**, the electron density of the carbon on **A** is less positive, but the ^{19}F-NMR chemical shift is more down field. The results suggest that the fluorine on **A** should be reactive in a nucleophilic aromatic substitution reaction and higher temperatures or longer reaction times may be needed.

3-4-2 Synthesis of Quinazoline Monomers

Quinazoline monomers were synthesized in three steps in moderate yield (Scheme 3-7). Finely ground anisidine was mixed well with isatoic anhydride and heated to 80°C. The reaction mixture was stirred for 30 minutes. The viscous black liquid gradually turned into a black dry solid with generation of bubbles of carbon dioxide. Recrystallization from toluene gave 2-amino N-(4-methoxyphenyl)benzamide **3.10** in 78% yield. **3.10** was then treated with 4-methoxybenzoyl chloride **3.11a** or 4-fluorobenzoyl chloride **3.11b** in diethyl ether in the presence of anhydrous potassium carbonate to yield 2-(4-methoxybenzamide)benzamide **3.12a** or 2-(4-fluorobenzamide)benzamide **3.12b** in 91% and 87% yield, respectively. The cyclization of o-amidebenzamides can be done by heating above their melting point until elimination of water is complete[15]. Cyclization sometimes can be done by heating the o-(benzamide)benzamide in the presence of base or acid[16].

Scheme 3-7 Synthesis of Quinazolinone Monomers 3.13a,b

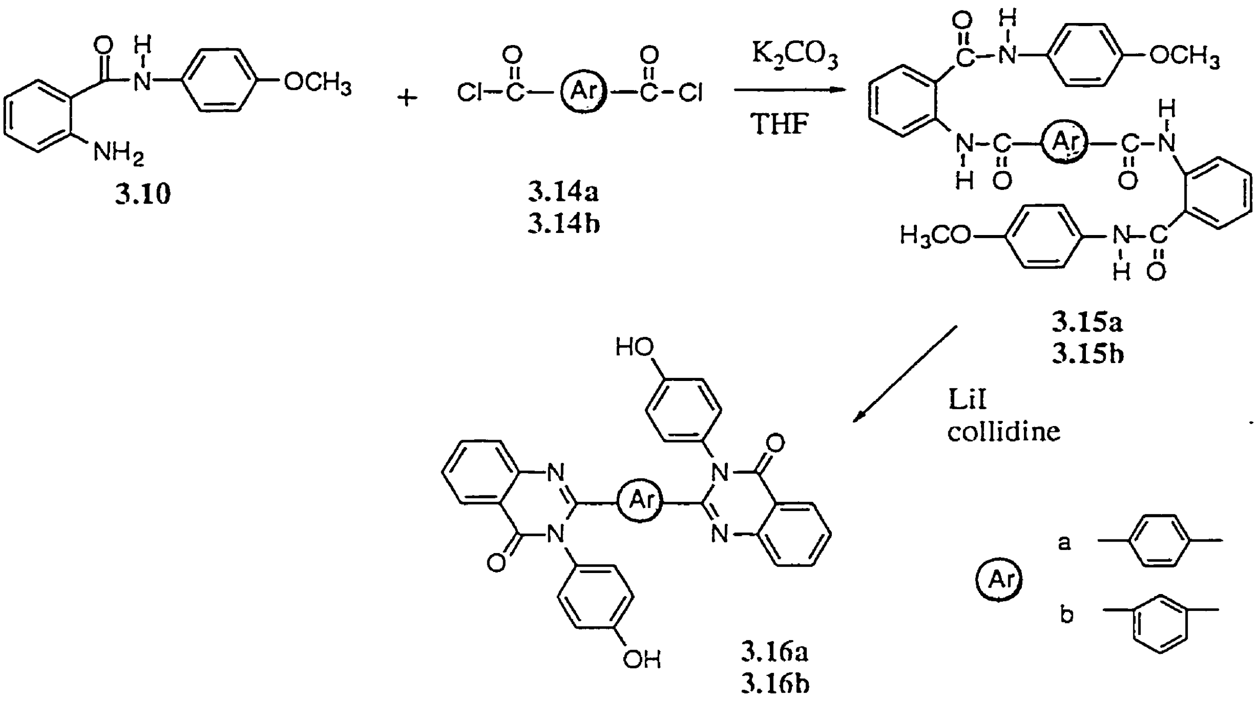


However, **3.12a,b** did not cyclize to quinazolinone under these conditions. The cyclization and deprotection of the methoxy groups were accomplished in one step by using either lithium iodide in collidine or pyridine hydrochloride. **3.12a** or **b** is stirred at 180°C for 18 hours in the presence of excess of lithium iodide in collidine affording quinazolinone monomer **3.13a,b** in 77, 85% yield, respectively. Alternatively, **3.12a** is stirred in a melt of pyridine hydrochloride at 200°C for 1 hour affording **3.13a** in 88 % yield. **3.13b** was obtained in 89 % in the same manner. The longer reaction time reduced the yield greatly and shorter reaction time causes incomplete demethylation.

3-4-3 Synthesis of Bisquinazolinone Monomers

Bisquinazolinone monomers were prepared because monomers **3.13** might form cyclic oligomers which terminated the polymerization reaction (Scheme 3-8).

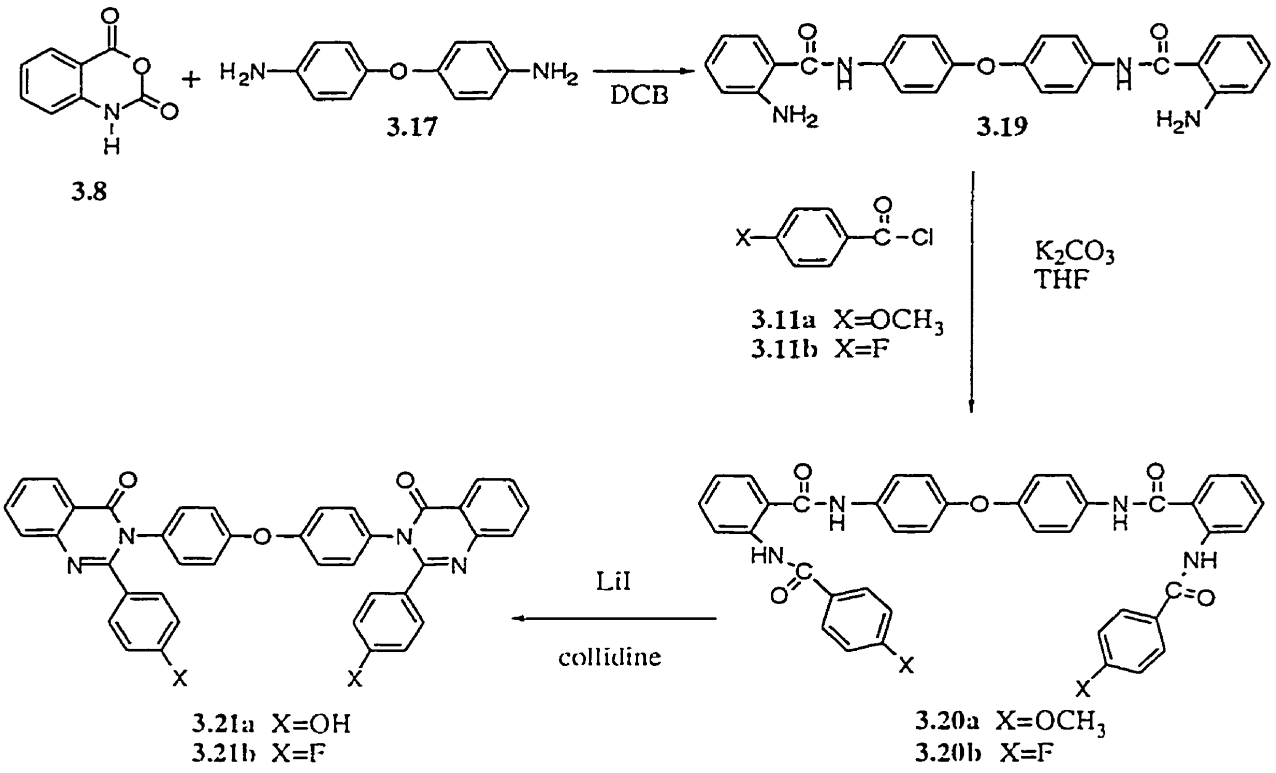
Scheme 3-8 Synthesis of Quinazolinone Monomers 3.16a,b



3.10 was reacted with terephthaloyl chloride **3.14a** or isophthaloyl chloride **3.14b** in THF in the presence of anhydrous potassium carbonate affording bis(benzamide)benzamide **3.15a, b** in 69%, 65% yield, respectively. When it reacted with excess of lithium iodide in collidine bisquinazolinone bisphenols **3.16a, b** were obtained in 52%, 45% yield, respectively. **3.15a, b** were reacted in a melt of pyridine hydrochloride; however, the yields for both **3.16a, b** were less than 30% yield.

Another type of bisquinazolinone monomer was prepared because the bisquinazolinone monomers above formed insoluble crystalline oligomers which came out of the solution during attempted polymerizations (Scheme 3-9). Isatoic anhydride **3.8** was reacted with 4,4'-oxydianiline **3.17** in o-dichlorobenzene at 130 C° affording diamine **3.19** in 75% yield.

Scheme 3-9 Synthesis of Quinazolinone Monomers 3.21a-b

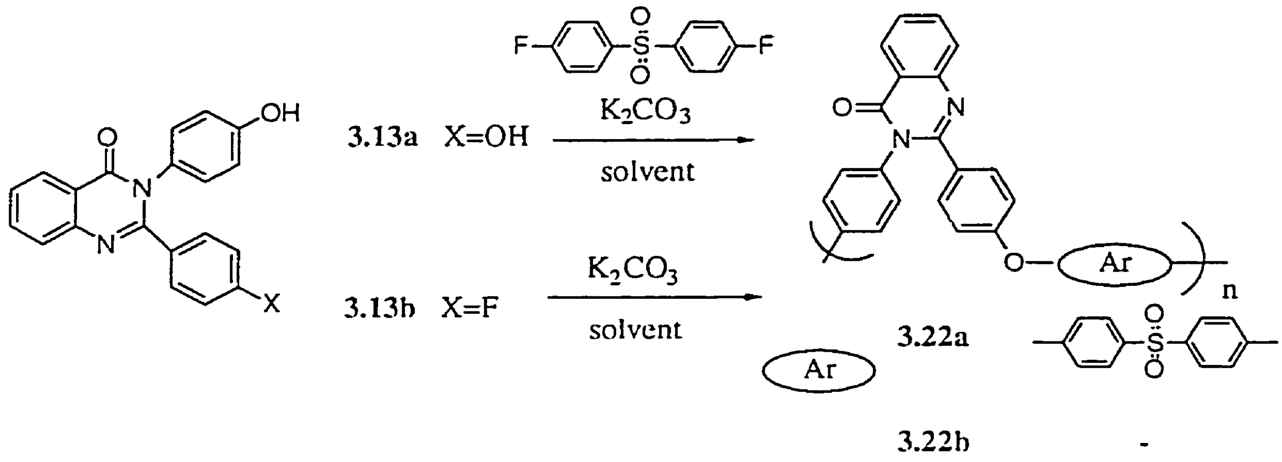


It was reacted with **3.11a** or **3.11b** in THF in the presence of anhydrous potassium carbonate to form **3.20a,b** in 65% and 68% yield, respectively. **3.20** was cyclized and demethylated in one step by lithium iodide in collidine affording bisquinazolinone monomer with a flexible ether linkage, **3.21a,b** in 45% and 68% yield, respectively.

3-5 Attempted Polymerization of Quinazolinone Monomers

A series of novel quinazolinone monomers were subjected to a nucleophilic displacement polymerization reaction in order to synthesize high molecular weight poly(arylene ether)s containing the quinazolinone moiety.

Scheme 3-10



Quinazolinone monomer **3.13a** was reacted with bis(4-fluorophenyl)sulfone in a dipolar aprotic solvent in the presence of potassium carbonate at 25 weight % solids (Scheme 3-10). The results of polymerization for **3.13a-b**, are shown in Table 3-2.

Table 3-2 Polymerization of **3.13a,b**

Polymer	Solvent	wt%	Temp. (°C)	Yield (%)	η_{inh}	M_w	M_n	pd
3.22a	NMP	25	190	85	1.1	6900	4900	1.4
3.22a	sulfolane	25	230	81	0.8	5500	2100	2.6
3.22a	sulfolane	40	230	83	1.2	4700	2500	1.9
3.22a	DMPU	30	250	82	0.9	4800	2400	2.0
3.22a	DPS	20	250	69	0.8	4000	1300	1.4
3.22b	DMAc	25	160	81	1.2	8700	4800	1.8
3.22b	NMP	25	190	79	1.3	8900	4700	1.9

AB-type quinazolinone monomer **3.13b** was reacted under the same conditions. Low molecular weight oligomers were obtained in 69-85 % yield. Weight average molecular weights (M_w) of the formed oligomers were 4000-8900 and inherent viscosities were 0.8-1.3. A typical GPC elution curve is shown in Figure 3-2. M_w, M_n, and the polydispersity (PD) values were taken from the highest molecular weight peak.

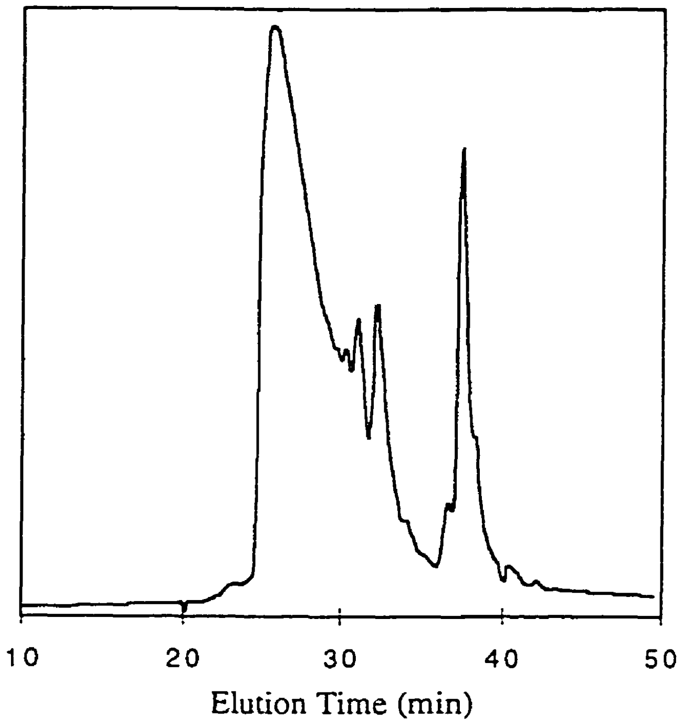


Figure 3-2 Typical GPC Elution Curve for **3.22a**

Besides the highest molecular weight peak, some lower molecular weight peaks, which seemed to correspond to dimer, trimer and so on, were observed. The peaks for phenolic OH in the monomer **3.13a** disappeared after polymerization (Figure 3-3). No fluorine groups were observed based in ^{19}F-NMR. Considering the geometry of the two functionalities, cyclic oligomers were likely to form. That might be the reason why high molecular weight polymers did not form. Polymerization therefore, was conducted in more concentrated solution; however, high molecular weight polymer could still not be obtained. Maldi-TOF MS is a powerful tool to characterize cyclic oligomers[17]. Extensive analysis of formed oligomers by Maldi-TOF with various matrices were carried out. No clear cyclic oligomer peaks were detected.

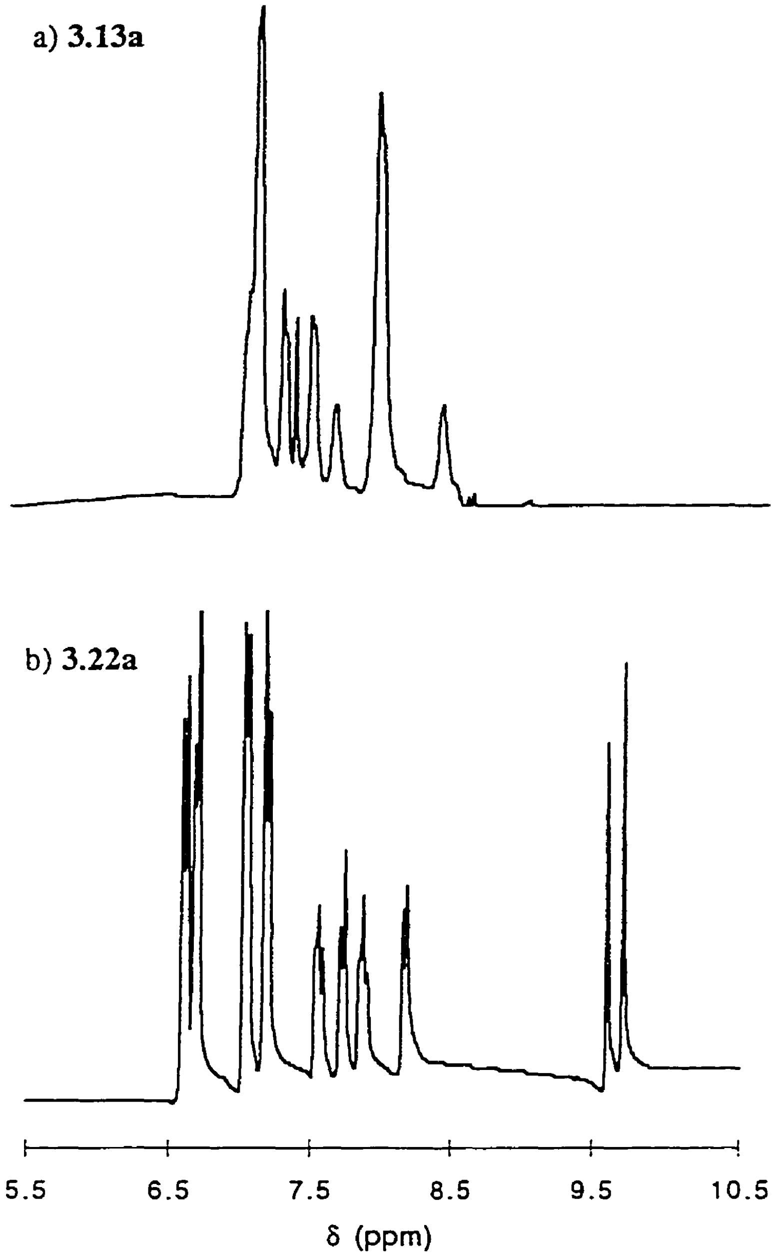
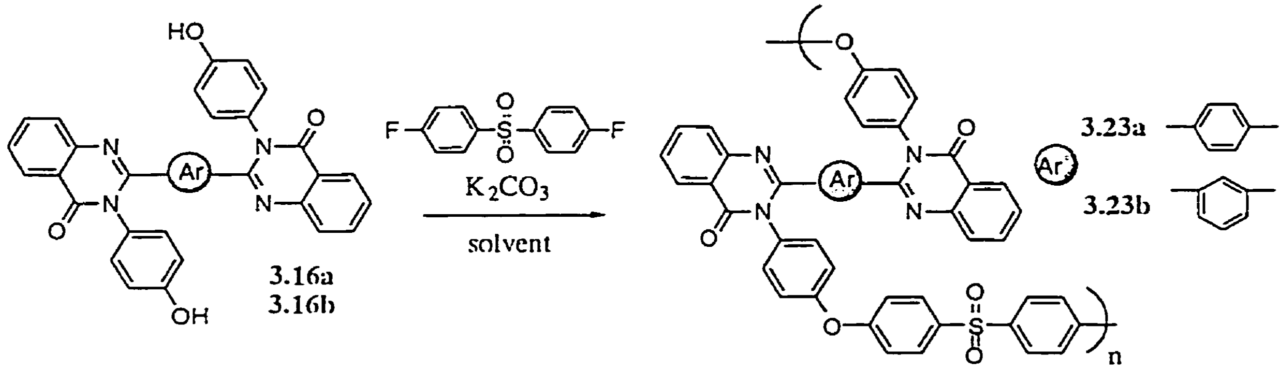


Figure 3-3 ^{1}H-NMR spectra of **3.13a** and **3.22a**

Biquinazolinone bisphenols **3.16a,b** were reacted with bis(4-fluorophenyl sulfone) under the same conditions (Scheme 3-11).

Scheme 3-11 Polymerization of 3.16a, b



In the polymerization of **3.16a, b**, insoluble oligomers came out from the solution in two hours regardless of the conditions. The formed polymers were soluble only in conc. H_2SO_4. Inherent viscosities in conc. H_2SO_4 were 0.10-0.11 (Table 3-3).

Table 3-3 Polymerization of **3.16a,b**

Monomer	Monomer	Solvent	Temp. (°C)	Yield (%)	η_{inh}	Condition
3.16a		NMP	190	91	0.11	precipitation
3.16a		sulfolane	230	88	0.10	precipitation
3.16a		DMPU	250	86	0.10	precipitation
3.16a		DPS	250	79	0.11	precipitation
3.16a (50%)	BPA (50%)	NMP	190	87	0.25	precipitation
3.16b		NMP	190	76	0.11	precipitation
3.16b		DMPU	250	69	0.10	precipitation
3.16b (50%)	BPA (50%)	NMP	250	77	0.21	precipitation

The structures of the oligomers were so rigid that they crystallized out from the solution before high molecular weight polymer formed. Copolymerization of **3.16a** with bisphenol A (BPA) was conducted. Insoluble oligomer with inherent viscosity of 0.21-0.25 still came out of the solution.

The monomers **3.21a,b**, which have flexible ether linkages would not be expected to form cyclic oligomers because the two functionalities are far from each other. **3.21a** was then reacted with bis(4-fluorophenyl)sulfone under the same conditions as **3.13a**. Molecular weight by GPC of the products were somewhat higher than **3.22a-b** (Table 3-4). **3.21b** was reacted with BPA. First BPA was reacted with anhydrous potassium carbonate and the formed water was removed by azeotropic distillation. **3.21b** was then reacted with the BPA potassium salt.

Scheme 3-12

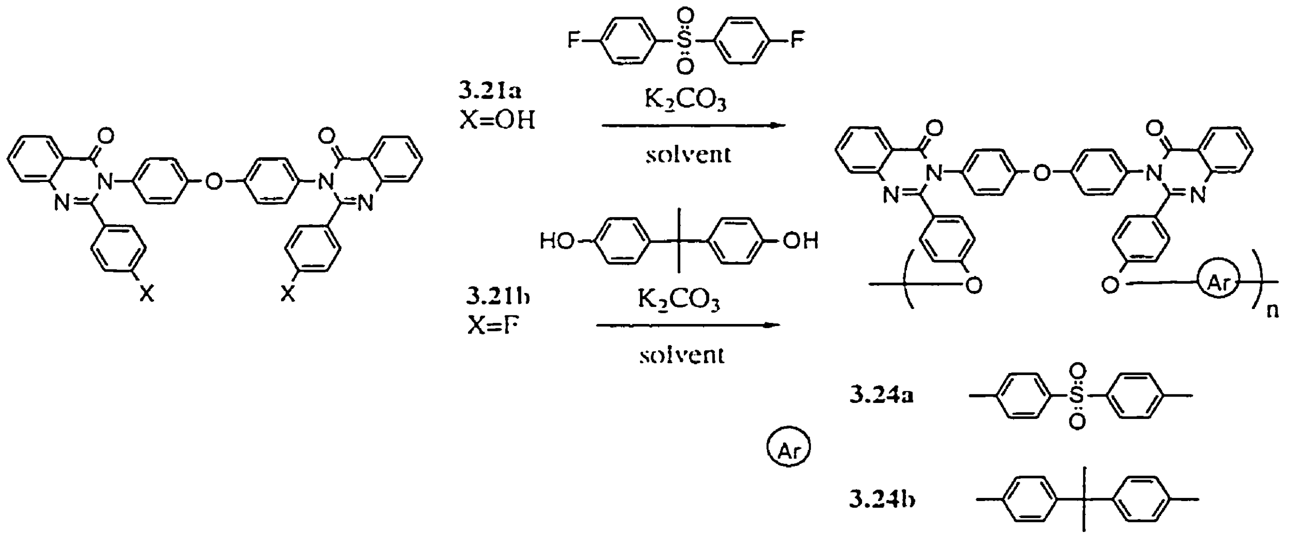


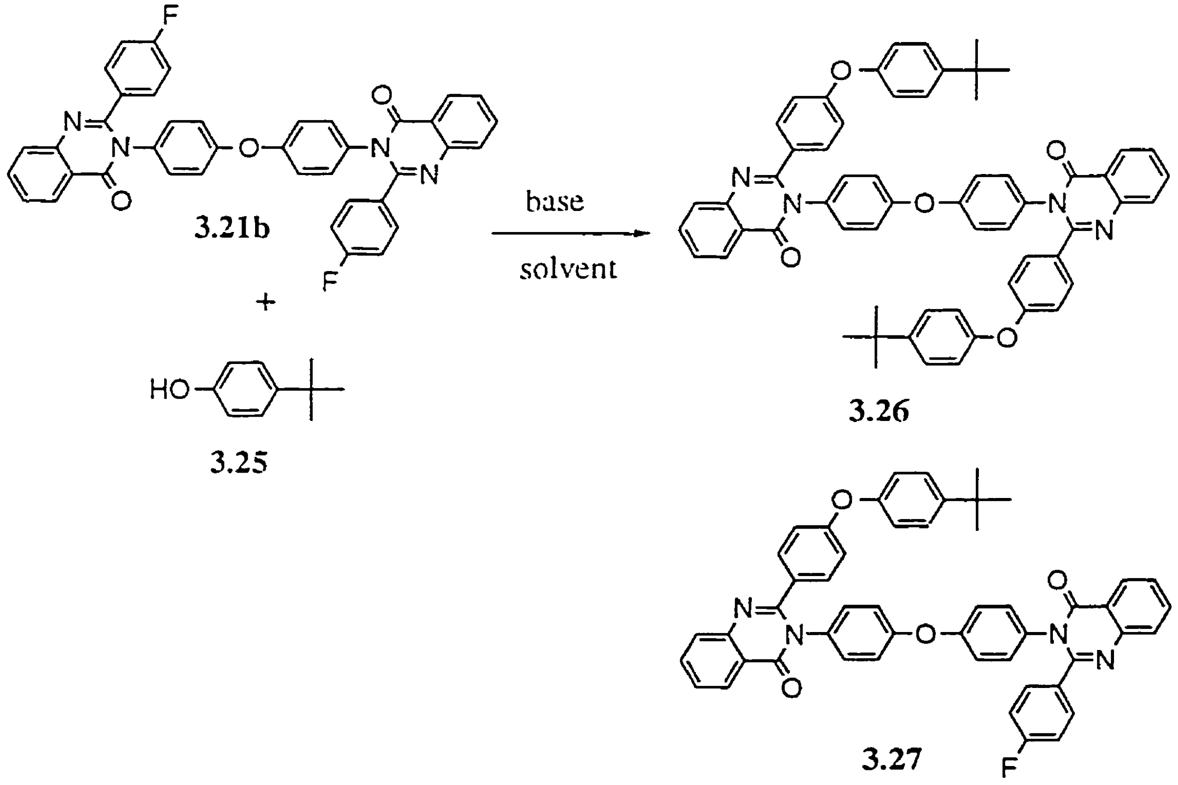
Table 3-4 Polymerization of **3.21a, b**

Polymer	Solvent	wt%	Temp. (°C)	Yield (%)	η_{inh}	M_w	M_n	PD
3.24a	NMP	25	190	77	0.11	8500	5900	1.4
3.24a	sulfolane	25	230	80	0.12	8900	6500	1.4
3.24a	DMPU	40	250	76	0.13	9900	4800	2.1
3.24a	DPS	30	250	74	0.09	6800	1400	4.9
3.24b	NMP	25	190	85	0.13	8800	4200	2.1
3.24b	sulfolane	25	230	84	0.13	8600	4100	2.1
3.24b	DMPU	25	250	75	0.12	7700	3200	2.4

The inherent viscosities of the products were 0.09-0.13, and M_w were 8500-9900 (Table 3-4).

To clarify the experimental results obtained for the polymers, model reactions were performed on **3.21b**, which gave the best result. **3.21b** was reacted with the potassium salt of t-butylphenol in DMSO at 150°C. The reactions were followed by HPLC and the reaction was stopped when the **3.21b** peak disappeared after 6 hours. Side product peaks were observed in HPLC (Figure 3-4) indicating decomposition of the monomer or oligomer occurred along with the substitution reaction. The solid yield after work up was only 66%. Mild reaction conditions were carried out using cesium carbonate at 120°C. In 9 hours the **3.21b** peak disappeared. Side product peaks still appeared along with substituted quinazolinones (Figure 3-5). The solid yield was 77%. Lower temperature reactions suppressed the side reactions, however not completely. **3.21b** was reacted with BPA at 120°C using cesium carbonate in DMSO for 20 hours. Low molecular weight oligomer with inherent viscosity of 0.16 formed.

Scheme 3-13 Model Reaction on 3.21b



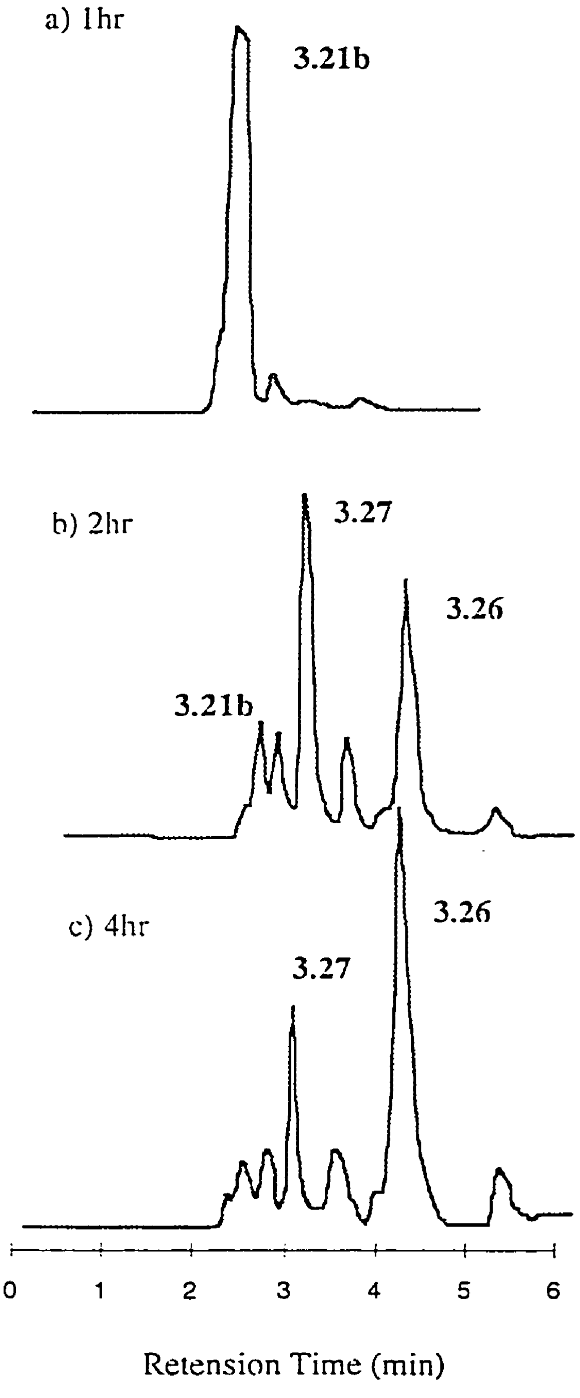


Figure 3-4 HPLC Elution Curves of the Model Reaction (K_2CO_3/DMSO)

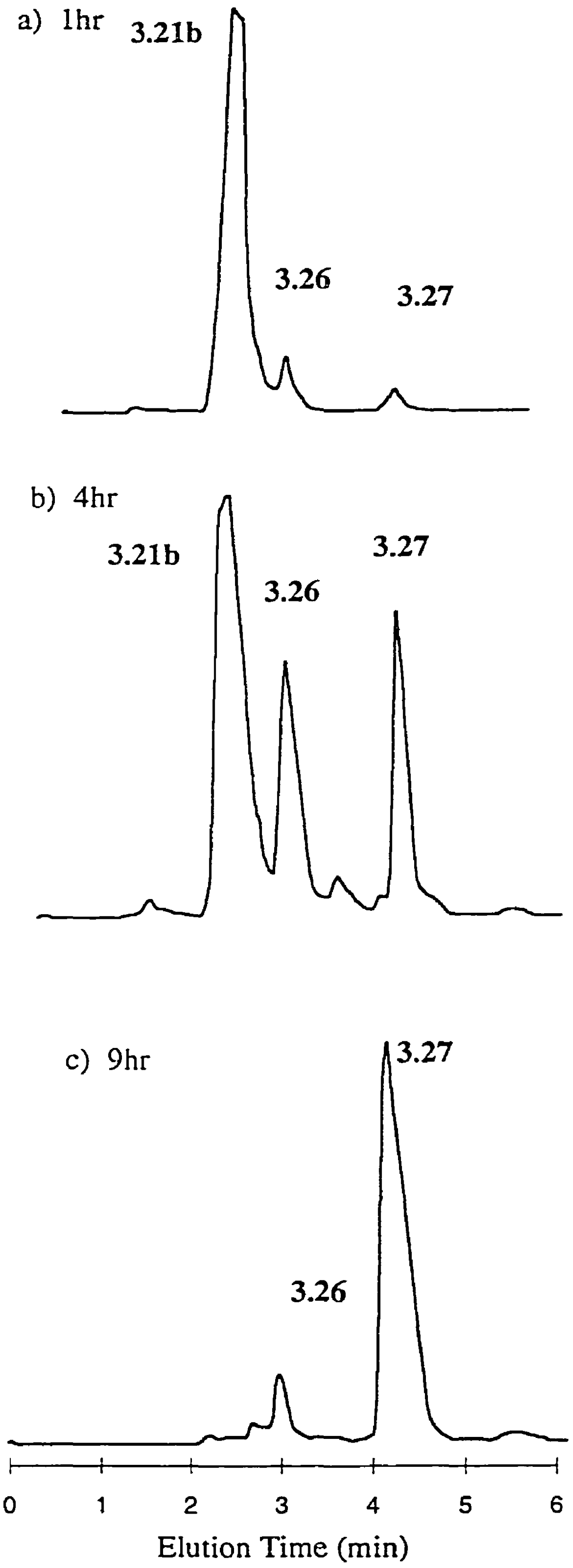


Figure 3-4 HPLC Elution Curves of the Model Reaction (Cs_2CO_3/DMSO)

Table 3-5 Nucleophilic Aromatic Displacement of 3.22b by t-Butylphenolate

Base	Solvent	Temp. (°C)	Time (h)	Solid Yield (%)
K_2CO_3	NMP	190	4	53
K_2CO_3	DMSO	120	24	-
K_2CO_3	DMSO	150	6	66
Cs_2CO_3	DMSO	120	9	77

3-6 Conclusions

N-arylation of quinazolinone was examined by model reactions under nucleophilic aromatic polymerization conditions. The nucleophilicity of the quinazolinone aza nitrogen anion was low and no reaction took place.

A number of quinazolinone containing bisphenols and difluorides were prepared from isatoic anhydride. The overall yields for the synthesis of these monomers were good. They were subjected to a nucleophilic displacement polymerization reaction in order to synthesize new poly(arylene ether)s containing the quinazolinone moiety. In all cases only low molecular weight oligomer formed in 70-90% yield. In HPLC analysis of the model reaction, side product peaks were observed. Presumably, due to the steric interaction of the 3,4-phenyl substituents of the quinazolinone, the quinazolinone monomers were unstable under the polymerization conditions so that decomposition reactions of the monomers competed with polymerization. Lower temperature reactions with cesium carbonate suppresses the side reaction, however, not completely.

3-7 Experimental

Materials

Anthranylonitrile, anisidine, isatoic anhydride, 4-methoxybenzoyl chloride, pyridine hydrochloride, lithium iodide, 4,4'-oxydianiline, t-butylphenol were purchased from the Aldrich Chemical Co. 4-Fluorobenzoyl chloride, collidine were obtained from Lancaster Chemical Co. All the reagents and solvents were used without further purification otherwise noted. Solvents N, N-dimethylacetamide (DMAc), 1-methyl-2-pyrrolidinone (NMP) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) were dried over 4Å molecular sieves for 24 hours before use.

Instrumentation

All ^{1}H- and ^{13}C- NMR were obtained on a JEOL 270 spectrometer. High pressure liquid chromartography (HPLC) analyses were carried out on a Milton Roy CM4000 pump equipped with a reverse phase silica column and a UV detector set at 254 nm; methanol was used as the eluent at a flow rate of 1 mL/min. GPC analyses were performed on a Waters 510 instrument equipped with a UV detector set 254 nm and four 5µm phenogel columns (3x500Å linear) arranged in series. All molecular weights were reference to polystyrene standards. Inherent viscosity data were from chloroform solution with a concentration of 0.5 g/dL in a calibrated Ubbelohde viscometer at 25°C. Matrix-assisted laser desorption ionization-time of flight-mass spectroscopy analyses were performed on a KOMPACT-MALDI-TOF-MS instrument. The analysis solution was prepared from 10 µl of sample solution and 100 µL of dithranol solution (matrix). The cyclic sample solution was prepared from 5 mg of sample of 1mL of chloroform. The matrix solution consisted of 10 mg of dithranol and 1 mL of chloroform. The sample solution (0.2 µL) was spotted on the sample slot and subjected to analysis. The laser power was selected as 90.

Synthesis

2-(4-Fluorobenzamide)benzonitrile. (3.3)

Anthranylonitrile (2.36 g; 0.02 mol) and anhydrous potassium carbonate (8.29 g; 0.06 mol) were suspended in 100 mL of diethyl ether. 4-Fluorobenzoyl chloride (3.17 g; 0.02 mol) was added dropwise with stirring at room temperature. Then the reaction mixture was brought to reflux and stirred for 2 hours. The solvent was removed under reduced pressure. The white powder left was washed with water. The light yellow residue was recrystallized from aqueous ethanol; yield 78% (3.46 g), white needles, m.p. 156-159°C (lit. 155-157°C)[10], ^{1}H-NMR (270MHz, DMSO-d_6) δ 7.19 (t, J_2=6.16, 1H), 7.56-7.62 (m, 2H), 7.80-7.89 (m, 3H), 8.17 (t, J_2=5.59, 1H), 8.70 (d, J_2=8.40, 1H), 12.96 (s, 1H)

4(3H)-2-(4-Fluorophenyl)quinazoline-4-one. (3.4)

2-(4-Fluorobenzamide)benzonitrile (0.96 g; 0.004 mol) **3.3** was stirred in 50 mL of ethyl acetate with 20 mL of 5N HCl for 30 min at room temperature. Basification with 10% NaOH solution, and evaporation of the dried organic layer gave 0.74 g of a white powder. It was recrystallized from 95% ethanol; white needles, yield 0.66 g (69 %), m.p. 218-220°C (lit. 218-9°C)[11], ^{1}H-NMR (270MHz, DMSO-d_6) δ 7.19 (t J_2=6.70, 1H), 7.50-7.67 (m, 3H), 7.82-8.03 (m, 3H), 8.16 (t, J_2=8.40, 1H), 8.70 (d, J_2=8.40, 1H), 12.96 (s, 1H)

2-Amino-N-(4-methoxyphenyl)benzamide. (3.10)

Finely ground anisidine (25.37 g, 0.206 mol) and isatoic anhydride (32.63 g, 0.20 mol) were mixed well and then heated to 80°C which the reaction mixture turned into viscous black liquid with generation of carbon dioxide. The reaction mixture turned dry black solid 30 minutes later. It was recrystallized from boiling toluene; yield 37.95 g (78.4 %), m.p. 115-118°C, ^{1}H-NMR (270MHz, DMSO-d_6) δ 3.74 (s, 3H), 6.34 (s,2H), 6.59 (t, J_2=7.18, 1H), 6.76 (d, J2=8.40, 1H), 6.91 (d-d, J_2=6.67, J_2=2.24, 2H), 7.19 (t, J_2=7.18, 1H), 7.63 (d-d, J_2=6.67, J_2=2.24, 2H), 9.90 (s, 1H)

2[(4-methoxyphenyl)oxomethylamino]-N(4-methoxyphenyl)benzamide. (3.12a)

To a 500 mL three-neck flask equipped with a mechanical stirrer, a dropping funnel and a thermometer were added **3.10** (6.05 g; 0.025 mol) and 10.37 g (0.075 mol) of potassium carbonate. in 120 mL of diethyl ether. *p*-Methoxy benzoyl chloride **3.11a** (4.35 g; 0.0255 mol) was dropped slowly into the suspension with stirring at room temperature. The resulting white slurry was refluxed with stirring for 2 hours. The solvent was removed under reduced pressure. The white powder left was washed twice in water. Recrystallization from DMF-water gave light purple needles; yield 8.55 g (91%), m.p. 211-213°C ^{1}H-NMR (270MHz, DMSO-d_6) δ 3.75 (s,3H), 3.83 (s, 3H), 6.97 (d, J_2=8.88, 2H), 7.11 (d, J_2=9.13, 2H), 7.31 (t, J_2=7.81, 1H), 7.61 (d, J_2=9.13, 2H), 7.88 (d, J_2=8.88, 2H), 8.56 (d, J_2=8.40, 1H), 10.46 (s, 1H), 11.85 (s, 1H)

3,4-Dihydro-2-(4-fluorophenyl)-3-(4-hydroxyphenyl)-4-oxo-(3H)quinazoline. (3.13a)

Method 1

To a 250 mL three-neck round bottom flask equipped with a water cooled condenser, a nitrogen inlet and a stir bar, were added 1.09 g (0.003 mole) of **3.12a** and 3.95 g (0.03 mole) of lithium iodide in 100 mL of collidine. The reaction mixture was stirred in an atmosphere of nitrogen at 190 °C (bath temperature) for 20 hours. A viscous dark gray semisolid separated. The mixture was poured into 500 mL of water and white powder separated was filtered. It was washed in water and recrystallized from DMF-water; yield 7.67 g (77%), m.p. 309°C (DSC)

Method 2

To a 100 mL three neck flask equipped with a nitrogen inlet a stir bar, a thermometer, and a water cooled condenser, were added 2.91 g (0.008 mole) of **3.12a** and 9.24 g (0.08 mole) of pyridine hydrochloride. The mixture was stirred at 200°C in an atmosphere of dry nitrogen for 1 hour. The dark brown viscous semi solid was poured into 600 mL of water after cooling down to room temperature. The light gray powder was washed in water until acid free.

Recrystallization from DMF-water gave white powder; yield 88 % (2.34 g) m.p. 309°C (DSC) Longer reaction times or higher reaction temperatures or older pyridine hydrochloride cause great yield reductions. ^{1}H-NMR (270MHz, DMSO-d_6) δ 6.67 (d, J_2=8.64, 2H), 7.07 (m, 4H), 7.40 (d, 8.64, 2H), 7.54 (t, J_2=7.40, 1H), 7.73 (d, J_2=7.42, 1H), 7.86 (t, 7.01, 1H), 8.17 (d, J_2=7.42, 1H), 9.62 (s, 1H)

2[(4-Fuorophenyl)oxomethylamino]-N(4-methoxyphenyl)benzamide. (3.12b)

This material was prepared by the reaction of **3.10** with 4-fluorobenzoyl chloride **3.11b** in the presence of anhydrous potassium carbonate in diethyl ether using the procedure described above for compound **3.12a**; yield 87%, white needles, m.p. 236-238°C, ^{1}H-NMR (270MHz, DMSO-d_6) δ 3.75 (s,3H), 6.95 (d, J_2=9.13, 2H), 7.32 (t, J_2=9.13, 1H), 7.42 (t, J_2=7.81, 2H), 7.61 (m, 3H), 7.96 (m, 3H), 8.48 (d, J_2=7.67, 1H), 10.45 (s, 1H), 11.86 (s, 1H)

3,4-Dihydro-2-(4-hydroxyphenyl)-3-(4-hydroxyphenyl)-4-oxo-(3H)-quinazoline. (3.13b)

This material was prepared by the reaction of **3.12b** with pyridine hydrochloride using the procedure described above for compound **3.13a**; yield 85%, m.p. 305°C (DSC), ^{1}H-NMR (270MHz, DMSO-d_6) δ 6.59 (d, J_2=8.64, 2H), 6.67 (d, J_2=8.64, 2H), 7.03 (d, J_2=9.37, 2H), 7.17 (d, J_2=8.64, 2H), 7.55 (t, J_2=7.40, 1H), 7.70 (d, J_2=7.91, 1H), 7.86 (t, J_2=6.94, 1H), 8.15 (d, J_2=7.40, 1H), 9.62 (s, 1H), 9.73 (s, 1H)

This material was also prepared by the reaction of **3.12b** with lithium iodide in collidine; yield 85%.

N,N'-Bis-[2-(4-methoxyphenylaminooxomethyl)phenylene]-1,4-benzenediamide. (3.15a)

To a 500 mL three neck flask equipped with a mechanical stirrer, and a thermometer, were added **3.10** (6.09 g; 0.030 mol) and anhydrous potassium carbonate (24.88 g; 0.18 mol) in 600 mL of THF. Finely ground terephthaloyl chloride **3.14a** was added slowly into the suspension with stirring at room temperature. The resulting white slurry was refluxed with stirring for 2 hours. The hot reaction mixture was filtered. The solvent was removed from the filtrate under reduced pressure. The light purple powder was washed with water. Recrystallization from DMF-water gave white powder; yield 16.82 g (69.0 %), m.p. 304°C (DSC), ^{1}H-NMR (270MHz, DMSO-d_6) δ 3.75 (s, 6H), 6.94 (d, J_2=9.15, 4H), 7.31 (t, J_2=7.67, 2H), 7.63 (d, J_2=6.67,4H), 7.94 (d, J_2=7.89, 2H), 7.95 (d, J_2=7.91, 2H), 8.07 (s, 2H), 8.48 (d, J_2=8.15, 2H), 10.44 (s, 2H), 11.93 (s, 2H)

1,4-phenylene-bis[2-(4-hydroxyphenyl)-1-oxo-quinazolin-3-yl]. (3.16a)

This material was prepared by the reaction of **3.15a** with lithium iodide in collidine using the procedure described above for compound **3.13a**; yield 68%. m.p. 445°C (DSC) ^{1}H-NMR (270MHz, DMSO-d_6) δ 6.66 (d, J_2=8.64, 4H), 7.03 (d, J_2=8.64, 4H), 7.26 (s, 4H), 7.58 (t, J_2=7.55, 2H), 7.77 (d, J_2=7.91, 2H), 7.87 (t, J_2=7.55, 2H), 8.17 (d, J_2=6.91, 2H), 9.61 (s, 2H)

N,N'-bis-[2-(4-methoxyphenylaminooxomethyl)phenylene]-1,3-benzenediamide. (3.15b)

This material was prepared by the reaction of **3.10** with isophthaloyl chloride **3.14b** in THF in the presence of anhydrous potassium carbonate using the procedure described above for compound **3.15a**. m.p. 224-6°C ^{1}H-NMR (270MHz, DMSO-d_6) δ 3.74 (s, 6H), 6.90 (d, J_2=6.67, 4H), 7.33 (t, J_2=7.89, 2H), 7.63 (d, J_2=6.67,4H), 7.95 (d, J_2=6.91, 2H), 8.10 (d, J_2=7.91, 2H), 8.48 (m, 2H), 10.44 (s, 2H), 11.95 (s, 2H)

1,3-phenylene-bis[2-(4-hydroxyphenyl)-1-oxo-quinazolin-3-yl]. (3.16b)

This material was prepared by the reaction of **3.15b** with lithium iodide in collidine using the procedure described above for compound **3.16a**; yield 45%. m.p. 285-287°C, ^{1}H-NMR (270MHz, DMSO-d_6) δ 6.66 (d, J_2=8.78, 4H), 6.89 (d, J_2=8.78, 4H), 7.01-7.25 (m, 4H), 7.53 (t, J_2=7.77, 2H), 7.70 (d, J_2=7.77, 2H), 7.87 (t, J_2=6.97, 2H), 8.15 (d, J_2=7.77, 2H)9.69 (s, 2H)

N-[oxy-bis-1,4-phenylene]-bis-[2-aminobenzamide]. (3.19)

Isatoic anhydride (34.25 g; 0.21 mol) and 4,4'-oxydianiline (20.02 g; 0.10 mol) were reacted in 300 mL of o-dichlorobenzene for 3 hours with stirring at 130 °C. As the reaction proceeded bubbles of carbon dioxgen were evolved and the reaction mixture changed from a dark purple slurry to a white slurry. The reaction mixture was cooled down to room temperature. The white powder was filtered, dried and recrystallized from DMF-water; yield 33.10 g (75%), m.p. 272-4 °C. ^{1}H-NMR (270MHz, DMSO-d_6) δ 6.32 (s, 4H), 6.59 (t, J_2=8.34, 1H), 6.75 (d, J_2=8.64, 1H), 6.98 (d, J_2=8.91, 2H), 7.19 (t, J_2=8.34, 1H), 7.62 (d, J_2=8.34, 1H), 7.70

N-(4-methoxyphenyl)-N'-[oxy-bis-1,4-phenylene]-bis-[1,2-benzenediamide]. (3.20a)

3.19 (13.15 g; 0.030 mol) and anhydrous potassium carbonate (24.88 g; 0.18 mol) were suspended in 350 mL of THF. **3.11a** (9.51 g; 0.06 mol) was slowly dropped into the reaction mixture. Then white slurry was brought to reflux and stirred for 3 hours. White powder was filtered off. The solvent was removed under reduced pressure from the filtrate. The white powder left was washed in water, dried, and recrystallized from DMF-water to give light purple powder; yield 13.28 g (65%), m.p. 274-6, ^{1}H-NMR (270MHz, DMSO-d_6) δ 7.02 (d, J_2=9.13, 4H), 7.30 (t, J_2=7.91, 2H), 7.41 (m, 4H), 7.65 (t, J_2=8.98, 2H), 7.70 (d, J_2=9.15, 4H), 7.98 (m, 6H), 8.43 (d, J_2=8.40, 2H), 10.57 (s, 2H), 11.70 (s, 2H)

Oxy-bis(1,4-phenylene)bis[3-(4-hydroxyphenyl)-1-oxo-quinazoline-2-yl]. (3.21a)

This material was prepared by the reaction of **3.20a** with excess of lithium iodide in collidine using the procedure described above for compound **3.16a,b**; yield 45%, white needles, m.p. 330 °C (DSC) ^{1}H-NMR (270MHz, DMSO-d_6) δ 6.63 (d, J_2=8.64, 4H), 6.90

(d, J_2=8.67, 4H), 7.20 (d, J_2=8.67, 4H), 7.32 (d, J_2=8.64, 4H), 7.57 (t, J_2=7.91, 2H), 7.75 (d, J_2=7.91, 2H), 7.89 (t-d, J_2=7.40, J_3=1.49, 2H), 8.03 (d, J_2=7.88, 2H), 9.77 (s, 2H)

N-(4-fluorophenyl)-N'-[oxy-bis-1,4-phenylene]-bis-[1,2-benzenediamide]. (3.20b)

This material was prepared by the reaction of **3.19** with **3.11b** in the presence of anhydrous potassium carbonate in diethyl ether using the procedure described above for compound **3.12a**; yield 68%, white needles; m.p. 274-6, ^{1}H-NMR (270MHz, DMSO-d_6) δ 7.02 (d, J_2=9.13, 4H), 7.30 (t, J_2=7.91, 2H), 7.41 (m, 4H), 7.65 (t, J_2=8.98, 2H), 7.70 (d, J_2=9.15, 4H), 7.98 (m, 6H), 8.43 (d, J_2=8.40, 2H), 10.57 (s, 2H), 11.70 (s, 2H)

Oxy-bis(1,4-phenylene)bis[3-(4-fluorophenyl)-1-oxo-quinazoline-2-yl]. (3.21b)

This material was prepared by the reaction of **3.20b** with lithium iodide in collidine using the procedure described above for compound **3.21a**; yield 69%, white needles, m.p. 308°C ^{1}H-NMR (270MHz, DMSO-d_6) δ 6.87 (d, J_2=8.26, 4H), 7.13 (t, J_2=8.91, 4H), 7.36 (d, J_2=8.64, 4H), 7.45 (dd, J_2=5.45, J_3=2.97, 4H), 7.61 (t, J_2=7.18, 2H), 7.78 (d, J_2=8.15, 2H), 7.91 (t, J_2=7.18, 2H), 8.21 (d, J_2=7.18)

Polymerization

Typical Method: To a 50 mL three neck round bottom flask, equipped with a Dean-Stark trap, a water cooled condenser, a nitrogen inlet, a thermometer, and stir bar, was added , cesium carbonate (0.326 g, 1.0 mmol) and BPA (0.114 g; 0.5 mmol) in 4 mL of DMSO and 10 mL of toluene. The mixture was refluxed for 4 hours at 110-130°C. The toluene was removed from the Dean-Stark trap. It was cooled down to room temperature and the **3.20b** (0.323g; 0.5 mmol) was added and the mixture was stirred a this temperature for 1 hour and slowly raised to 120°C over 2 hours and maintained at this temperature for 16 hours. After cooling to room temperature it was poured into a mixture of 300 mL methanol and 100 mL of water. The white powder was filtered and dried to give 0.367 g (88 %) of product.

Model Reaction

To a 50 mL three neck round bottom flask, equipped with a Dean-Stark trap, water cooled condenser, a nitrogen inlet, a thermometer, and stir bar, added were *t*-butylphenol (0.150 g; 1.0 mmol), cesium carbonate (0.326 g, 1.0 mmol) in 4 mL of DMSO and 10 mL of toluene. The mixture was refluxed for 4 hours at 110-130°C. The toluene was removed from the Dean-Stark trap. It was cooled down to room temperature and the **3.20b** (0.323g; 0.5 mmol) was added. Temperature was increased gradually to 100°C. The mixture was stirred at 100°C. The reaction was followed by HPLC. The **3.20b** peaks disappeared in 6 hours. The mixture was poured into 500 mL of water. The white powder was washed in water, dried at 80°C under reduced pressure over night. Solids yield 78%.

3-8 References and Notes

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Chapter 4

Polyimides Containing a Quinazolinone Moiety

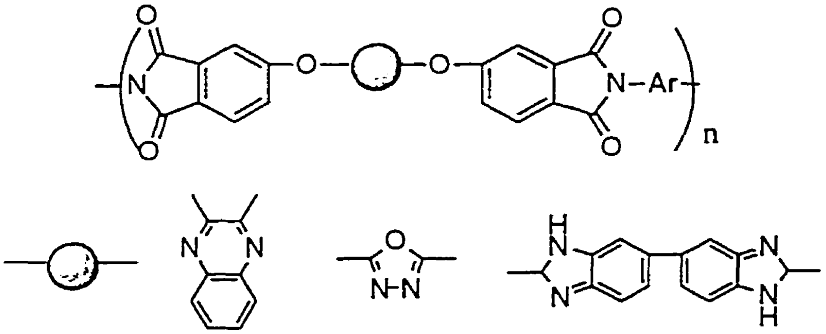
4-1 Introduction

Aromatic polyimides possess outstanding thermal, mechanical, and electrical properties as well as excellent chemical resistance. A large number of new polyimides with unique properties have been introduced for various industrial and consumer product applications since their commercialization in the beginning of the 1960's.[1-9] One of the directions in the development of new polyimides is the synthesis and study of extended rod or rigid rod-like aromatic polyimides because such polyimides have potential as materials for thermally stable, high-modulus, high- strength fibers, as materials with low thermal expansion coefficient (TEC) for packaging materials in microelectronic applications, or as materials for gas separation membranes. In general, rod-like polymers, due to strong enthalpic interactions and the minimal increase in conformational entropy associated with their dissolution or melting, are basically intractable or only processable under extreme conditions[10]. To overcome these difficulties, structural modifications of the polymer backbone, such as the addition of bulky lateral substituents[11-15], flexible alkyl side chains[16], noncoplanar biphenylene moieties[17] and kinked comonomers[18,19] have been utilized to modify the polymer properties, either by lowering the interchain interactions or reducing the stiffness of the polymer backbone. Fluorine containing polyimides have received a great deal of attention because fluorine lowers the TECs. Rigid rod polyimides from fluorinated benzenetetracarboxylic dianhydrides[20], from 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl[20-22], from 2,2'-bis(fluoroalkoxy)benzidine[23] have been prepared and all of these polymers had high moduli, and low TEC.

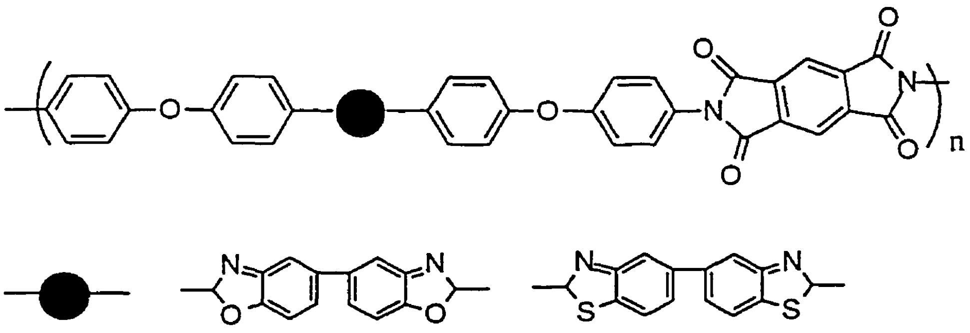
The effect of linearity and rigidity of polyimide chains and moduli of polyimide films have been investigated using uniaxially stretched polyimide films[24]. The linearity of the polymer chain is more important for high modulus than rigidity. The relationship between molecular packing coefficient or free volume and modulus has also been studied[25]. Large packing coefficients tends to increase the moduli for the polyimides, but the rod-like polyimides with side groups, which have small packing coefficients, have high moduli. The X-ray scattering study suggests a high degree of liquid crystallinity or crystalline ordering results in high modulus[26, 27] .

Some efforts have been reported on incorporation of heterocyclic units into polyimides to increase the rigidity of the polyimide backbone or to provide strong intermolecular associations which generally result in increased glass transition temperatures. A recent major approach has been the introduction of amine functionality or dianhydrides into the heterocyclic ring by formation of ether linkages by a nucleophilic aromatic substitution reaction. Benzothiazole[28], quinoxaline[29-31], and benzimidazole[28], have been incorporated into polyimides in this manner and formed high modulus films (Figure 4-1).

Figure 4-1 Previous Heterocyclic Polyimides



P.M. Hergenrother, S.J.Havens
Macromolecules 1994, 27, 4659



J. L. Hedrick
Polymer, 33, 1399

4-2 Strategy and Goals

In the previous chapter, attempted synthesis of poly(arylene ether)s containing the quinazolinone moiety was described. Because of the instability of the monomers under the reaction conditions used, high molecular weight polymers could not be obtained. If reaction conditions are considered, polyimides or polyamides can be synthesized under milder conditions; the polymerization reaction can be carried out at room temperature and stoichiometric amounts of base are not necessary.

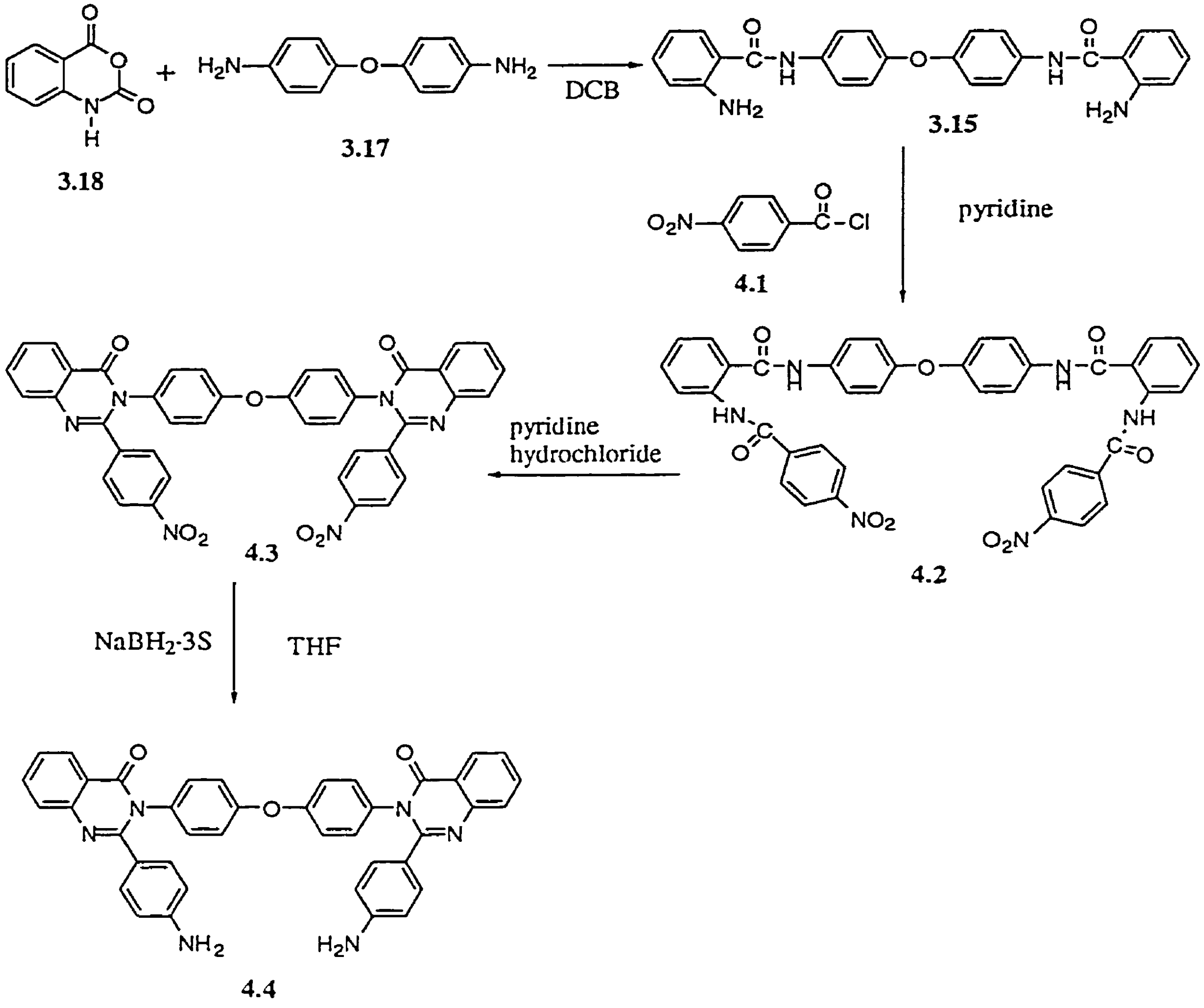
The goal of this chapter is to synthesize novel polyimides or polyamides containing the quinazolinone moiety. The polymers containing the quinazolinone moiety are expected to possess high themooxidative stabilities and high T_gs. In addition, more interesting properties are expected because of hydrogen bonding ability of the quinazolinone. Novel new quinazolinone diamines are designed, and synthesized from inexpensive starting materials. The polymerization conditions are optimized and finally, the polymers are characterized and the effect of the incorporation of the quinazolinone moiety on the properties is discussed.

4-3 Monomer Synthesis

4-3-1 Attempted Synthesis of Oxy-bis(1,4-phenylene)-bis[3-(4-aminophenyl)-1-oxo-quinazolin-2-yl]

As mentioned in Chapter 3, one of the motivations to make quinazolinone containing monomers is that they can be synthesized from isatoic anhydride, which is inexpensive. The first attempt at synthesis of a bisquinazolinone amine was by the synthetic scheme similar to Scheme 3-9 in Chapter 3 (Scheme 4-1). Isatoic anhydride **3.18** was reacted with 4,4'-oxydianiline **3.17** in o-dichlorobenzene at 130°C affording o-aminodiamide **3.15**, which was reacted with *p*-nitrobenzoyl chloride **4.1** in pyridine affording bis(4-nitrobenzamide)benzamide **4.2**.

Scheme 4-1

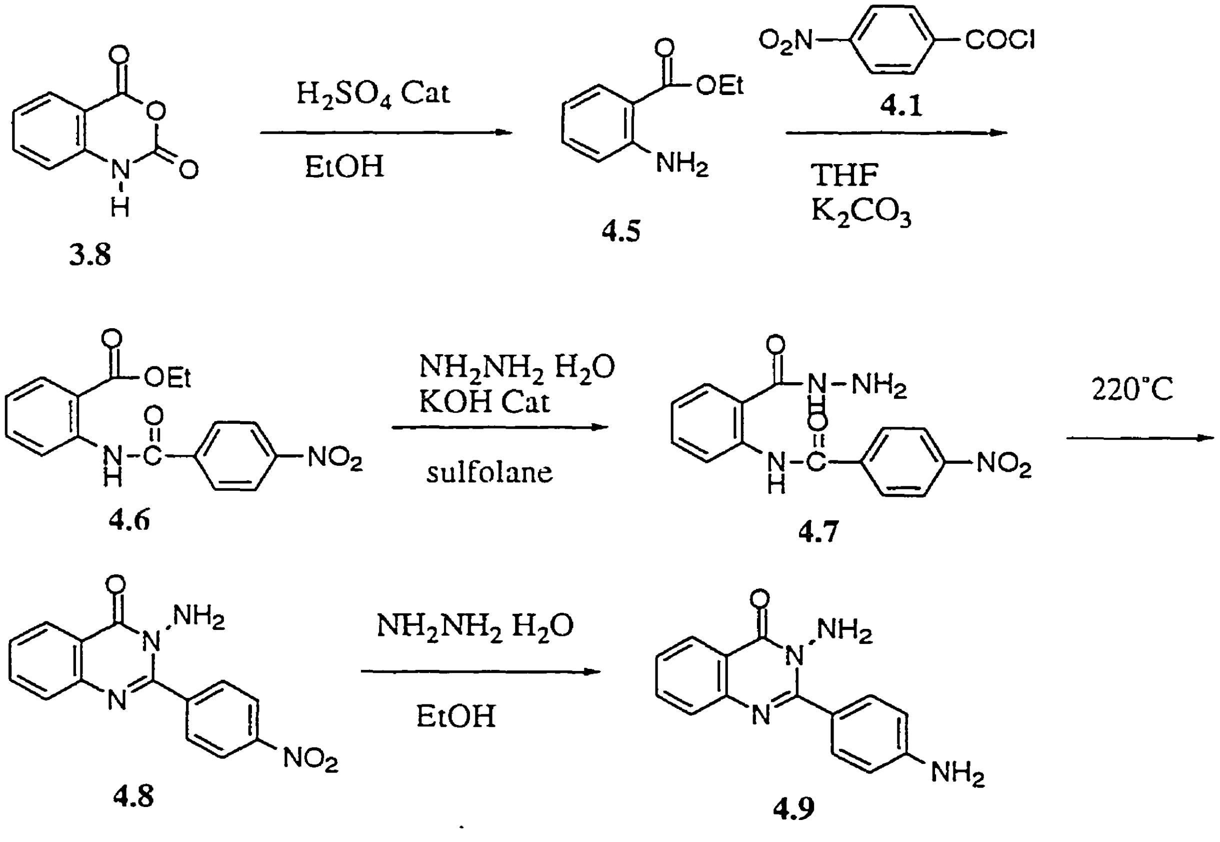


The benzamide **4.2** was cyclized to bisquinazolinone **4.3** in pyridine hydrochloride at 200°C. Reduction by $NaBH_2$•3S gave diamine **4.4**. Bisquinazolinone amine **4.4**, purity by HPLC was 95%, was obtained in 56% yield. However, it decomposed in solution and could not be purified to monomer grade material i.e. over 99%. Purification by column was tried but it reacted in the column. The steric interaction between 2,3-substituted phenyl rings makes the quinazolinone unstable and presumably decomposition starts with the attack of the amino group on the quinazolinone carbonyl group.

4-3-2 Synthesis of 2-(4-Aminophenyl)-3-amino-4(3H)-quinazolinone

The results in Chapter 3 and our first diamine synthesis suggest that quinazolinones containing 2,3-diphenyl rings are unstable and therefore not useful as monomers. Therefore, another diamine from isatoic anhydride **3.8** was designed (Scheme 4-2). **3.8** was reacted with ethanol in the presence of an acid catalyst affording anthranyl ethylate **4.5** in good yield. It was reacted with *p*-nitrobenzoyl chloride **4.1** in THF in the presence of anhydrous potassium carbonate as an acid acceptor. The amide ethylate **4.6** was reacted with hydrazine monohydrate in the presence of a catalytic amount of potassium hydroxide in sulfolane affording hydrazide **4.7**.

Scheme 4-2



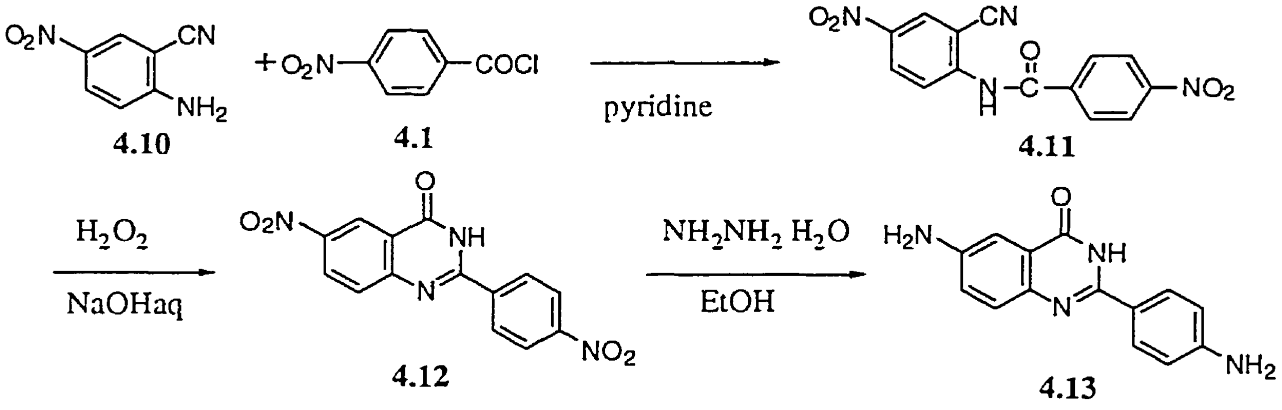
The hydrazide **4.7** was melted at 220°C to cyclize to 3-aminoquinazolinone **4.8**. The nitro group was then reduced by hydrazine monohydrate in ethanol affording 2-(4-aminophenyl)-3-

amino-4(3H)-quinazolinone **4.9**. The yields in each step were very high and the reactions were clean. Each intermediate was easily purified by recrystallization.

4-3-3 Synthesis of 2-(4-Aminophenyl)-6-amino-4(3H)-quinazolinone

The isomer of the diamine monomer **4.9**, 2-(4-aminophenyl)-6-amino-4(3H)-quinazolinone **4.13**, was prepared in three steps from readily available starting materials in high yield (Scheme 4-3). 2-Amino-5-nitrobenzonitrile **4.10** was reacted with 4-nitrobenzoyl chloride **4.1** in pyridine at reflux overnight. The formed N-(2-cyano-4-nitrophenyl)-4-nitrobenzamide **4.11** was cyclized to dinitro quinazolinone **4.12** in the presence of potassium hydroxide and hydrogen peroxide. The reduction with hydrazine monohydrate/Pd-C gave 2-(4-aminohenyl)-6-amino-4(3H)-quinazolinone **4.13**. The yields in each step were very high.

Scheme 4-3

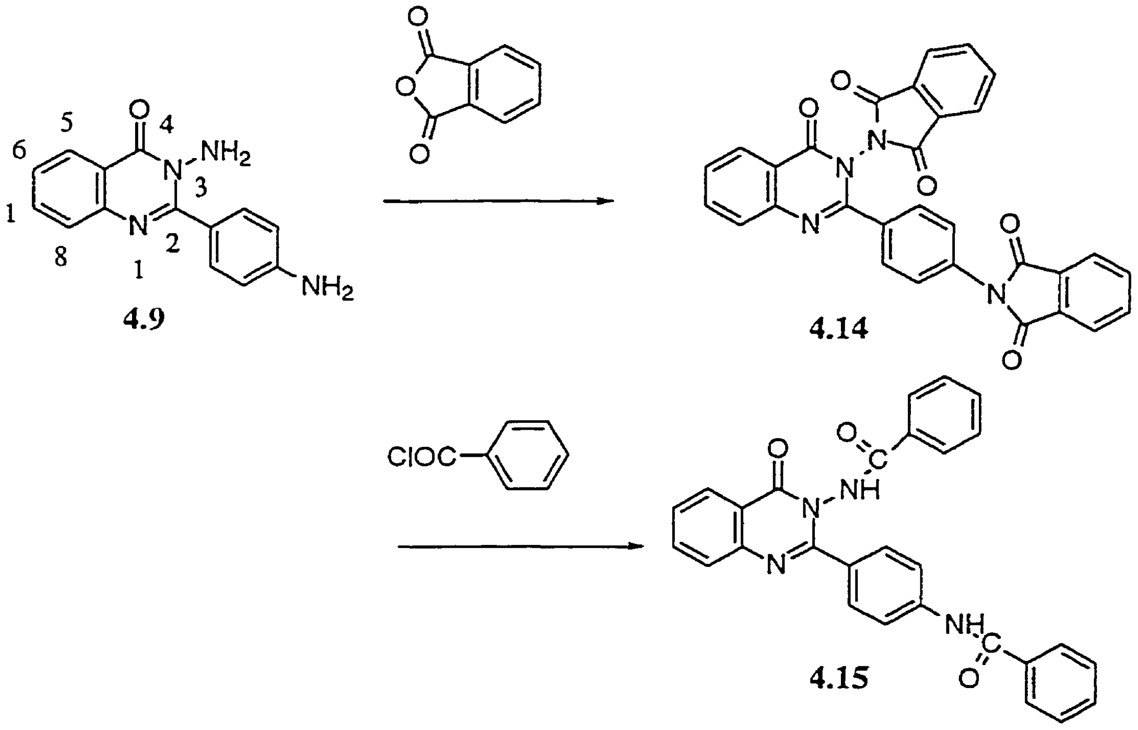


4-4 Polymer Synthesis

4-4-1 Attempted Polymerization of 2-(4-Aminophenyl)-3-amino-4(3H)-quinazolinone

The reactivity of the two amino groups of the diamine monomer **4.9** and the stability of the bisimide product under conditions similar to those used in the polyimide formation reaction were investigated in model reactions (Scheme 4-4). First, **4.9** was reacted with phthalic anhydride at 80°C in *m*-cresol for 24 hours. The solid yield of the diimide product was 60%. Secondly **4.9** was reacted with phthalic anhydride at room temperature in DMAc for 24 hours. The yield of the diamic acid was 80%. Since the yield of the second model reaction is high, polymerization with BPA dianhydride was performed in DMAc at room temperature for 24 hours. The inherent viscosity of the poly(amic acid) in DMAc was less than 0.1. Both of the amino groups are deactivated by the electron-withdrawing quinazolinone group. In addition, the amino group at the 3-position of the quinazolinone is sterically hindered because of the phenyl group in the 2-position.

Scheme 4-4



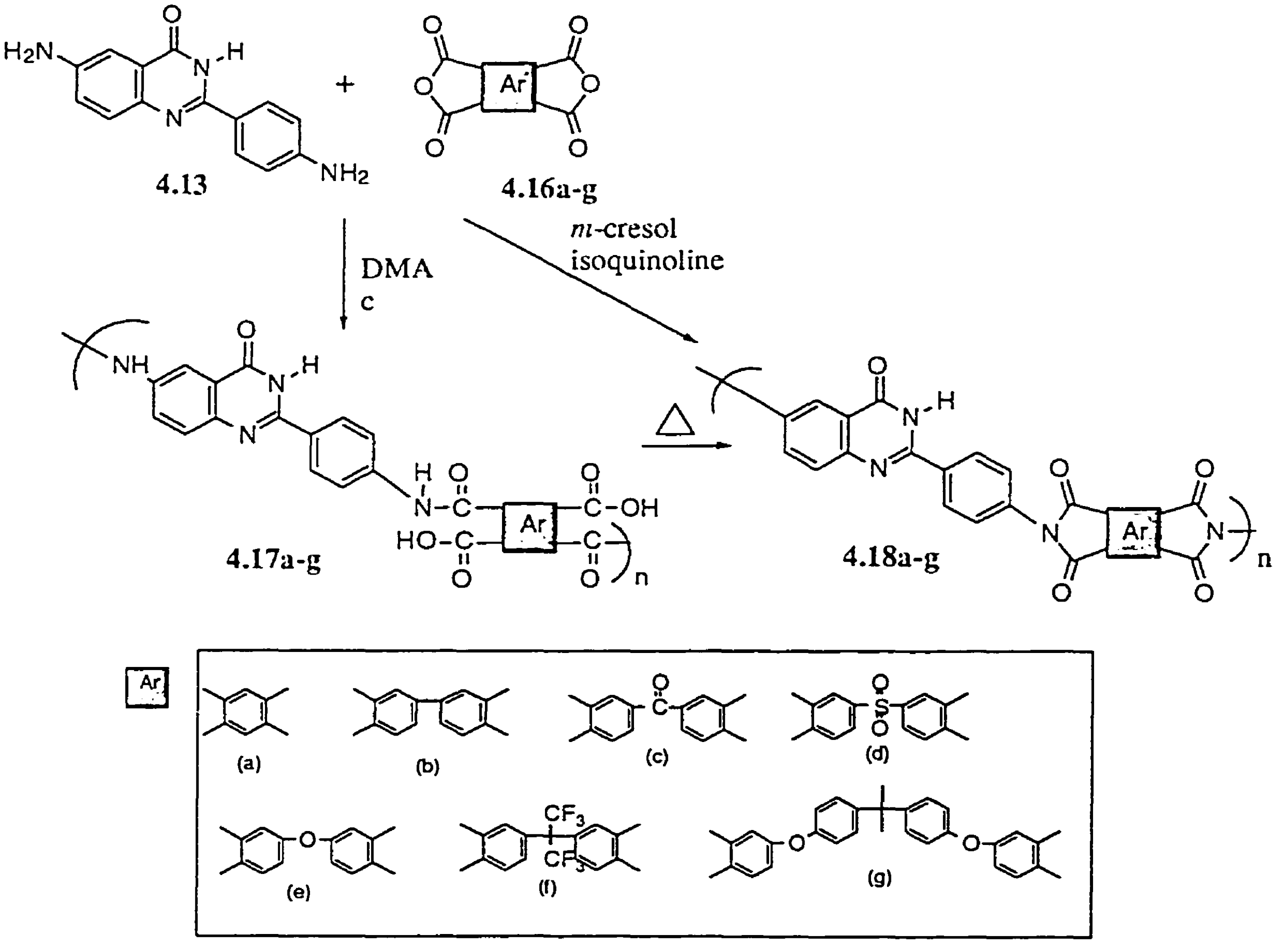
For these reasons, the reactivity of the amino groups in **4.9** is low and high molecular weight polymer could not be obtained. The low temperature reaction showed higher yield of the two model reactions. This suggested that the product was unstable and decomposed under the reaction conditions, presumably due to the steric hindrance of the bulky imide substituents on the 2- and 3- position

A model reaction for polyamide synthesis was also carried out. **4.9** was reacted with benzoyl chloride in pyridine at room temperature for 24 hours. The yield after work up was less than 30%. In NMP, the yield was less than 20%.

4-4-2 Polymerization of 2-(4-Aminophenyl)-6-amino-4(3H)-quinazolinone

There are two major methods used for the preparation of polyimides. One procedure involves a two-step process via poly(amic acid) intermediates, the other is a one-step solution polymerization.

Scheme 4-5



The one step method has some advantages over the two step method. Polyimides in bulk are more easily produced, and polyimides with higher crystallinity can be more readily obtained[32]. The one-step method is also useful for unreactive diamines and dianhydrides which cannot form high molecular weight poly(amic acid)s by the two step method[33]. Since the quinazolinone diamine should be deactivated by the electron-withdrawing heterocyclic, we first tried, the one-step solution method even though with some of the dianhydrides we would expect to form insoluble polyimides because of the rigid structure. The quinazolinone diamine **4.13** and a series of dianhydrides were then reacted in *m*-cresol or *p*-chlorophenol in the presence of a catalytic amount of isoquinoline (Scheme 4-5). A homogeneous, yellow to orange clear solution was formed after 8 hours at room temperature. The temperature was raised slowly to 220°C and maintained at that temperature for 24 hours. The water formed during imidization was removed continuously with a stream of nitrogen. Depending on the rigidity of the dianhydrides, the reaction mixture became either a homogeneous solution, a clear gel or a heterogeneous slurry due to the precipitation of the polymer in the later stages of the reaction.

Table 4-1 Synthesis of Polyimides from **4.13** (One-step Method)

Polymer	Solvent	Conc.(wt%)	Conditions[a)]	η_{inh}(dL/g)[b)]	film
4.18a	p-chlorophenol	5	ppt	0.63	-
4.18b	p-chlorophenol	5	gel	0.46	-
4.18c	p-chlorophenol	5	gel	0.64	-
4.18d	m-cresol	5	ppt	0.23	-
4.18d	p-chlorophenol	5	gel	0.49	-
4.18e	m-cresol	5	ppt	0.53	-
4.18f	m-cresol	8	sol	0.59	flexible
4.18g	m-cresol	8	sol	0.44[c)]	flexible

a) sol: clear, viscous solution. gel: no precipitation, but gelation occurred during polymerization. ppt: precipitaion of polymer occurred during polymerization
b) 0.5 g/dL in conc. H_2SO_4 at 25°C. c) 0.1g/dL in *m* -cresol at 50°C

With dianhydrides, **4.16a-d**, the polymer precipitated from *m*-cresol solution, so *p*-chlorophenol was used as a solvent. A clear gel formed and polyimides with higher viscosity were obtained for **4.18b-d**. With **4.16a**, even in *p*-chlorophenol, polymer came out from the solution as a powder. Using dianhydrides which have flexible linkages, **4.16f**, **4.16g**, the polymer stayed in *m*-cresol solution and high molecular weight polyimides were obtained even though precipitation or gelation took place in some cases. Moderately high molecular weight polyimides with inherent viscosities of 0.44-0.63, were obtained (Table 4-1). Presumably the molecular weight was built up in the early stage of the polymerization as a poly(amic acid) before imidization. Polymers **4.18f**, **4.18g** can be cast into free-standing transparent films, which indicates the formation of high molecular weight polymers. IR and TGA analysis indicated that complete imidization of the polymers was attained.

Polyimides were synthesized by the conventional two-step procedure, involving ring-opening polyaddition and subsequent thermal cyclodehydration.

Table 4-2 Synthesis of Polyimides from **4.13** (Two-step Method)

Ar	η_{inh}(dL/g)		film
	PAA[a)]	PI[b)]	
a	1.41	0.91	brittle
b	0.95	0.89	slightly flexible
c	0.81	0.72	slightly flexible
d	1.11	0.88	slightly flexible
e	0.84	0.83	slightly flexible
f	1.07	0.86	flexible
g	0.63	0.57[c)]	flexible

a)PAA; poly(amicacid), 0.5 g/dL in DMAc at 25°C.
b) PI; polyimide, 0.1 g/dL in conc. H_2SO_4 at 25°C
c) 0.1 g/dL in m-cresol at 50°C

Dianhydrides **4.16a-g** were added to a solution of the quinazolinone amine **4.13** in DMAc at room temperature (Scheme 4-5). The solids composition was maintained at 15 weight % except for **4.17a** (10 weight %). High molecular weight poly(amic acid) solutions with inherent viscosities of 0.63-1.40 were obtained in 24 hours (Table 4-2). Transparent yellow, flexible films of the poly(amic acid)s could be obtained by casting the resulting polymer solutions at 80°C for 24 hours. The thermal conversion to polyimides was carried out by heating the polyamic acid films at 100°C for 15 min, 140°C for 20 min, 200°C for 25 min, 250°C for 30 min, 280°C for 30 min, 300°C for 1 hour, and 320°C for 30 min. More rapid temperature elevation resulted in cracked or brittle films. The poly(amic acid)s, **4.17b-4.17g** formed free-standing films. However, poly(amic acid) from **4.16a** formed a brittle film. Crystallization of **4.18a** was very rapid so that a film could not be obtained. Poly(amic acid)s prepared in NMP solution were cast into films and heated up in the same manner, **4.17a-e** formed brittle or cracked films despite the high viscosity of the poly(amic acid) solutions. The polyimide films were transparent, and dark red brown in color. The films shrank to about 90% of their original dimension after thermal imidization. The inherent viscosities in concentrated sulfuric acid were somewhat lower than those of the poly(amic acid)s. Complete imidization was confirmed by FTIR and TGA.

4-5 Properties of the Quinazolinone Polyimides

Solubilities

The solubilities of the poly(quinazolinone imide)s are shown in Table 4-3. The polyimides prepared by the one-step method and those by the two-step method have the same solubilities. All of them are soluble in concentrated sulfuric acid at room temperature after 3 days. They are insoluble in common organic solvents except polyimides **4.18f** and **4.18g**, which dissolve in hot *m*-cresol. When the polyimide solutions in *m*-cresol were cooled to room temperature, they formed a clear gel even at 3 weight %. The solution behavior and solubility suggest strong interchain association presumably because of hydrogen bonding of the quinazolinone

Table 4-3 Solubilities of Polyimides **4.18a-g**[a)]

Polymer	Solvent					
	H_2SO_4	*m* -cresol	NMP	DMAc-LiCl	DMSO	pyridine
4.18a	+	-	-	-	-	-
4.18b	+	-	-	-	-	-
4.18c	+	-	-	-	-	-
4.18d	+	-	-	-	-	-
4.18e	+	-	-	-	-	-
4.18f	+	+-	-	-	-	-
4.18g	dec.	+-	-	-	-	-

a) +; soluble at room temperature; +-, soluble in hot solvent; -, insoluble

Thermal Properties

The thermal properties of the polyimides were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Table 4-4). The data shown are for the polyimide films prepared by the two-step method. The results of the TGA analyses showed the general excellent thermal stability of the polyimides (Figure 4-2). The 5% weight losses in nitrogen were 540-588 °C. In air these temperatures were in all cases similar, suggesting high thermooxidative stability. Generally, the thermal stability of a polymer backbone will be determined by the strength of its weakest bond. The order of thermal stability of polyimides from the different dianhydrides is **4.16a>4.16b>4.16e>4.16c>4.16d**[5]. The 5% weight losses of the polyimides **4.18a-g** followed this order and no weight losses were observed under 400°C. These results suggest a high thermal stability of the quinazolinone ring.

Table 4-4 Thermal Properties of Polyimides **4.18a-g**

Polymer[a)]	T_g(°C)	T_m(°C)	TGA(°C)[b)]	
			N_2	air
4.18a	-[c)]	-[c)]	583	581
4.18b	-[c)]	465	588	585
4.18c	339	-[c)]	568	571
4.18d	350	-[c)]	540	545
4.18e	338	-[c)]	588	589
4.18f	360	-[c)]	544	546
4.18g	298	356	540	537

a) Prepared by 2-step method. b) Reported for 5% weight loss. c) Not detectable

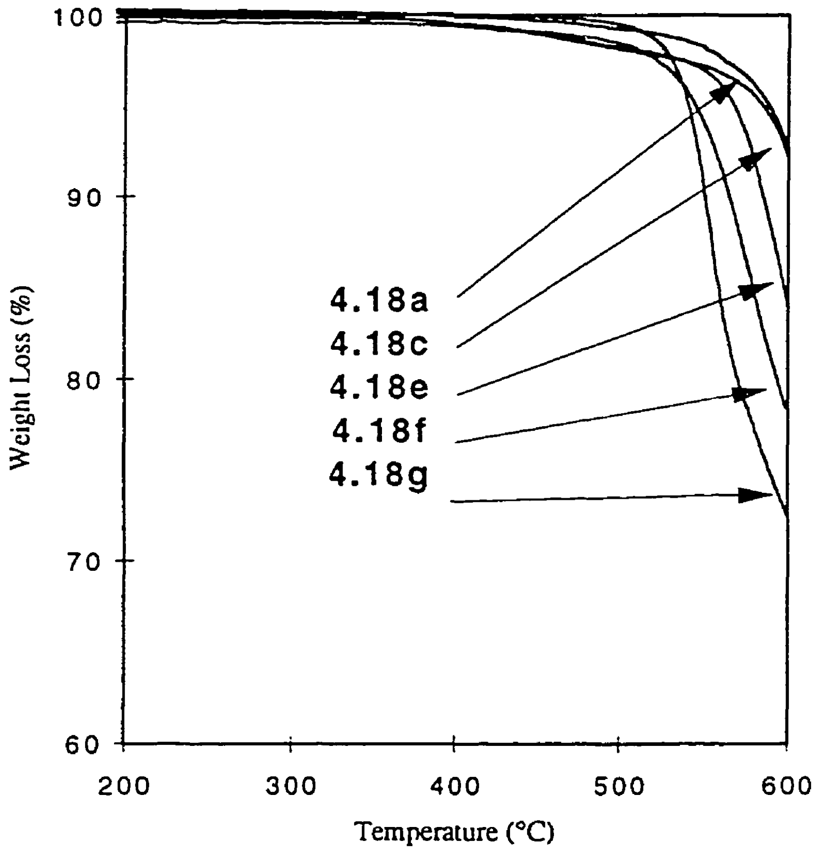


Figure 4-2 TGA Thermograms of Polyimides **4.18a, c, e, f, g**

Thermal transitions were investigated by DSC in the temperature range from 100 to 530 °C. Due to the chain stiffness, transitions were not observed for polymers **4.18a-d** at the rate of 20 °C/min. A distinct glass transition was observed for **4.18g** at 298°C (Figure 4-7). This polyimide was semicrystalline. The melting endothermic peak had its maximum at 356°C. At a rate of 30°C/min, thermal transitions of the polyimides **4.18b-f** were detected. No clear transition was observed for **4.18a**. Polyimide **4.18b** was semicrystalline and showed a melting endothermic peak at 465°C. T_gs of **4.18c-4.18f** ranged from 338°C to 342°C (Figure 4-3). Polymer **4.18a**, **4.18c**, **4.18d**, **4.18f** showed broad exothermic behavior above 400°C. This may be attributed to the crystallization that occurs in the semicrystalline polymers above their glass transition temperatures. The other possible explanation is a crosslinking reaction.

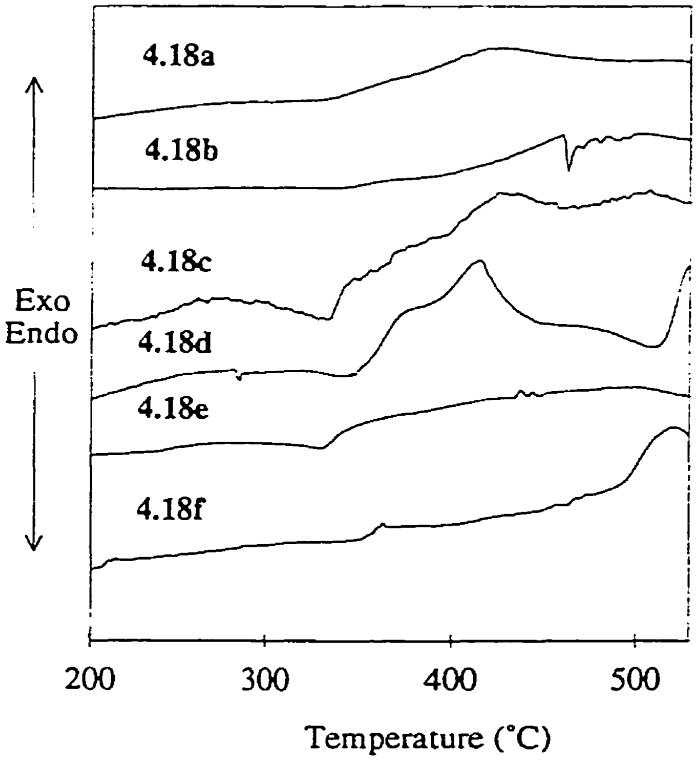


Figure 4-3 DSC Thermograms of Polyimides **4.18a-f**

Themomechanical Properties

Young's moduli (E'), maximum values of loss moduli (E"), and maximum values of tan δ of the polyimide films are tabulated in Table 4-5. They were measured by TMA in the tensile stress-strain mode. Loads were chosen such that a linear stress-strain relationship was obtained. These films had very high moduli 2.34-4.89 and maintained the high moduli at high temperatures. The flexible polyimides **4.18f**, **4.18g** showed lower moduli than the rigid polyimides. Typical TMA curves are shown in Figure 4-4,5,6. The rigid polyimide **4.18b** showed high a modulus and the E' values dropped gradually at high temperature and did not show clear maxima for tan δ and E" (Figure 4-4). Polyimide **4.18c**, which has the carbonyl linkage as a spacer, showed the highest modulus. In this case rapid decrease in the modulus took place and it exhibited a maximum of tan δ at 343°C, which corresponds to the T_g (Figure 4-5).

Table 4-5 Thermomechanical Properties of the Polyimides 4.18a-g

Polymer	Preparation	Modulus(GPa) at		tanδ(max)	E"(max)
		25°C	200°C	(°C)	(°C)
4.18b	2 step	3.19	2.26	388	353
4.18c	2 step	4.89	3.13	362	332
4.18d	2 step	3.99	2.44	355	334
4.18e	2 step	3.61	2.23	343	320
4.18f	1step	1.48	0.89	400	350
4.18f	2step	2.65	1.64	413	374
4.18g	1step	2.25	1.41	293	282
4.18g	2step	2.34	1.61	308	290

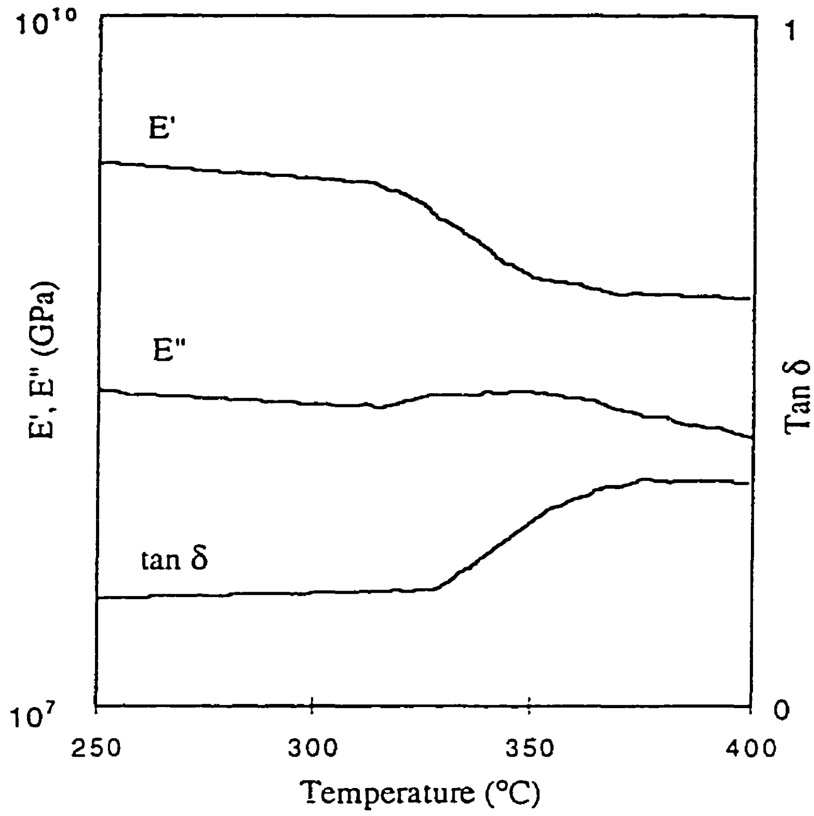


Figure 4-4 Thermomechanical Analysis of Polyimide **4.18b**

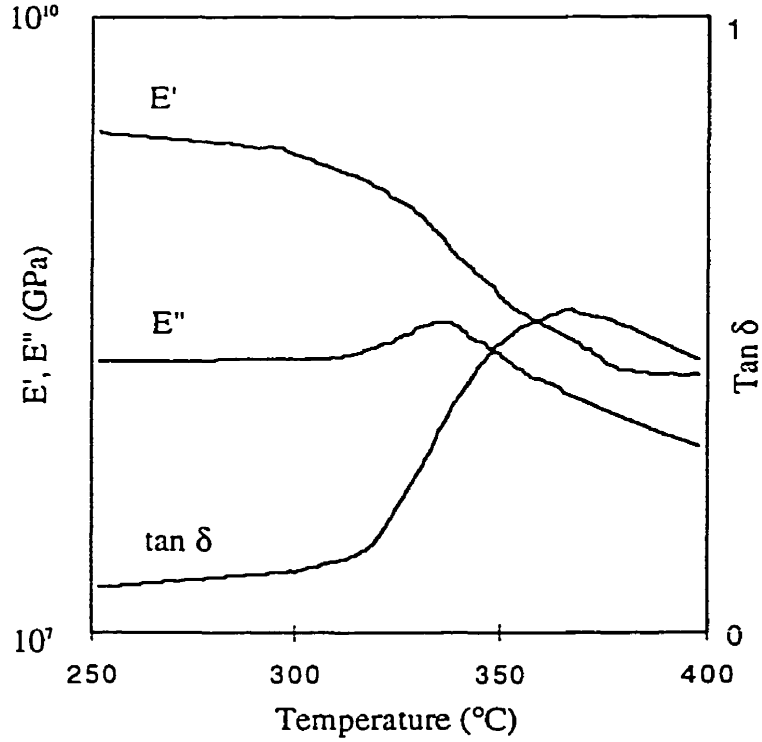


Figure 4-5 Thermomechanical Analysis of Polyimide **4.18c**

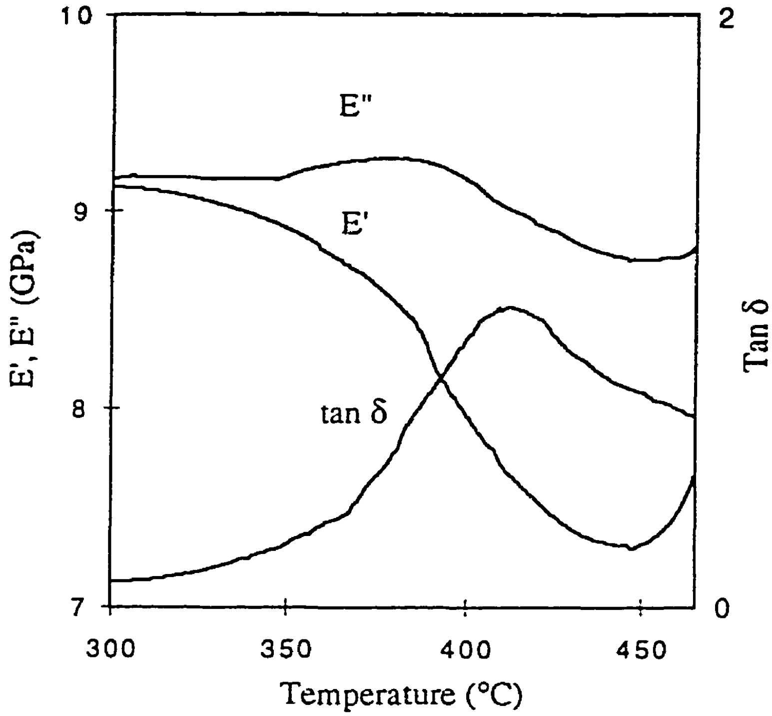


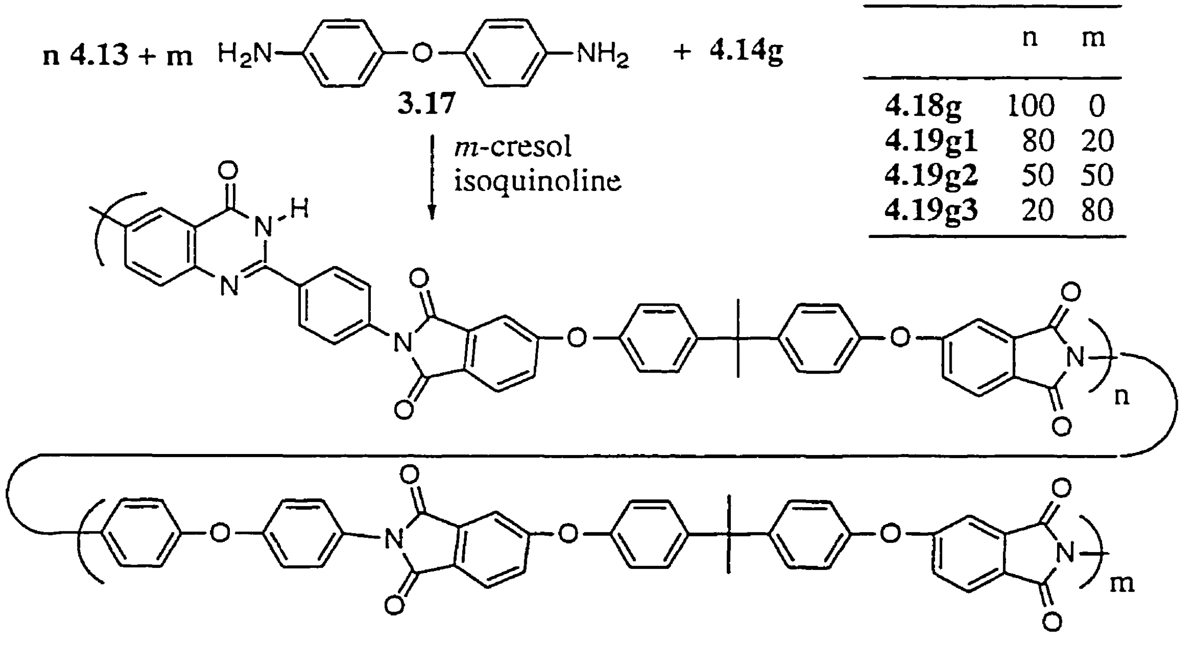
Figure 4-6 Thermomechanical Analysis of Polyimide **4.18f**

T_gs by TMA for **4.18d**, **4.18e**, **4.18g** agreed with the T_g s determined by DSC. However, T_gs by TMA for **4.18c** and **4.18f** were considerably higher than those determined by DSC. There might be a crosslinking reaction occurring even though no weight loss was observed below 400°C by TGA. Polyimides containing the benzimidazole group have been shown to crosslink on heating[27].A modulus increase over 350 °C was observed for **4.18f** (Figure 4-6). A modulus increase above T_g was also observed for the polyimde from PMDA and 4,4'-oxydianiline[33], which suggested side reactions in these polyimides resulting in crosslinking occurring at elevated temperature. The films of the polyimides prepared by the one-step method showed lower E' values for **4.18f** and **4.18g**. This can be explained by a difference in morphology of the films resulting from the thermal history or an effect due to a small amount of residual *m*-cresol.

Copolymerization

Copolymerization of **4.13** with 4,4'-oxydianiline (ODA) **3.17** and bisphenol A dianhydride **4.16g** was carried out (Scheme 4-6). High molecular weight polymers with inherent viscosities over 0.87 were obtained (Table 4-6). Transparent yellow flexible tough films could be obtained by casting from *m*-cresol. Polymers **4.19g1-3** were only soluble in *m*-cresol and the solutions behave similar to the homopolyimides. Even when 20% of quinazolinone was incorporated in BPA-dianhydride-ODA polyimide copolymers, they were insoluble in common organic solvents. This suggested a strong influence of hydrogen bonding of the quinazolinone structure. T_gs (Figure 4-7) and moduli increased as quinazolinone content increased. Thermooxidative stability also increased as quinazolinone content increased as indicated by the 5% weight losses in TGA.

Scheme 4-6



	n	m
4.18g	100	0
4.19g1	80	20
4.19g2	50	50
4.19g3	20	80

4.19g1-3

Table 4-6 Copolymerization of **4.13** with 4,4'-Oxydianiline

Polymer	n	η_{inh}^a)	T_g	T_m	TGA(°C)^b)		Modulus(GPa)		Tanδ(max)
	mol%	dL/g	°C	°C	N_2	Air	20°C	200°C	°C
4.18g	100	0.44	298	356	540	537	2.34	1.61	283
4.19g1	80	0.92	282	-	533	533	2.22	1.89	280
4.19g2	50	0.83	263	-	537	533	1.96	0.99	256
4.19g3	20	0.87	240	-	509	502	0.89	0.76	227

a) Intrinsic viscosity measured in m-cresol at 50°C at a concentration of 0.1 g/dL.
b) Reported for 5% weight loss

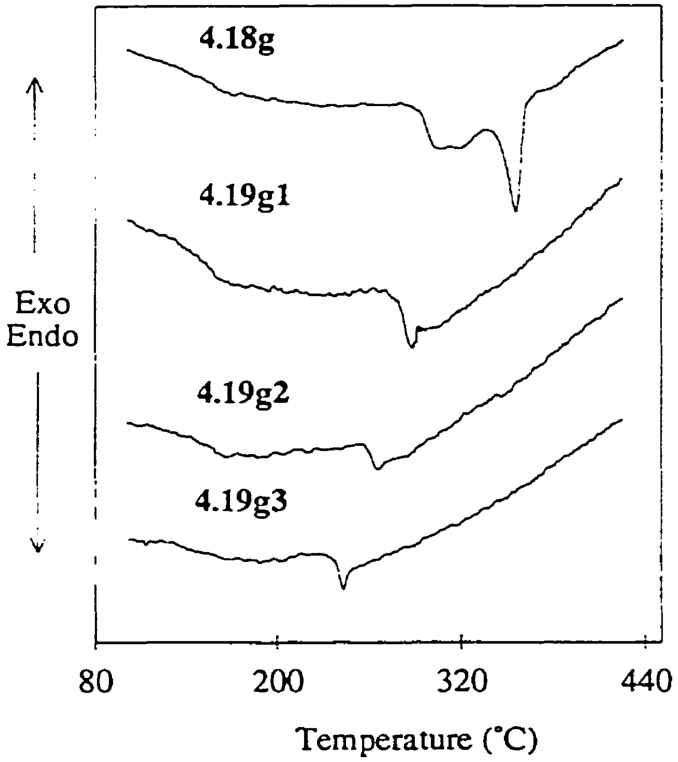


Figure 4-7 DSC Thermograms of the Polyimides **4.18g, 4.19g1-3**

4-6 Conclusions

Three new aromatic diamines, oxy-bis(1,4-phenylene)-bis-[3-(4-aminophenyl)-1-oxo-quinazolin-2-yl] **4.4**, 2-(4-aminophenyl)-3-amino-4-quinazolinone **4.9**, 2-(4-aminophenyl)-6-amino-4(3H)-quinazolinone **4.13** were synthesized from readily available compounds in high yield. Monomer **4.4** was unstable in solution and could not be purified to monomer grade. The reactivities of the two amino groups of **4.9** were too low to form high molecular weight polymer because they were deactivated by the electron-withdrawing quinazolinone moiety and because the amino group on the 3-position of the quinazolinone was sterically hindered by the phenyl group on the 2-position. In addition, the diimide product seemed to decompose because of steric hindrance of the bulky imide substituents on the 2,3- position of the quinazolinone.

A series of high molecular weight, polyimides containing the quinazolinone moiety were synthesized from **4.13**. All polyimides synthesized had very high glass transition temperatures, and excellent thermal stabilities. Films made from the polyimides had high moduli and maintained the high moduli to high temperatures.

4-7 Experimental

Materials.

2-Amino-5-nitrobenzonitrile, 4-nitrobenzoyl chloride, hydrazine monohydrate, *m*-cresol, and hydrogen peroxide were purchased from Aldrich Chemical Co. and used as received. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA, **4.16b**; from CHRISKEV), 4,4'-oxydiphthalic anhydride (ODPA, **4.16e**; from CHRISKEV), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, **4.16c**; from TCI), 4,4'-sulfonyl diphthalic anhydride (SDPA, **4.16d**; from CHRISKEV), 4,4'-hexafluoroisopropylidine diphthalic anhydride (CF_3DA, **4.16f**, Hoechst), were dried at 150 °C under reduced pressure before use. Bisphenol-A-dianhydride (BPADA, **4.16g**; from General Electric) was recrystallized from acetic anhydride. Pyromellitic dianhydride (PMDA, **4.16a**; from TCI) was sublimed before use. NMP (Lancaster), and DMAc (Aldrich) were vacuum distilled with P_2O_5 before use. Other common organic solvents were reagent grade unless otherwise stated.

Characterization.

The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL 270 spectrometer in DMSO-d_6 using tetramethylsilane as an internal reference. The chemical shift (δ) and coupling constant (J) data were quoted in ppm and Hertz, respectively. The following abbreviations were used to describe peak patterns where appropriate: s=singlet, d=doublet, m=multiplet, and br=broad. Melting points (m.p.) were measured on a Fisher-Johns melting point apparatus or a Mettler FP800 DSC (determined by taking peak of endothermic peak.) and were uncorrected. IR spectra were performed on a Analet AQS-60 FTIR spectrophotometer. Microanalyses were obtained from Galbraith Laboratories Inc., Knoxville, TN. Low-resolution mass spectroscopy data were recorded on a ZAB2FHS spectrometer, ion source 240°C and 70-eV electron impact, direct inlet: m/e (assignment).

The T_g's and T_m s of the polymers were obtained using a Seiko 220 DSC instrument at a heating rate of 20°C/min, or 30°C/min for rigid polyimides in N_2 (160 mL/min). The T_g was taken from the midpoint of the change in slope of the baseline. The T_m was taken from the onset of the change in slope to the minimum of the endothermic peak. The weight loss data were obtained from a Seiko TGA/DTA instrument at a heating rate of 20°C/min in N_2 and air (200 mL/min). For all DSC and TGA measurements, polymer pellets were pressed under 5 tons of pressure with a small-scale version of a KBr die. Inherent viscosity data were obtained with a calibrated Ubbelohde viscometer. The measurements were done in concentrated sulfuric acid at 25°C or in *m*-cresol at 50°C for the polyimides, DMAc or NMP at 25°C for the poly(amic acid)s with a 1B (205) viscometer.

Film casting.

Polymer films were cast from *m*-cresol solution. A typical procedure is as follows: 130 mg of polymer was dissolved in 2-5 mL of *m*-cresol on heating. This solution was transferred into a glass ring (diameter = 3.5 cm, height = 2 cm, thickness = 0.4 cm) located on a glass plate. The solvent was slowly evaporated in a forced-air oven at 130°C for 24 hours to yield tough and flexible films (thickness = 0.070-0.120 mm) which were fingernail creasable. If the films could not be removed from the glass plate, they were placed into a beaker of hot water for 1-10 h, followed by drying at 220°C in vacuo for 24 hours. Typical film thickness was in the range 0.080-0.120 mm.

Measurement of Mechanical Properties.

A typical procedure to obtain Young's modulus measurements was performed as follows: a stamp was used to cut out a film strip (length = 5 mm, width = 2 mm, thickness = 0.15-0.22 mm) which was mounted between two chucks in a Seiko TMA/SS 120 instrument. For Young's modulus at 25°C, the parameters were set as offset load = 10-20 g, load amplitude = 5-10 g, and cycling frequency = 0.05 Hz. After these data were collected for 30 min, the same film was used without changing the parameters to measure Young's modulus (E') variation with temperature by heatiing to 450°C at a ramp rate of 3°C/min in static air.

Synthesis of Diamine 4.4

N'-(Oxy-bis-1,4-phenylene)-bis-(2-amino-benzamide) (3.15)

In a 2000 mL three neck flask fitted with a mechanical stirrer and a thermometer were placed, 63.13 g (0.40 mole) of isatoic anhydride **3.1**, 40.04 g (0.20 mol) of 4,4'-oxydianiline **3.2** and 400 mL of o-dichlorobenzene. The mixture was heated up gradually on an oil bath. Bubbles of carbon dioxide evolved about 130°C and a white powder came out as the reaction proceeded. The reaction mixture was stirred at this temperature for 2 hours. The reaction mixture was cooled down to the room temperature. The white mass was filtered, washed with methanol, dried and recrystallized from DMF-water. White needles. Yield: 62.36 g (71.0 %), m.p. 263.1 °C (DSC); ^{1}H-NMR (270MHz, DMSO-d_6) δ 6.32 (s, 4H), 7.59 (t, J_2=8.91, 2H), 6.74 (d, J_2=8.91, 2H), 6.98 (d, J_2=8.91, 4H), 7.19 (t, J_2=8.15, 2H), 7.62 (d, J_2=7.91, 2H), 7.71 (d, J_2=8.67, 4H), 10.00 (s, 4H)

N-(4-Nitrophenyl)-N'-(oxy-bis-1,4-phenylene)-bis-(1,2-benzenediamide) (4.2)

To the mixture of 200 mL of pyridine and 31.18 g (0.071 mol) of **3.15**, which is a light purple slurry, was added 26.39 g (0.142 mol) of *p*-nitrobenzoyl chloride **4.1** in small portions at room temperature in a 4L beaker. An exothermic reaction took place and the reaction mixture became a dark purple solution. It was stirred for 30 minutes at room temperature, then a yellow powder came out of solution. 2L of water was added to it and then acidified by concentrated hydrochloric acid. The yellow chunks formed were filtered, dried, and recrystallized from DMF-water to give a yellow powder; yield 31.66 g (60.5 %), m.p. 290 °C (DSC) : ^{1}H-NMR (270MHz, DMSO-d_6) δ 6.99 (d, J_2=9.15, 4H), 7.34 (t, J_2=7.64, 2H), 7.62 (t, J_2=7.91, 2H), 7.69 (d, J_2=8.91, 4H), 7.93 (d, J_2=7.43, 2H), 8.14 (d, J_2=8.91, 4H), 8.34 (d, J_2=8.40, 2H), 8.40 (d, J_2=8.88, 4H), 10.57 (s, 2H), 11.78 (s, 2H)

Oxy-bis(1,4-phenylene)bis[3-(4-nitrophenyl)-1-oxo-quinazolin-2-yl] (4.3)

4.2 (31.66 g) was stirred at 200°C in 74.55 g (0.645 mol) of pyridine hydrochloride for one hour in 250 mL 3 neck-flask equipped with a thermometer and a nitrogen inlet. The purplish black viscous half solid was cooled down to room temperature, and then washed in excess of water to form a white powder. It was washed in water thoroughly until acid-free. The white powder was filtered, dried and recrystallized from DMF-water to give a white powder; yield 11.43 g (50.7 %), m.p. 338 °C; ^{1}H-NMR (270MHz, DMSO-d_6) δ 6.87 (d, J_2=8.67, 4H), 7.39 (d, J_2=8.64, 4H),7.62-7.73 (m, 6H), 7.80 (d, J_2=7.67, 2H), 7.93 (t, J_2=7.67, 2H), 8.14 (d, J_2=8.40, 4H), 8.23 (d, J_2=7.40, 2H),

Oxy-bis(1,4-phenylene)bis[3-(4-aminophenyl)-1-oxo-quinazolin-2-yl] (4.4)

To a 500 mL flask, were added 1.44 g (4.5 mmol) of elemental sulfur and 0.568 g (1.5 mmol) of sodium borohydride. The mixture was stirred in 40 mL of dried dioxane for 15 minutes. To the yellow suspension, was added 10.50 g (1.5 mmol) of **4.3** with 40 mL of dried THF. The reaction mixture, a yellow suspension, was heated up to boiling and stirred for 24 hours. The reaction mixture was cooled down to room temperature and dioxane was removed under reduced pressure at room temperature. 20 mL of concentrated hydrochloric acid was added to the yellow chunks and the mixture stirred for 30 minutes. 20 mL of water was added and a gray powder was filtered off. The yellow solution was brought to pH11 by adding 30% sodium carbonate solution to precipitate light yellow powder. It was filtered, dried and recrystallized from acetone-hexane. Yield 6.92 g (72 %; purity by HPLC 97%) m.p. 325°C (DSC), ^{1}H-NMR(270MHz, DMSO-d_6) δ 5.46 (s, 4H), 6.35 (d, J_2=8.21, 4H), 6.92 (d, J_2=8.91, 4H), 7.03 (d, J_2=8.15, 4H), 7.30 (d, J_2=8.91, 4H), 7.53 (d, J_2=7.91, 2H), 7.72 (t, J_2=7.43, 2H), 7.85 (t, J_2=7.91, 2H), 8.14 (d, J_2=7.43, 2H)

Synthesis of Diamine 4.9

2-Aminoethylbenzoate (4.5)

Isatoic anhydride (32.92 g; 0.20 mol) was suspended in 500 mL of absolute ethanol in a 1L three-necked flask fitted with a magnetic stirbar and nitrogen inlet. 10 mL of concentrated sulfuric acid was added to the mixture. The reaction mixture was stirred at reflux for 2 hours. It became a dark brown homogeneous solution. Ethanol was removed under reduced pressure. Brown powder was recrystallized from ethyl acetate to give white needles; yield 85 % (53.43 g), m.p. 109-114°C. ^{1}H-NMR (270MHz, DMSO-d_6) δ 1.27 (t, d_2=7.16, 3H), 4.25 (t, d_2=6.91, 2H), 6.83 (t-d, d_2=7.53, d_3=1.24, 1H), 7.00 (d, d_2=7.64, 1H), 7.38 (t-d, d_2=7.90, d_3=1.49, 1H), 7.79 (d, d_2=6.67, 1H), 8.57 (s, 2H)

2-[(4-Nitrophenyl)oxomethylamino]benzethylate (4.6)

The reaction was conducted in a 1L three-neck round-bottom flask equipped with a nitrogen inlet, a condenser, and a thermometer and a magnetic stirring bar. The reaction vessel was charged with 18.56 g (0.01 mol) of **4.5**, 16.50 g (0.01 mol) of 4-nitrobenzoyl chloride, **4.1**, 41.46 g (0.03 mol) of anhydrous potassium carbonate and 300 mL of THF. The resulting mixture was stirred under reflux for 2 hours. A white powder was filtered off from the hot reaction mixture. THF was removed from the filtrate to form a white powder. It was recrystallized from 95% ethanol to form light yellow needles. Yield 94% (29.55 g), m.p. 143-146°C . ^{1}H-NMR (270MHz, DMSO-d_6) δ 1.29 (t, J_2=7.16, 3H), 4.32 (q, J_2=7.07, 2H), 7.31 (t, J_2=7.49, 1H), 7.79 (t, J_2=8.88, 1H), 7.99 (d, J_2=8.88, 1H), 8.39-8.45 (m, 3H), 11.58 (s, 1H)

2-[(4-Nitrophenyl)oxomethylamino]benzohydrazide (4.7)

To a 250 mL three neck flask equipped with a water cooled condenser, a magnetic stir bar, and a thermometer, were added 6.50 g (0.0207 mol) of **4.6**, 2 drops of 10 % NaOH aq in 50 mL of sulfolane. To the yellow slurry, 15 mL of hydrazine monohydrate was added dropwise. The orange slurry was heated to 80°C. In five minutes the reaction mixture turned into a homogeneous dark red solution. The reaction mixture was then cooled down to room temperature. A yellow powder precipitated. The yellow powder was filtered and washed with dilute formic acid. Recrystallization from ethanol gave 5.92 g (95.3%) of **4.7**. m.p. 220°C (DSC, cyclized to **4.8**). ^{1}H-NMR (270MHz, DMSO-d_6) 5.67 (s, 2H), 7.18 (t, J_2=7.67, 1H), 7.61 (d, J_2=7.67, 1H), 7.79 (d, J_2=7.67, 1H), 8.15 (d, J_2=8.88, 2H), 8.49 (d, J_2=8.89, 2H), 8.61 (d, J_2=6.99, 1H), 11.58 (s, 1H),

2-(4-Nitrophenyl)-3-amino-4-quinazolinone (4.8)

To a 250 mL round bottom flask, was added **4.7** (5.92 g; 0.021 mol). The yellow powder was heated up to 250°C in a salt bath. As soon as the yellow powder melted, it turned into yellow prisms. Temperature was raised to 270°C and the prisms melted. After all the prisms melted completely, it was cooled down to room temperature. Recrystallization from DMF-water gave 5.11 g (92.0%) of yellow needles, m.p. 255-257°C. ^{1}H-NMR (270MHz, DMSO-d_6) 5.64 (s, 2H), 7.60 (t, J_2=7.16, 1H), 7.75 (d, J_2=5.45, 1H), 7.87 (t, J_2=7.16, 1H), 8.04 (d, J_2=9.12, 2H), 8.19 (d, J_2=5.45, 1H), 8.32 (d, J_2=9.12, 2H)

2-(4-Aminophenyl)-3-amino-4-quinazolinone (4.9)

To a 250 mL three-neck round bottom flask equipped with a water cooled condenser, a dropping funnel, a stir bar and a thermometer, were added 5.11 g (0.018 mol) of **4.8** and 0.02 g of 5% palladium on activated carbon in 150 mL of 95% ethanol. Hydrazine monohydrate (9.07 g; 0.18 mol) was added dropwise to the mixture at reflux from a dropping funnel over 15 minutes. The mixture was stirred at reflux for 18 hours. It was then filtered through celite. Ethanol was removed from the filtrate under reduced pressure. Recrystallization from ethanol gave pale yellow needles; yield 3.89 g (85%) m.p 227-229°C . ^{1}H-NMR (DMSO-d_6) δ 5.62 (s, 2H, NH_2), 5.72 (s, 2H, NH_2), 6.60 (d, J_2=8.67, 2H), 7.47 (t, J_2=5.43, 1H), 7.63-7.70 (m, 3H), 7.78 (t, J_2=5.43, 1H), 8.11 (d-d, J_2=6.43, J_3=1.49, 1H), C^{13}-NMR (270MHz, DMSO-d_6) 112.76, 119.86, 121.85, 126.28, 126.48, 127.64, 132.09, 134.50, 147.60, 151.11, 155.80, 161.75, MS (m/e, relative intensity %): 251.99 (M^+, 100), 250.99 (69.8), 222.99 (34.7)

Synthesis of Diamine 4.14$^{32)}$

N-(2-Cyano-4-nitrophenyl)-4-nitrobenzamide (4.11)

A mixture of 24.47 g (0.15 mol) of 2-amino-5-nitrobenzonitrile **4.10**, 27.83 g (0.15 mol) of 4-nitrobenzoyl chloride **4.1** and 200 mL of pyridine was heated under reflux for 6 hours, cooled and poured into 1.5 L of 2% HCl. The separated orange solid was collected by filtration, washed well with water and dried. Recrystallization from aqueous DMF yielded a yellow powder; yield 40.15 g (86.5 %), m.p. 200-203 °C, ^{1}H-NMR (270MHz, DMSO-d_6) δ 7.90 (d, J_2=9.15, 1H), 8.25 (d, J_2=8.91, 2H), 8.45 (d, J_2=8.91, 2H), 8.59 (d-d, J_2=9.43, J_3=2.73, 1H), 8.82 (d, J_3=2.73, 1H), 11.38 (s, 1H). MS (m/e, relative intensity %): 312 (M, 49.4), 150 (100). 104 (56.3) Analysis calc'd for $C_{13}H_8N_4O5$: C, 53.85; H, 2.58; N, 17.94; O, 26.62; found: C, 53.95 H, 2.54 ;N, 17.99

2-(4-Nitrophenyl)-6-nitro-4(3H)-quinazolinone (4.12)

To a three-neck round bottom flask equipped with a mechanical stirrer and a water cooled condenser, were added 31.22 g (0.10 mol) of N-(2-cyano-4-nitro-phenyl)-3-nitrobenzamide, **4.11**, 500 mL of 16% sodium hydroxide and 1 L of 3% hydrogen peroxide. The orange suspension was heated cautiously until the initial vigorous reaction subsided and then refluxed gently for 1 hour. The mixture turned to a dark orange solution and then to an orange slurry. It was cooled to room temperature, an additional 600 mL of 3% hydrogen peroxide added and the reaction mixture was refluxed and stirred for 30 minutes. The cooled mixture was then filtered and the collected yellow solid was suspended in 5% sulfuric acid and stirred for several minutes. Filtration, drying, and recrystallization from aqueous DMF gave a yellow powder; yield 27.79 g (89 %), m.p. 319.8 °C (DSC). ^{1}H-NMR (270MHz, DMSO-d_6) δ 7.96 (d, J_2=8.96, 1H), 8.37-8.45 (m, 4H), 8.58 (d-d, J_2=8.98, J_3=2.81, 1H), 8.83 (d, J_3=2.81, 1H),13.1-13.3 (br). MS (m/e, relative intensity %): 312 (M, 100), 282 (39.2). Analysis calc'd for $C_{14}H_8N_4O_5$: C, 53.85; H, 2.58; N, 17.94; O, 25.62; found: C, 53.99 H, 2.54 ;N, 17.93

2-(4-Aminophenyl)-6-amino-4(3H)-quinazolinone (4.13)

To a dispersion of **4.12** (24.72 g, 0.079 mol) in ethanol (600 mL) was added 5% palladium on charcoal (1.0 g). Hydrazine monohydrate (15.84 g) was added to the stirred mixture dropwise at 85°C over 15 minutes. After addition was completed, the mixture was stirred at 85°C for another 8 hours. The solution was then filtered to remove Pd-C. The crude product was recrystallized from 95% ethanol to give pale yellow needles; yield 18.16 g (91 %), m.p. 303.5 °C (DSC). ^{1}H-NMR (270MHz, DMSO-d_6) δ 5.51 (s, 2H), 5.66 (s, 2H), 6.60 (d, J_2= 8.67, 2H), 7.05 (d-d, J_2= 8.67, J_3=2.73, 1H), 7.17 (d, J_3=2,73, 1H), 7.36 (d, J_2=8.64, 1H), 7.85 (d, J_2=8.67, 2H), 11.71(s, 1H). ^{13}C-NMR (270MHz, DMSO-d_6) δ 106.93, 113.66, 120.33, 121.88, 123.12, 128.40, 128.83, 140.93, 147.42, 148.41, 151.71, 162.80.

MS (m/e, relative intensity %): 252 (M, 100), Analysis calc'd for $C_{14}H_{12}N_4O$: C, 66.66; H, 4.79; N, 22.21; O, 6.34; found: C, 66.37 ;H, 4.67 ;N, 22.07

Polymerization:1-step solution method

Polyimides were prepared following a general procedure from the dianhydrides and free diamines in either *m*-cresol or *p*-chlorophenol with isoquinoline as a catalyst. The polymer concentration was 5 or 8 weight %. To a 50-mL three-neck round bottom flask equipped with a nitrogen inlet and a water-cooled condenser was added 2-(4-aminophenyl)-6-amino-4-quinazolinone **4.13** (0.3784 g; 1.50 mmol), 2 drops of isoquinoline and 23.18 g of *m*-cresol. Bisphenol A dianhydride (0.7806 g; 1.50 mmol) was added to the reaction mixture in small portions with vigorous stirring at room temperature. The flask was purged with nitrogen and the solution was stirred for 8 hours under a N_2 atmosphere at room temperature. During this period in all cases a clear yellow homogeneous solution was formed. The solution became viscous as the poly(amic acid) formed, The reaction system was slowly heated to reflux at 220°C (salt bath temperature) with stirring for 24 hours. The water formed in imidization was removed by slow stream of nitrogen with the solvent. In some cases, depending on the polyimide and solvent, the polymer precipitated as powder or formed clear gel. The reaction mixture was cooled and precipitated into 400 mL of methanol and collected by filtration. **4.2f** and **4.2g** were isolated as fibrous polymer, the others were yellow powders. The polymers were extracted with acetone for 24 hours and dried under high vacuum at 200°C for 24 hours. The yield was about 90%. The polyimide structure and complete imidization was confirmed by FTIR spectroscopy.

Polymerization:2-step method

Poly(amic acid) synthesis

A typical example of polymerization is as follows. The solids composition was maintained at 15 weight % except for PMDA (10 weight %). Into a 50 mL round bottom three-neck flask equipped with a nitrogen inlet and a stir bar, 0.3784 g (1.50 mmol) of 2-(4-aminophenyl)-6-amino-4(3H)-quinazolinone **4.13** was charged by washing in with 8.62 g of

DMAc under a strong nitrogen flow. To this solution, 0.4833 g (1.50 mmol) of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, **4.2b**) was added with slow stirring, and the reaction mixture was stirred at room temperature in nitrogen atmosphere affording a viscous polymer solution after 24 hours. The inherent viscosities of the poly(amic acid)s were subsequently determined at a concentration of 0.5 g/dL in DMAc at 25°C.

Thermal conversion of poly(amic acid)s to polyimides

About 1.5 g of the poly(amic acid) solution was spread on a glass plate and dried at 80 °C for 24 hours in a forced air oven. The films on glass were then converted to the polyimide by heating in air at 100 °C for 15 min, 140 °C for 20 min, 200 °C for 25 min, 250 °C for 30 min, 280 °C for 30 min 300 °C for 1 hour, and 320 °C for 30 min. The film was stripped from the plate by soaking in hot water. The films were dried at 120 °C in vacuo before mechanical testing. The average film thickness was 0.20 mm.

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Chapter 5

Poly(arylene ether)s Containing 1,5-Dibenzoylnaphthalene Units

5-1 Introduction

Aromatic poly(arylene ether ketone)s (PAKs) are an important class of high performance polymers displaying excellent thermal and chemical stabilities and excellent mechanical properties. Since the commercialization of poly(ether ether ketone) (PEEK) by ICI a number of new PAKs have been synthesized in an effort to improve overall properties[1,2]. Much effort has been expanded in the development of new PAKs with high glass transition temperatures (T_g) because PEEK has a relatively low T_g of 145°C.

Many new PAKs have been synthesized to study the influence of the substitution pattern of the aromatic cyclic units on bulk properties of PAKs. Para-substituted cyclic units have received most of the attention[3,4]. Deviations in chain linearity such as crankshaft aromatic units, or kinks or bends in the polymer main chain, disorder the linear configuration and reduce polymer crystallinity. Introduction of meta-directed bonding in phenylene units into PAKs lowers the T_gs of the polymers[5,6]. Effects of biphenyl substitution patterns on PAK's properties have also been studied[7-9].

Synthesis of high performance polymers containing naphthalene units is of recent interest because of its availability and its rigid symmetrical structure which gives enhanced thermal stability to the polymers. In the PAK synthesis area, some new PAKs with naphthalene units have been synthesized and structure-property relationship has been studied (Figure 5-1). Hergenrother synthesized PAKs containing the 2,6-naphthalene unit. These PAKs possess higher T_gs but lower solubilities in common organic solvents[10]. Wang has synthesized PAKs containing unsymmetrical benzoylnaphthalene units [11,12] and 1,8-dibenzoyl naphthalene units[13], which have high T_gs and improved solubilities. Endo reported PEKs containing the 2,6-dimethyl-1,5-naphthalene unit, which have higher T_gs but decreased thermooxidative stabilities[14,15]. In this work methyl substituents play an important role both in enhancing the T_g and in decreasing the thermal stability. Bottino has synthesized PAKs and poly(ether sulfone)s containing 2,6- or 1,5-naphthalaene units with methyl substituted biphenyl-4,4'-diols[16]. The polymers show high T_gs but decreased thermooxidative stabilities.

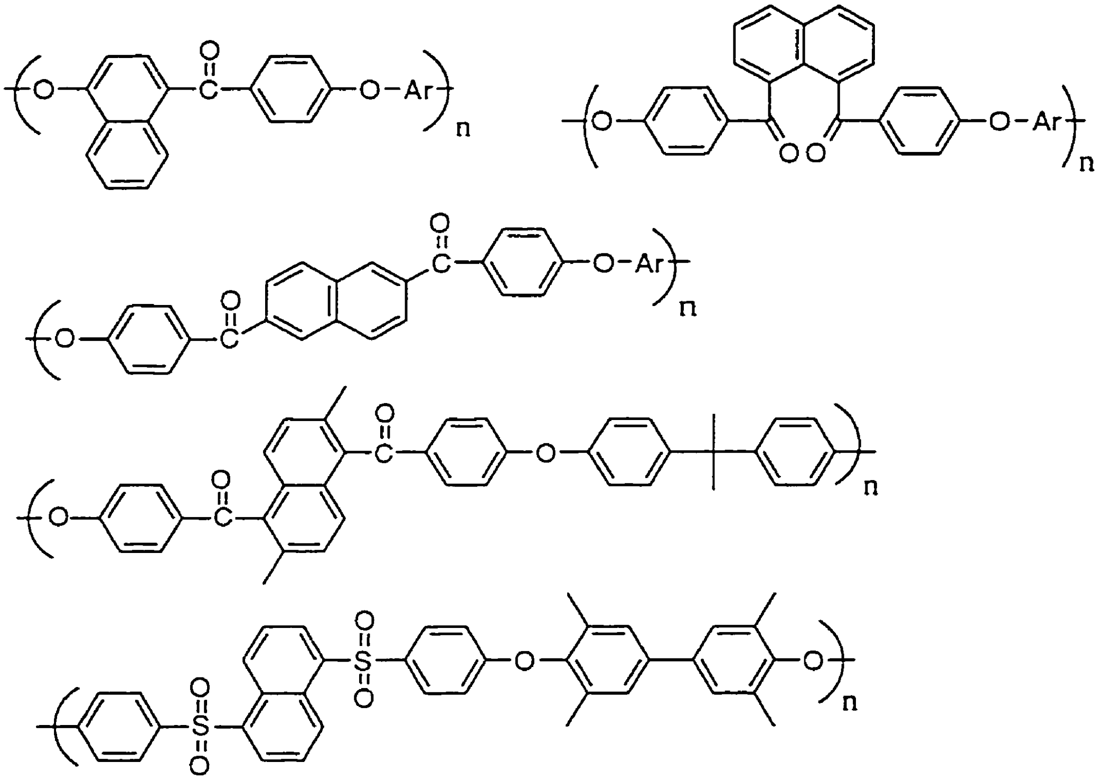


Figure 5-1 Previous PAKs Containing Naphthalene Units

5-2 Strategy and Goals

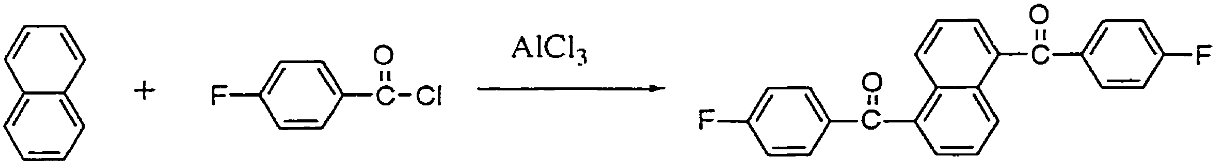
Some PAKs with a naphthalene moiety have been synthesized. The rigid naphthalene structure improved both physical and chemical thermostability[10]. However, the polymers were so insoluble that processing became difficult. Kinked structures, such as the 2,3-naphthalene unit, raised T_gs of the PAKs and enhanced solubility[13]. Some PAKs with 1,5-dibenzoyl units with methyl substituents have been synthesized[15]. They exhibited high T_gs but thermooxidative stability decreased greatly. Since methyl substitution raises the T_gs of polymers, the effect of the 1,5-naphthalene linkage on T_g is not clear. In addition, methyl substitution reduces thermooxidative stability.

In order to expand the study of the effects of structural symmetry and the substitution pattern in naphthalene containing PAKs, we have synthesized PAKs containing 1,5-dibenzoyl naphthalene units without any aliphatic substituents. The absence of aliphtic substituents should improve the thermooxidative stability of the polymer. 1,5-dibenzoyl naphthalene units, which disorder linearity, should reduce the crystallinity so that the polymers are more soluble.

5-3 Synthesis of the Monomer

Friedel-Crafts reactions of naphthalene with 4-fluorobenzoyl chloride in the presence of a Lewis acid such as aluminum trichloride in solvents such as nitrobenzene gave only the monoacylated product under all conditions used. We synthesized 1,5-bis(4-fluorobenzoyl)naphthalene, **5.1**, by Friedel-Crafts acylation of naphthalene with a slight excess of 4-fluorobenzoyl chloride in the absence of solvent at 80°C in 68% yield (Scheme 5-1).

Scheme 5-1



5.1

5-4 Polymer Synthesis

Polymerizations were carried out in a dipolar aprotic solvent using a stoichiometric ratio of monomers in the presence of excess potassium carbonate at a concentration of 25 weight% (Scheme 5-2). The water, formed by deprotonation of the bisphenols **5.2a-e**, was removed by azeotropic distillation with toluene at 130°C during the early stages of the reaction. High molecular weight polymers with inherent viscosities of 0.69-0.88, were obtained from bisphenols **5.2b**, **5.2c**, **5.2d** in NMP at 190°C for 18 hours (Table 5-1). In the case of **5.2a** and **5.2e**, somewhat lower molecular weight polymers formed in NMP. It has been known that fluoride anion cleaves the ether linkages in the synthesis of amorphous poly(ether ketone)s over prolonged reaction times[17]. To avoid this, polymerization reactions were run in DMAc at 160°C and high molecular weight polymers were obtained.

Scheme 5-2

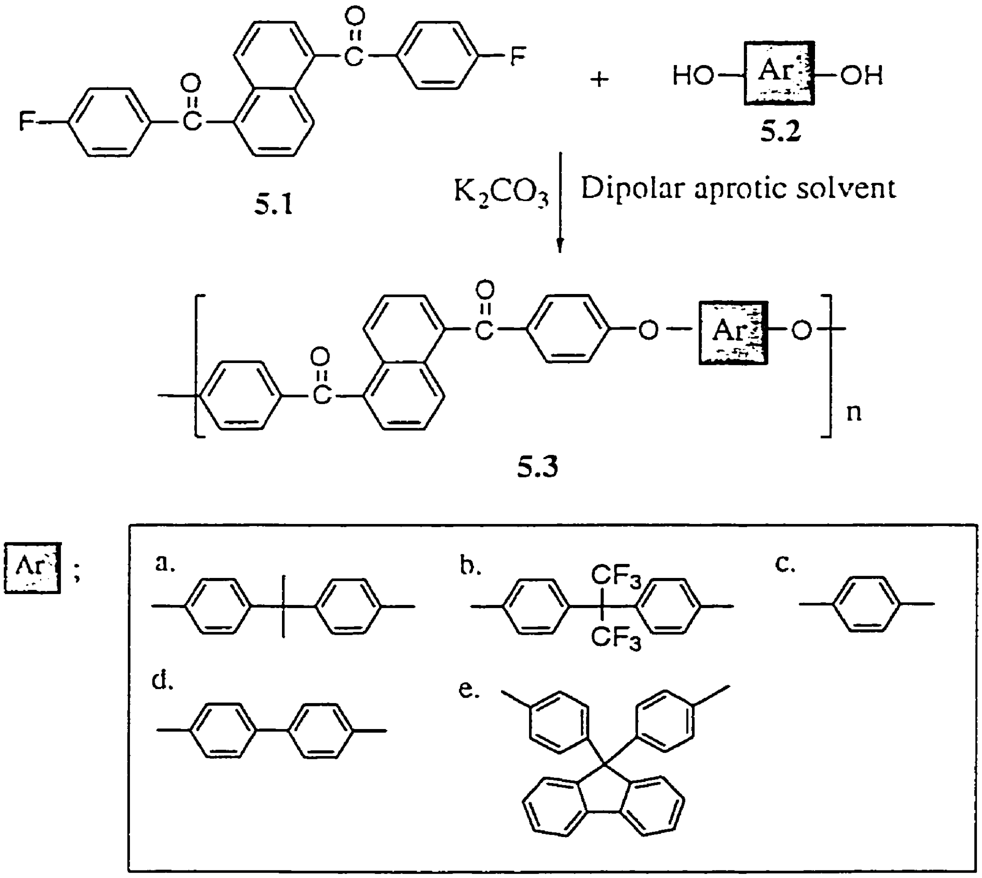


Table 5-1 Polymerization of **5.1** with Bisphenols **5.2a-e**

Polymer	Solvent	Yield (%)	η_{inh} a)	M_n b)	M_w	M_w/M_n
5.3a	NMP	89	0.27	29300	92300	3.2
5.3a	DMAc	92	0.45	55500	121000	2.2
5.3b	NMP	87	0.69	68200	150000	2.2
5.3c	NMP	93	0.86	-	-	-
5.3d	NMP	97	0.88	-	-	-
5.3e	NMP	91	0.37	27000	88000	3.3
5.3e	DMAc	89	0.51	64100	137000	2.1

a) Inherent viscosity was measured at a concentration of 0.5g/dL in NMP at 25°C.
b) Molecular weight was determined by GPC in chloroform based on polystyrene standards.

5-5 Properties of the Polymers

Polymer Solubilities

The solubilities of the resulting polymers are shown in Table 5-2.

Table 5-2 Solubilities of Polymers **5.3a-e** a)

Polymer	Solvent				
	m-cresol	TCE	chloroform	NMP	THF
5.3a	+	+	+	+	+-
5.3b	+	+	+	+	-
5.3c	+	+	+-	+	-
5.3d	+	+	+-	+	-
5.3e	+	+	+	+	-

a) Solubility: +, soluble at room temperature; +-, partially soluble; -, insoluble.

Polymers containing flexible chains such as **5.3a**, **5.3b** are soluble in chloroform at room temperature. As the chain rigidity increases, the solubility decreased; **5.3d** is soluble in TCE, while **5.3c** is soluble in dipolar aprotic solvents such as NMP.

Thermal Properties

The polymers were investigated with respect to their thermal properties by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). These results are summarized in Table 5-3 and illustrated in Figure 5-2, 5-3.

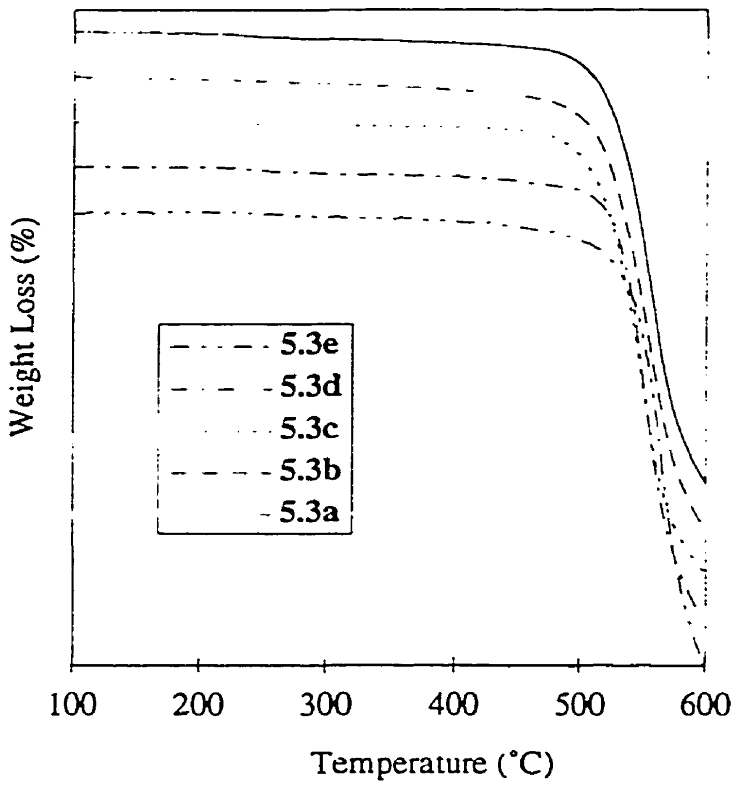


Figure 5-2 TGA Thermograms of Polymers **5.3a-e**

The results demonstrated the general excellent thermal stability of these poly(arylene ether)s. The 5% weight losses in nitrogen were in most cases around 500-520°C. In air these temperatures were up to 30°C lower. No polymers showed weight losses up to 400°C. Thermal transitions were investigated by DSC in the temperature range from 100°C to 400°C.

Table 5-3 Thermal Properties of Polymers 5.3a-e

Polymer	T_g(°C)[a]	TGA(°C)[b]	
		N_2	Air
5.3a	199	523	450
5.3b	208	516	507
5.3c	207[c]	506	456
5.3d	213	521	512
5.3e	259	535	467

a) T_g was determined by DSC at heating rate 20°C/min under nitrogen (160 mL/min), the values were reported from the second scan. b) Reported for 5% weight loss at heating rate 20°C/min under air or nitrogen (flow rate 200mL/min). c) T_m at 288°C after annealing at 220°C for 1h.

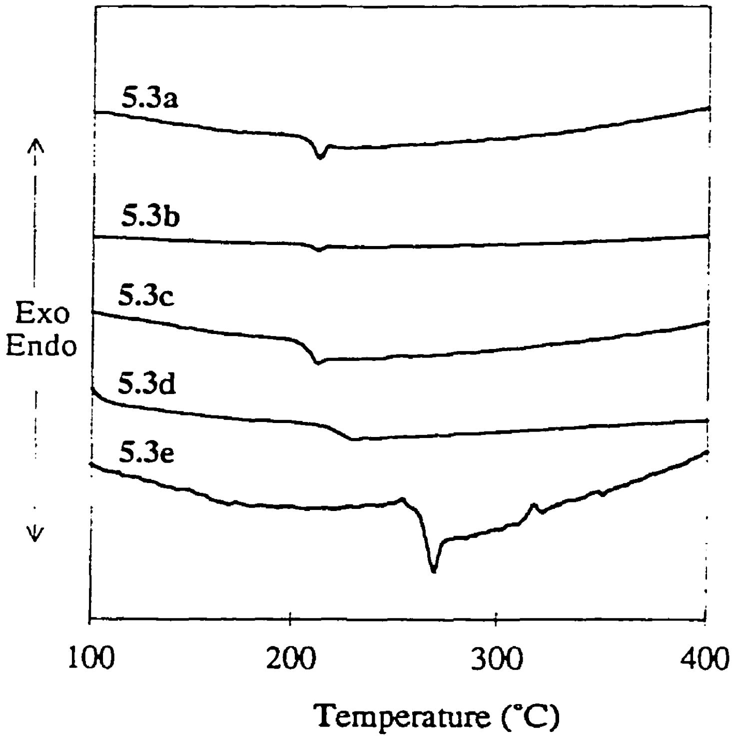


Figure 5-3 DSC Thermograms of Polymers 5.3a-e

With increasing chain stiffness the detection of the glass transition by DSC became more difficult as shown with **5.3b**, **5.3d** (Figure 5-3). The most flexible polymer with a BPA unit in the main chain showed the lowest T_g at 199°C. Polymer **5.3e** which contains the bulky fluorene group showed the highest T_g at 259°C. Polymers **5.3a**, **5.3b**, **5.3d**, appeared to be amorphous since none of them showed any crystalline behavior even after extensive annealing above the T_g. Polymer **5.3c** showed a melting endothermic peak at 288°C after annealing at approximately 10°C above T_g for 1 hour.

Mechanical Properties

The solvent cast thin films of these polymers were clear, creasable, and tough. Young's moduli were measured by TMA in the tensile stress-strain mode (Table 5-4).

Table 5-4 Themomechanical Properties of Polymers **5.3a-e**

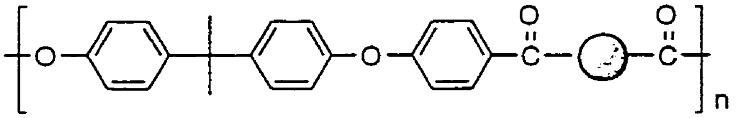
Polymer	Young's Modulus (GPa)		Tanδ (°C)
	20°C	200°C	
5.3a	1.78	0.92	183
5.3b	1.99	1.21	200
5.3c	2.18	1.33	194
5.3d	2.03	1.22	192
5.3e	1.87	1.14	248

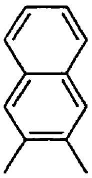
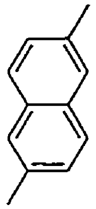
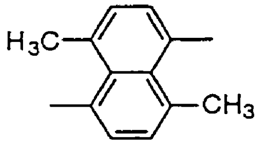
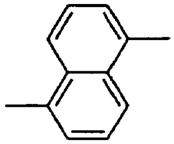
They maintained dimensional integrity from room temperature to close to their T_gs. The T_gs as determined by TMA agreed with those determined by DSC. The Young's moduli from TMA/SS were in the range 0.92-2.18 Gpa between 25-190°C. These values are typical for engineering thermoplastics such as polysulfones and poly(ether imide)s.

Comparison with Other Naphthalene Containing PAKs

The comparison of the thermal properties of napthalene-containing PAKs is shown in Table 5-5. T_gs of poly(ethylene naphthalene dicarboxylate)s decrease in the order of 2,6-< 1,5-,<1,4- [18]. In other words, T_gs increase with increasing linearity of the polymer chain. T_gs of PAKs containing dibenzoylbiphenyl moieties also increase with increasing linearity of the dibenzoylbiphenyl unit except for the 2,2'-substituted PAKs[7]. This is because of the sterically restricted motions in the biphenyl unit caused by the 2,2'-substitution. In dibenzoyl naphthalene containing PAKs, the T_gs increase in the order of 2,3->1,5->2,6-.

Table 5-5 Properties of Naphthalene Containing PAKs



				
T_g	215	185	238	199
$T_{d5\%}$	475	522	457	501
Solubility	$CHCl_3$	NMP	$CHCl_3$	$CHCl_3$
Reference	13	10	15	

T_gs decreased with increasing linearity of the naphthalene unit. This is probably because the naphthalene ring is so bulky that steric interaction, which inhibits the chain motion, controls the T_g values. Compared to poly(ethylene naphthalene dicarboxylate)s, steric interaction is more important since naphthalene-containing PAKs have more benzene rings instead of aliphatic chains. Therefore the order of T_gs is reversed. Molecular symmetry increases the crystallinity of polymers and enhances thermooxidative stability and decreases the solubility. This pattern followed the 5% weight losses in TGA ($T_{d5\%}$) and solubilities for napthalene-containing PAKs. The order of $T_{d5\%}$ is 2,6->1,5->2,3- and solubility increases in order of 2,6->1,5->2,3-. Compared with PAKs with 1,5-dibenzoyl-4,8-dimethyl units, they showed lower T_gs, higher thermostabilities and less solubility. Methyl substitutions cause "crowding" of the atoms of the side groups, hinder the motions of polymer chains, increase the chain stiffness and cause T_g to increase. Methyl substitution also decreases crystallinity and increases solubility. However, thermooxidative stability is reduced greatly.

5-6 Conclusions

A series of novel poly(arylene ether ketone)s have been synthesized. These polymers are amorphous, except for the polymer **5.3c** which shows semicrystalline behavior. The glass transition temperatures are in the range of 199°C-252°C, and they exhibit 5% weight losses around 500°C in nitrogen, and 480°C in air by TGA. High thermostability should allow the polymers to be melt processable. Many of these polymers are soluble in common organic solvents such as chloroform. The mechanical properties are typical of high performance engineering thermoplastics (modulus=1.78-2.18 GPa) and the properties are maintained up to T_g.

5-7 Experimental

General Methods

Melting points were recorded on a Fisher-Johns melting point apparatus. Inherent viscosity data was obtained using 1,1,2,2-tetrachloroethane (TCE) solution at a concentration of 0.5g/dL in a calibrated 1Å (176) Ubbelohde dilution viscometer at 25°C. A Waters 150u-styragel HT Linear 10 um column was used to determine apparent molecular weights by gel permeation chromatography using polystylene standards with chloroform as a solvent. Glass transition temperatures (T_g)s were measured using a Seiko 220 differential scanning calorimeter (DSC) instrument at a heating rate of 20°C/min under nitrogen atmosphere. The T_g was taken as the midpoint of the change in slope of the baseline. All values reported are from the second run otherwise noted. Thermogravimetric analyses (TGA) were obtained using a Seiko 220 TGA/DTA instrument. The 5% weight loss points were recorded using a heating rate of 20°C/min under atmospheres of nitrogen and air. All polymer samples were dried under a nitrogen atmosphere at the T_g (as determined by DSC) for 1 hour before performing TGA measurements. Young's moduli were recorded using a Seiko TMA/SS120. The polymer films used for these measurements were prepared as follows: 200 mg of polymer was dissolved in 3 mL of TCE. The films were cast from TCE solutions onto glass plates using circular glass molds, 1 inch in diameter. The solvent was allowed to evaporate and the films were dried at 100°C for 24 hours in a forced air oven. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Materials

4-Fluorobenzoyl chloride (Lancaster), naphthalene, aluminum trichloride (Omega), methanol (ACP), toluene (A&C Chemicals) were used as received. Dimethylacetamide (DMAc), N-methylpyrrolidinone (NMP) (Aldrich) are distilled over phosphorus pentoxide before use.

Monomer Synthesis

1,5-Bis(4-fluorobenzoyl)naphthalene (5.1)

In a flame-dried 500 mL three-neck flask equipped with a thermometer and a calcium chloride tube and a mechanical stirrer, was placed 37.64 g (0.25 mol) of 4-fluorobenzoyl chloride. Anhydrous aluminum chloride (53.34 g; 0.40 mol) was added slowly and then the temperature was raised to 70°C. To the yellow slurry, was added 12.82 g (0.10 mol) of naphthalene portionwise with care, at 60-65°C. The reaction mixture turned into a reddish black viscous liquid. It was stirred at 70°C for 18 hours. Then the reaction mixture was slowly added to water to form tan yellow chunks, which were washed thoroughly until acid free and filtered. Recrystallization from toluene gave 24.92 g (67 %) of tan yellow plates. ^{1}H-NMR (270 MHz, DMSO-d_6) 7.36-7.47 (m, 4H), 7.64-7.72 (m, 4H), 7.86-7.93 (m, 4H), 8.09 (d-d, J_2=7.64, J_3=1.73, 2H); m.p. 216-8°C; MS (EI, 250°C) 372.14 (M^+, 100), 277.07 (42.0), 249.08 (90.9); Analysis calc'd for $C_{24}H_{14}F_2O_2$: C, 77.41; H, 3.79; ; found: C, 77.56 ;H, 3.79

Polymer Synthesis

Polymerizations were typically carried out in a 50-mL, three-necked flask equipped with a stir bar, a Dean-Stark trap fitted with a condenser, and a nitrogen inlet. The following is a typical procedure. A flask was charged with **5.1** (0.558 g; 1.5 mmol), bisphenol A **5.2a** (0.342 g; 1.5 mmol), potassium carbonate (0.230 g; 1.65 mol), NMP (4.5 mL), and toluene (10 mL). The reaction mixture was heated to a gentle reflux (135 °C) and this temperature was maintained for 2 hours to ensure complete dehydration. The reaction temperature was increased to 190°C by distilling the toluene into the Dean-Stark trap. The reaction was discontinued when the solution viscosity increased dramatically. The solution was diluted with 5 mL of DMAc and coagulated into 300 mL of methanol containing several drops of glacial acetic acid. The recovered polymer was dissolved in chloroform and filtered hot through a thin pad of Celite. The chloroform solution was concentrated and the polymer was coagulated in methanol (250 mL). The solid polymer was recovered by filtration and dried in vacuo for 24 hours.

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Chapter 6

Synthesis of a Benzopyrenequinone Containing Monomer and Attempts to Polymerize It

6-1 Introduction

6-1-1 Chemistry of Dyes and Pigments[1-5]

A dye is a compound which is added to give color to a normally colorless material, for instance natural or artificial fibers. Besides serving merely as colorants, functional organic dyes have become increasingly important in material science. In principle, dyes are extremely versatile materials and may be utilized in many ways. The important properties of a dye chromophore are light absorption, light emission, light induced polarization, photoelectrical properties, and chemical and photochemical reactivities. Most of these properties are related to the ability of dyes to interact strongly with visible electromagnetic radiation, leading to such phenomena as color, fluorescence and various photochemical and photoelectrical processes. Infrared absorbing dyes can be applied in the following fields: laser optical recording systems, laser printing systyems[6], laser thermal writing displays[7], infrared photography, organic solar cell[8] and medical and biological applications. Phthalocyanine, azo compounds and, perylene compounds are important dyes and applied to these fields.

6-1-2 Synthesis of Pigmentary Polymers[9]

A significant effort has been devoted to incorporating dye molecules into the backbone or side chain of polymers because these polymers could combine the good properties of polymers and functionalities of dye molecules (Figure 6-1). Dye molecules are inherently very insoluble so that if soluble polymers with covalently bound dye molecules are developed, many new applications would be possible. In addition, polymer pigments have many advantages over low molecular weight dyes, such as ease of fabrication, thermal stability, low cost etc.

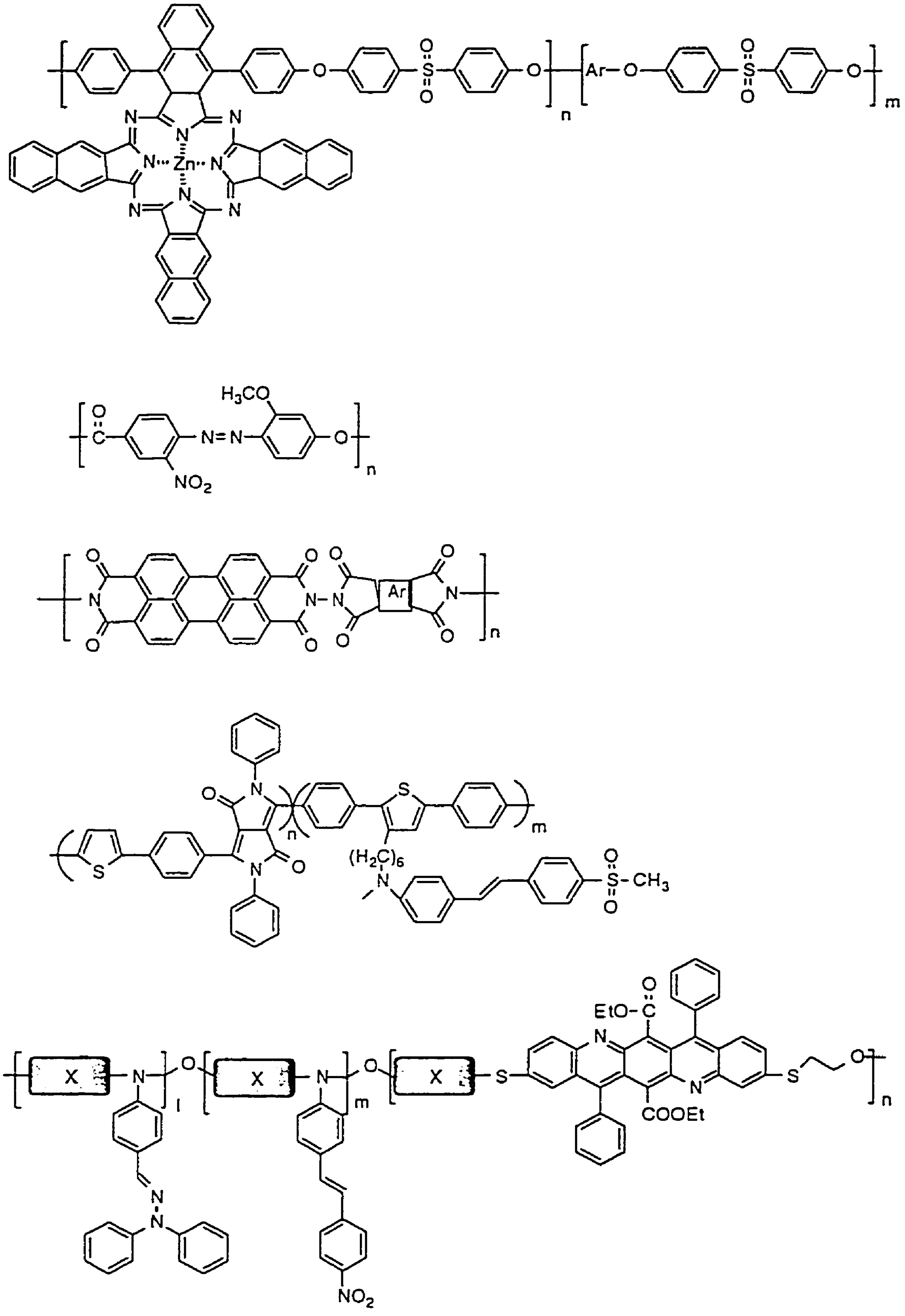


Figure 6-1 Polymers Containing Dye Molecules

Azobenzene was introduced into side chains of the polystyrene[10] or polyacrylate[11]. Hall has synthesized azobenzene main chain polyesters and polyacrylates with azobenzene on the side chain[12] for non linear optical materials. Rehahn reported the first soluble rigid-rod polyimides with dye-containing pendant groups[13]. Our group has synthesized novel colored polymers which are potential charge generating materials for xerography. Red pigmentary polyimides from N,N'-diamino-3,4,9,10-perylenetetracarboxylic acid bisimide and bisphenol A dianhydride were synthesized. The polymers were soluble in organic solvents and could be cast into flexible red colored transparent films[14]. Thermally stable poly(aryl ether)s bearing covalently bound zinc(II) the naphthalocyanine unit[15] or the tetrapyrazinoporphyrazine[16] unit were also synthesized. The polymers were soluble in organic solvents and had almost the same maximum absorption wavelength as naphthalocyanine and tetrapyrazinoporphyrazine, respectively. Novel photorefractive polymers containing dye molecules have been synthesized. These polymers contained a non-linear optical chromophore, a charge generator, a transporting material, which were all covalently linked to the polymer backbone. The conjugated backbone could play the multiple role of charge generator, charge transporter and backbone[19].

6-2 Strategy and Goals

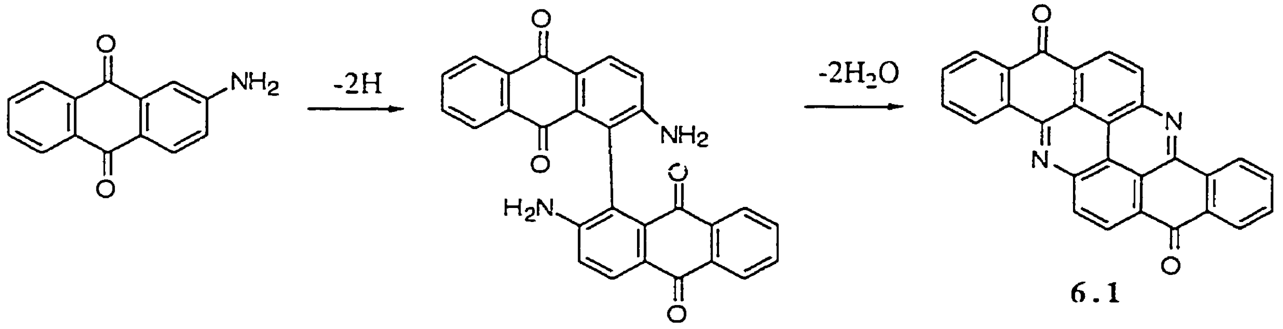
In chapter 4, we described the synthesis of the new monomer, 1,5-bis(4-fluorobenzoyl)naphthalene. The commercial dye molecule, Indanthrene Golden Yellow GK, has a dibenzopyrenequinone structure. If 1,5-bis(4-fluorobenzoyl)naphthalene can be cyclized in the same manner as the commercial dye, the product would be a monomer for poly(arylene ether)s because the two fluorines should be activated toward a nucleophilic aromatic substitution reaction due to the carbonyl groups in the *p*-position to the fluorines. Polymers from this monomer with bisphenols should have solubility, thermooxidative stability as well as interesting optical properties. We, therefore, synthesized the new monomer 2,3:7,8-bis(4-fluorobenzo)pyrene-1,6-quinone and investigated its polymerization with bisphenols.

6-3 Synthesis of 2,3;7,8-bis(4-fluorobenzo)pyrene-1,6-quinone

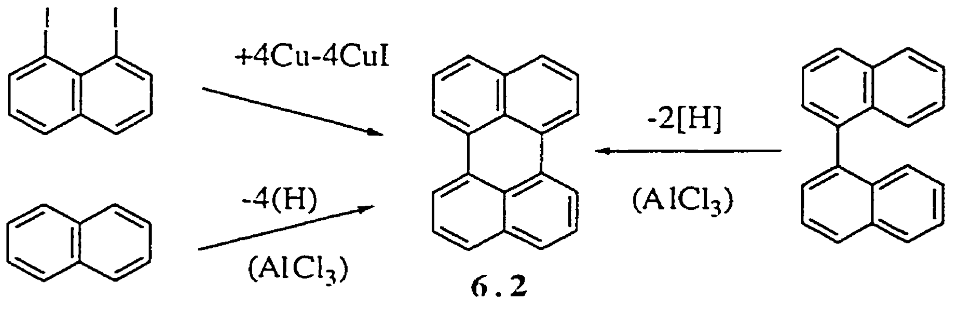
6-3-1 Scholl Reaction [20, 21]

The Scholl reaction is the process in which elimination of two aryl-bound hydrogens is accompanied by the formation of an aryl-aryl bond under the influence of a chemical catalyst-oxidant combination. In many cases, Friedel-Crafts catalysts are used. The Scholl reaction has been intensively studied because of its practical importance for the dyestuff industry. The synthesis of the vat dye flavanthrone **6.1** by fusion of 2-aminoanthraquinone in the presence of aluminum chloride[22] (Scheme 6-1), and perylene **6.2** formation by three different paths[23,24] are early examples of the Scholl reaction (Scheme 6-2). Oxidative polymerization of benzene to poly(*p*-phenylene) by treatment with aluminum chloride/copper chloride is also a related reaction[25].

Scheme 6-1

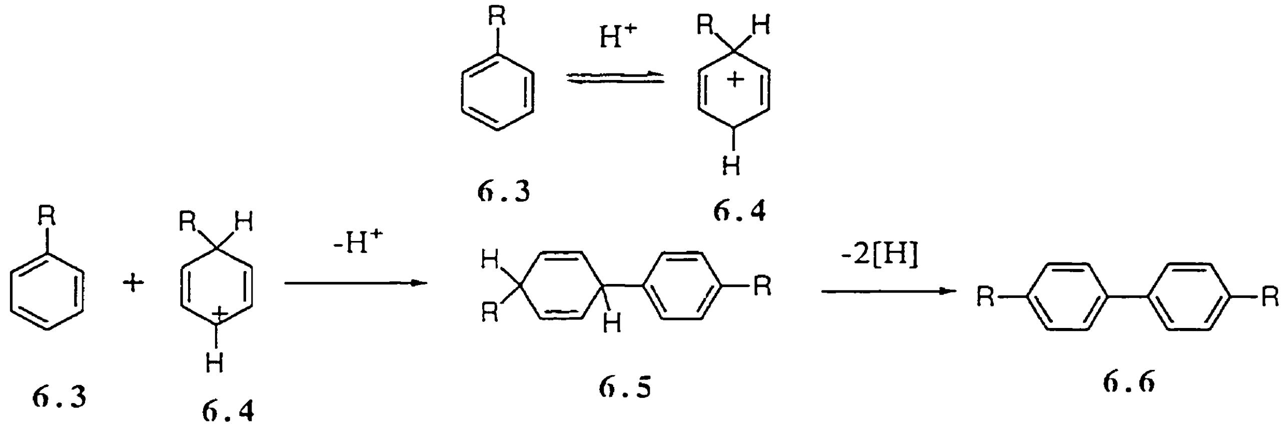


Scheme 6-2

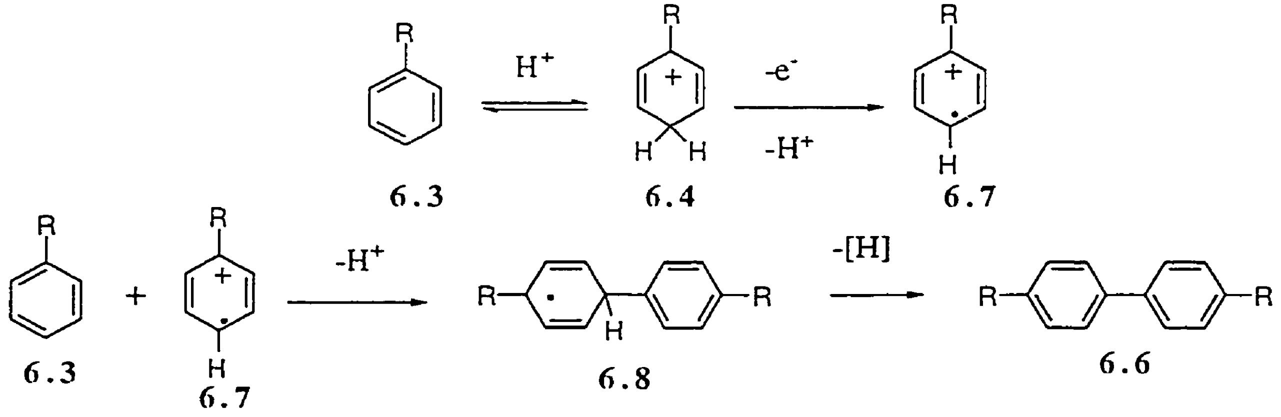


Two mechanisms for the Scholl reaction have been proposed. One is a radical cation intermediate mechanism, the other proposal involves a σ complex intermediate. In some cases more than one mechanism may pertain depending upon the substrate and conditions. In the σ complex intermediate mechanism, the reaction is an electrophilic substitution of an aromatic **6.3** by its conjugated acid **6.4**. The dihydro derivative **6.5**, formed as an intermediate, is subsequently dehydrogenated to a biaryl **6.6**.

Scheme 6-3



Scheme 6-4

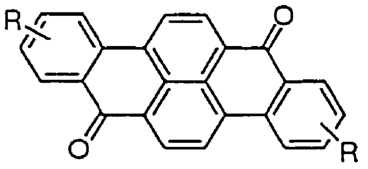


In the radical cation mechanism, the electophilic species is the radical ion **6.7**. The two hydrogens are eliminated stepwise, one before and one after linkage of the two aryl residues. It is very difficult to decide between the two mechanisms.

Generally the reaction conditions in the Scholl reactions are more drastic than in the Friedel-Crafts reactions. The catalyst is usually used in stoichiometric or even larger amounts. Aluminum chloride is the most common catalyst. Other metallic chlorides have also been used; $TiCl_4$, $SbCl_5$, $SnCl_4$, $FeCl_3$, and $CuCl_2$. Many reactions are run in carbon disulfide or in benzene. However, the usual temperature is above 100°C. A melt of a mixture of aluminum chloride and sodium chloride or a complex of sodium hydrogen sulfite with copper chloride, which is liquid at 40°, are used as a solvent. In these cases, oxygen is bubbled into the reaction mixture. Besides air or oxygen, nitrobenzene, potassium *m*-nitrobenzene sulfonate, manganese dioxide have been used as oxidizing agents. Recently the Scholl reaction using $NaNO_2$ with CF_3SO_3H or using SbF_5 to effectively form binaphthyl derivatives was reported[26].

6-3-2 Synthesis of 2,3;7,8-bis(4-fluorobenzo)pyrene-1,6-quinone

Indanthrene Golden Yellow GK is an example of the dibenzopyrenequinone type dyes formed by cyclization of 1,5-dibenzoylnaphthalene in a mixture of aluminum and sodium chloride using either oxygen or potassium *m*-nitrobenzene sulfonate as the oxidizing agent [27]. The cyclization does not take place in $AlCl_3$-NaCl melt at 140°C. On introduction of oxygen the reaction proceeds giving 2,3;7,8-dibenzopyrene-1,6-quinone **6.19a** (Scheme 6-7).



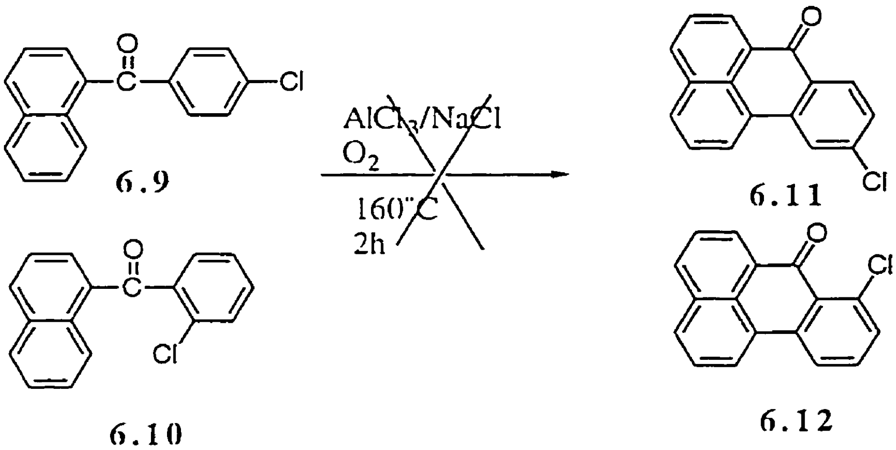
R=H; CI Vat Yellow 4
R=Br; CI Vat Orange

Figure 6-2 Indanthrene Golden Yellow GK

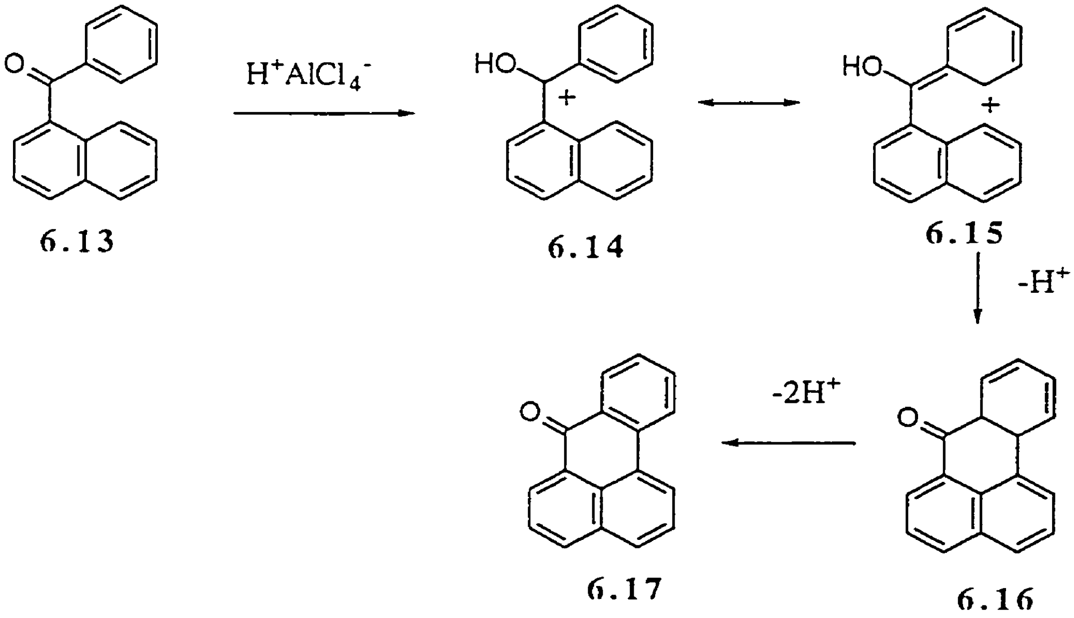
Bromination improves the fastness of the dye and gives Indanthrene Golden yellow GK (Figure 6-2).

In 1922, the Scholl reaction of 1-(4-chlorobenzoyl)naphthalene **6.9** was unsuccessfully tried[28] (Scheme 6-5). The mechanism shown in scheme 6-6, which was σ complex intermediate mechanism, was proposed.

Scheme 6-5



Scheme 6-6

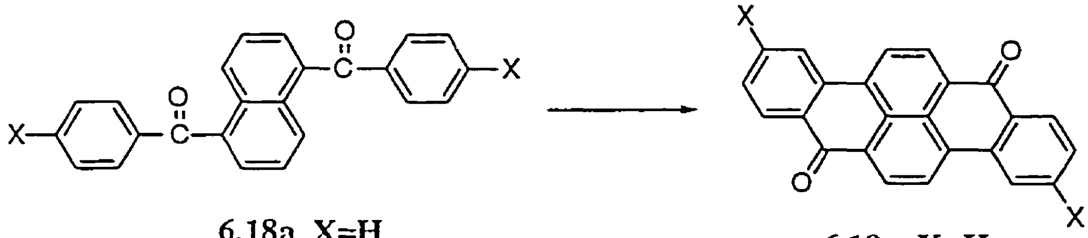


There were two reasons why the σ-complex mechanism was chosen. One was that HCl is necessary for the reaction to proceed. If HCl was expelled by a stream of oxygen, the reaction did not take place, but started on introduction of HCl gas. A strong protonic acid, $HF+BF_3$ or $HHal+AlHal_3$, was needed for the first step of the mechanism, the conjugate acid formation. It was known that radical ions were produced with Lewis acids alone. The other reason was that dihydroderivatives **6.5** were formed in similar systems. The negative result of the reaction was explained by destabilization of the intermediate cation **6.14** by chlorine substitution.

Since the Scholl reactions of interest were studied a long time ago, the reaction conditions were not clearly explained and the characterization of the products was limited. We, therefore, first performed the Scholl reaction on 1,5-dibenzoylnaphthalene **6.18a**. We investigated many super acid systems, radical cation generating agents, or various oxidizing agents to synthesize 2,3;7,8-bis(4-fluorobenzo)pyrene-1,6-quinone **6.19b** (Scheme 6-7).

6.18a was reacted in a melt of $AlCl_3$-NaCl at 140°C for 4 hours in the presence of an oxidizing agent. The golden yellow product was obtained in high yield (Table 6-1, Figure 6-2). Three kinds of oxidizing agent were used. The yields for each oxidizing agent were good. The reaction with oxygen was hard to handle because the reaction mixture was highly viscous and the introduction of oxygen was difficult on a small scale. 1,5-Bis(4-fluorobenzoyl)naphthalene **6.18b** did not cyclize under the same conditions regardless of the oxidizing agent used (Table 6-1).

Scheme 6-7



6.18a X=H
6.18b X=F

6.19a X=H
6.19b X=F

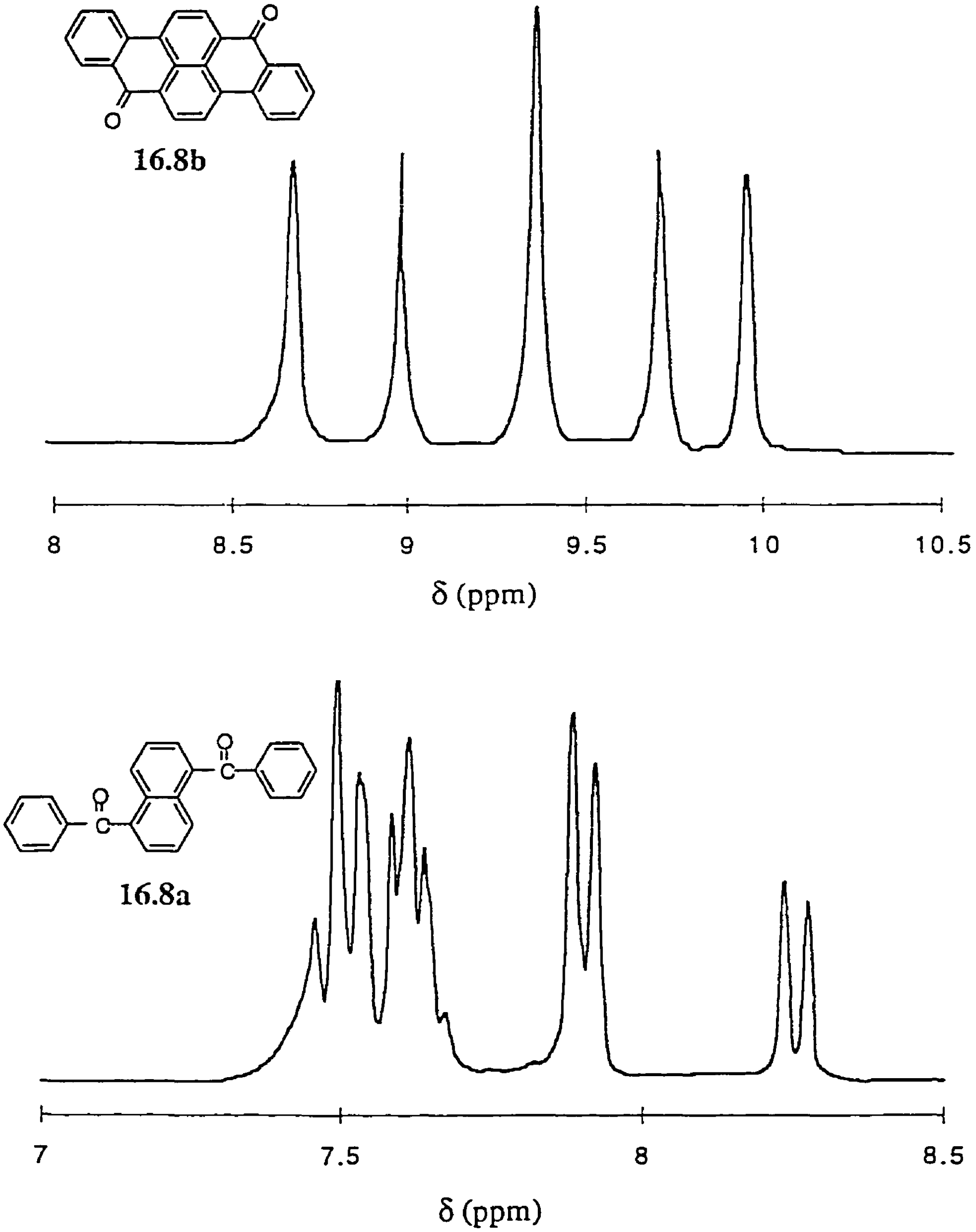


Figure 6-2 NMR spectra of **6.18a** (DMSO-d_6) and **6.19a** (D_2SO_4)

Table 6-1 Cyclization of **6.18a, b** with Various Oxidizing Agents

X	Oxidant	Yield (%)
H	O_2	77
H	m-$(NO_2)C_6H_4SO_3K$	89
H	2,4-$(NO_2)_2C_6H_3Cl$	85
F	O_2	NR
F	m-$(NO_2)C_6H_4SO_3K$	NR
F	2,4-$(NO_2)_2C_6H_3Cl$	NR
F	CuCl	NR
F	DDQ	NR
F	Chloranil	NR

In a melt of $AlCl_3$/NaCl. 140°C, 4 hours

The intermediate should be destabilized because of the electron withdrawing fluorines as described for **6.9** in the old paper . Therefore, the Scholl reaction was attempted with various Lewis acids, or strong protonic acids (Table 6-2).

Table 6-2 Cyclization of **6.18a,b** with Various Acids

Acid	Yield (%)
Polyphosphoric acid	NR
FSO_3H	NR
CF_3SO_3H	Dec.
CF_3SO_3H-SbF_5	Dec.
$AlCl_3$-NaCl	trace
$FeCl_3$-NaCl	Dec.
$AlCl_3$-$FeCl_3$(1:1)-NaCl	trace
$SbCl_5$	NR
SbF_5	56

In a melt of $AlCl_3$/NaCl, 140°C, 4 hours

In super acid systems such as CF_3SO_3H, decomposition took place. **6.18b** cyclized in antimony pentafluoride at 140°C for 4 hours affording orange colored **6.19b** in 56% yield (Figure 6-3). Optimization of the Scholl reaction with antimony pentafluoiride was carried out (Table 6-3). Addition of an oxidizing agent was not necessary. Some antimony pentafluoride worked as an oxidizing agent. The optimum temperature for cyclization was between 120°C and 160°C. At 120°C it took 20 hours to obtain a high yield. At 160°C some side reactions took place and the product became darker colored and insoluble. At least 10 equivalents of antimony pentafluoride were needed to obtain a high yield.

Table 6-3 Optimization of Cyclization of **6.18b** with antimony pentafluoride

SbF_5 (eq)	Oxidant	Temp. (°C)	Time (hr)	Yield (%)
5	m-$(NO_2)C_6H_4SO_3K$	140	4	33
5	O_2	140	4	56
5	-	140	4	61
10	-	140	4	72
10	-	120	20	70
10	-	160	2	0*

*Dark color insoluble product formed

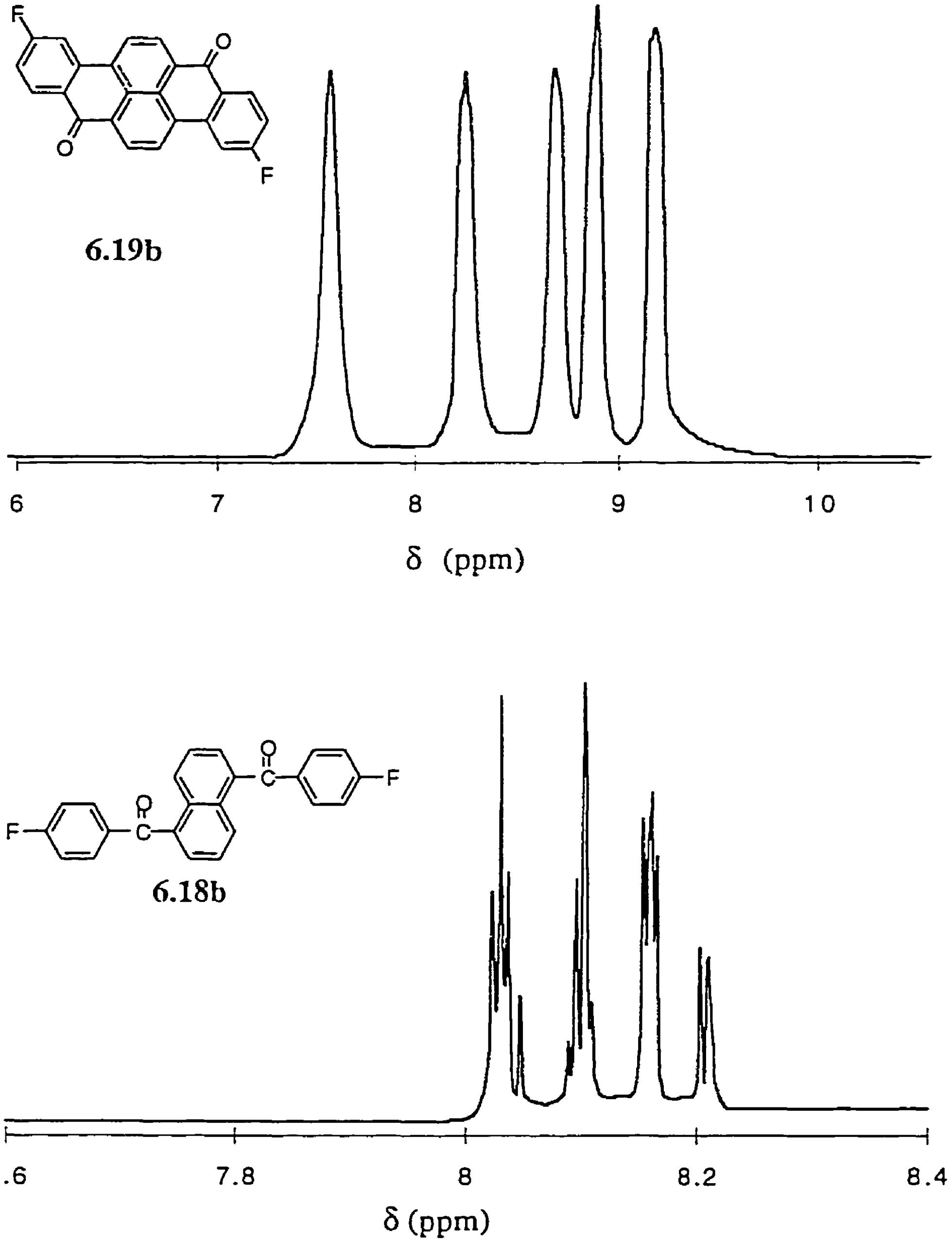


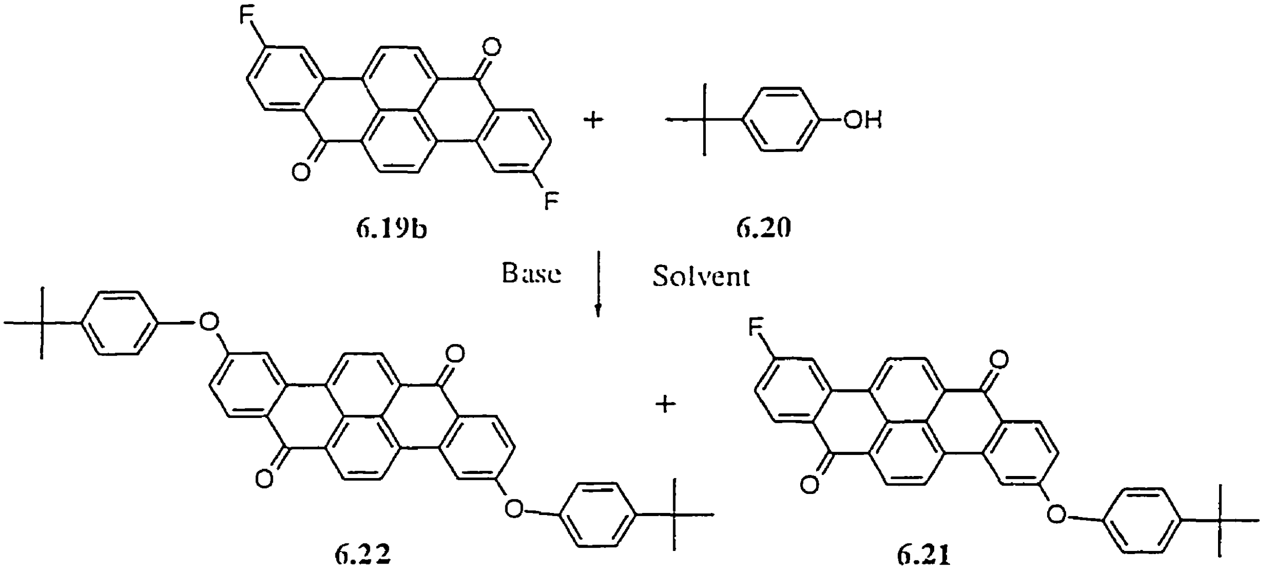
Figure 6-3 200MHzNMR Spectra of **6.18b** (DMSO-d_6) and **6.19b** (D_2SO_4)

6-4 Attempted Polymerization of 2,3;7,8-bis(4-fluorobenzo)pyrene-1,6-quinone

6-4-1 Nucleophilic Substitution on Monomer 6.19b

Model reactions for polymerization, reactions between **6.19b** and t-butylphenol **6.20**, were carried out. **6.20** was reacted with a base and formed water was removed by azeotropic distillation with toluene. Then, **6.19b** was reacted with the t-butylphenolate (Scheme 6-8).

Scheme 6-8.



The potassium carbonate-DMAc system was first attempted. The product, a dark orange residue, was insoluble in all common organic solvents. The soluble part was analyzed by MALDI TOF mass spectrometry and ^{1}H-NMR in D_2SO_4. The ^{1}H-NMR of the soluble part of the product showed some peaks for a methyl group and the MALDI-TOF spectrum showed the product peak as well as other product peaks. A mass peak for the starting material, **6.19b**, appeared at 368.6. Peaks for the mono substituted product (**6.21**) and disubstituted product (**6.22**) appeared 497.8, 626.2 respectively (Figure 6-4 (a)).

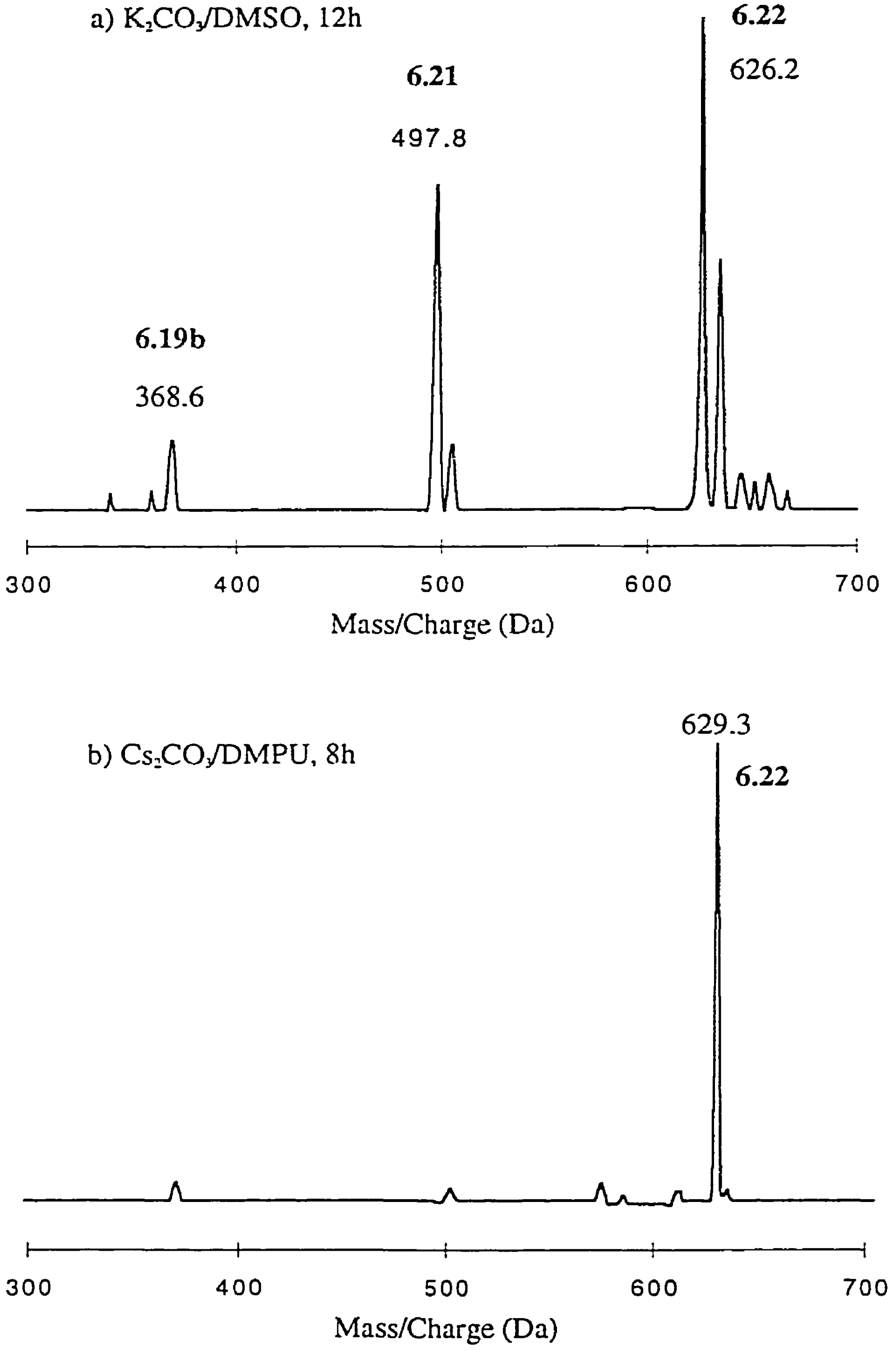


Figure 6-4 Maldi-TOF MS Analysis of the Model Reactions

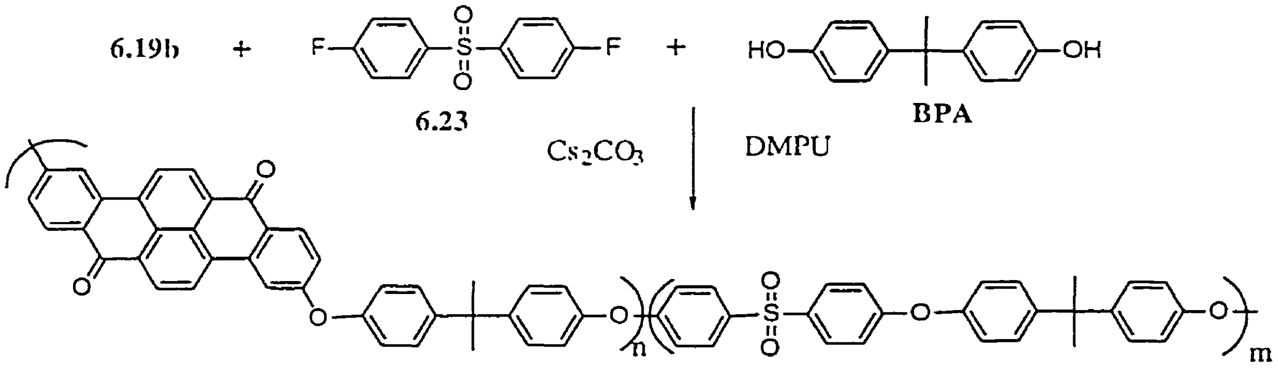
Table 6-4 Nucleophilic Substitution on **6.19b** by t-Butylphenolate

Base	Solvent	Temp(°C)	Time (hr)	Side Product peak
K_2CO_3	DMAc	150	16	yes
Cs_2CO_3	DMSO	140	12	yes
Cs_2CO_3	DMSO	120	24	yes
Cs_2CO_3	DMPU	120	8	no

These results strongly suggested that side reactions, presumably on the carbonyl groups of the monomer, had taken place. To avoid the side reactions, the reaction temperature was lowered and more reactions using cesium carbonate instead of potassium carbonate were attempted. The substitution proceeded at about 120°C. As the reaction proceeded the monomer gradually went into the solution. t-Butylphenol disappeared in 24 hours in DMSO, and in 8 hours in DMPU as followed with MALDI-TOF MS analysis of the reaction mixture. DMPU is the better solvent for **6.19b** and reaction time was shortened. The color of the product improved and the MALDI TOF mass spectrum of the product showed a single peak (Figure 6-4 (b)).

Polymerization with cesium carbonate at 120°C in DMPU was carried out (Scheme 6-9).

Scheme 6-9



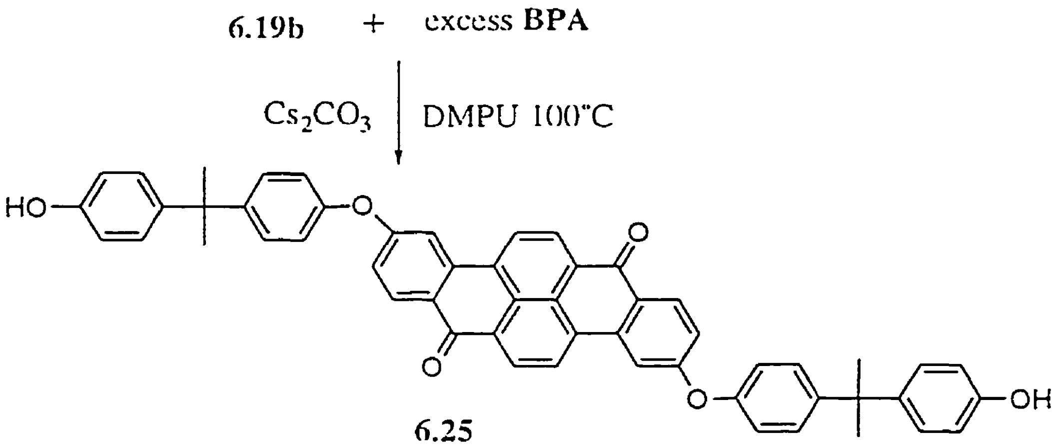
6.24

A reddish black insoluble product, which cannot be analyzed, came out from the solution in 15 hours. Copolymerization with 4,4'-bis(4-fluorophenyl)sulfone **6.23** was then carried out. However, the ^{1}H-NMR spectrum of the soluble part of the product did not show any peaks for benzpyrenequinone. Because of the insolubility of the monomer, BPA reacted selectively with bis(4-fluorophenyl)sulfone and a random copolymer **6.24** could not be obtained.

6-4-2 Modification on Monomer 6.19b

Modification of the monomer was tried to make it soluble. The monomer was reacted with excess of **BPA** in DMPU in the presence of cesium carbonate to synthesize soluble BPA end capped monomer **6.25**.

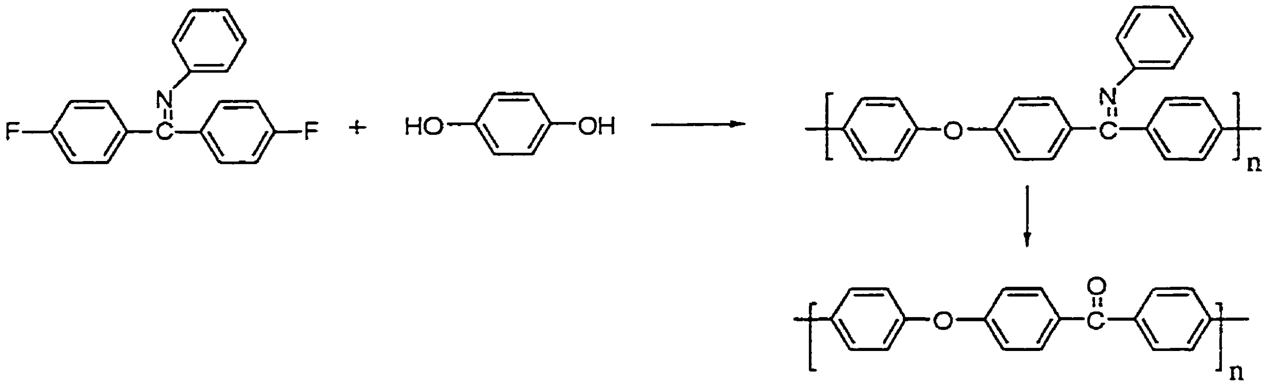
Scheme 6-9



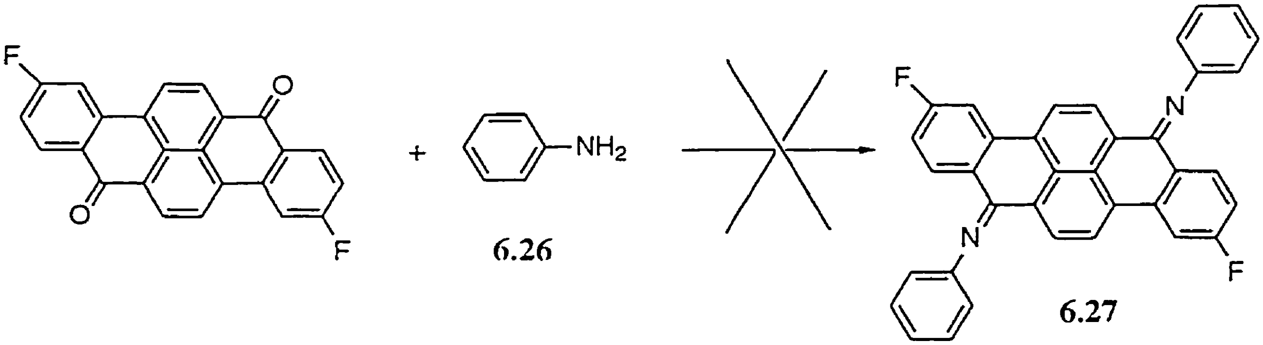
6.25

The monomer **6.25** was soluble in dipolar aprotic solvents such as DMSO, DMAc, and NMP. Polymerization was performed under several conditions as well as copolymerization reaction. The polymerization reactions with this monomer **6.25** resulted in insoluble dark colored solids regardless of the conditions. Copolymerization with **6.23** also did not go well because of insolubility of the monomer compared to BPA **6.22** .

Scheme 6-10



Scheme 6-11



The synthesis of soluble precursors of PEEK (poly(ether ether ketone)s) and the conversion to PEEK have reported. Soluble precursor polymers of PEEK have been synthesized from 2-*t*-butylhydroquinone[29], 4,4'-difluoro(N-benzohydroxylidene aniline) (Scheme 6-10)[30], and the ketal of 4,4'-dihydroxybenzophenone[31] . To solubilize the monomer and prevent side reactions on the carbonyl group, aniline **6.26** was reacted with the monomer **6.19b** in 1,2,4-trichlorobenzene. Molecular sieves, trifluoroacetic acid, titanium chloride[32], tributyltin chloride[33] were used as catalysts. The reactivity of the carbonyl group was so low that no reaction took place.

6-5 Conclusions

A new dye monomer, 2,3;7,8-bis(4-fluorobenzo)pyrene-1,6-quinone, was synthesized by the Scholl reaction of 1,5-bis(4-fluorobenzoyl)naphthalene with antimony pentafluoride. It was subjected to nucleophilic displacement polymerization reactions in attempt to synthesize a new colored polymer. Model reactions were performed by the reaction of t-butylphenol with the monomer and the insoluble products were analyzed by MALDI-TOF mass spectrometry. The results of the model reaction showed that the nucleophilic substitution reaction as well as side reactions, presumably reactions on the carbonyl group, took place. The use of cesium carbonate at low temperatures suppressed the side reactions. Polymerization reactions with BPA were tried but only insoluble residues formed, regardless of the conditions used. Copolymerization reactions were also unsuccessful because of the insolubility of the monomer. Therefore, modifications of the monomer was tried. Protection of the carbonyl group by reactions with aniline to give the anil was not successful. Both ends of the monomer were also capped with BPA by reaction with excess of BPA. Polymerization and copolymerization under mild conditions were attempted , but in both cases, only insoluble residues formed.

6-6 Experimental

General methods

N-Methylpyrrolidinone (NMP; Aldrich), dimethyl sulfoxide (DMSO; BDH), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) were distilled over posphorous pentaoxide and stored over 4Å molecular sieves. 4,4'-Isopropylidenediphenol (BPA), polycarbonate, were kindly supplied in high purity from the General Electric Company and were used as received. Antimony pentafluoride was obtained from Aldrich and used as received. All common solvents and reagents were reagent grade and used as received otherwise noted.

^{1}H- and ^{13}C-NMR were obtained on a JEOL 270 or XL-200 spectrometer. Matrix-assisted laser desorption ionization-time of flight-mass spectroscopy analysis was performed on a KOMPACT-MALDI-TOF-MS instrument. The analysis solution was prepared from 10 μl of sample solution and 100 μL of dithranol solution (matrix). The cyclic sample solution was prepared from 5 mg of sample of 1 mL of chloroform. The matrix solution consisted of 10 mg of dithranol and 1 mL of chloroform. The sample solution (0.2 μL) was spotted on the sample slot and subjected to analysis. The laser power was selected as 90.

1,5-Dibenzoylnaphthalene (6.18a)

To a 500 mL three neck flask equipped with a mechanical stirrer a thermometer, and a calcium chloride tube was placed benzoyl chloride (38.5 g; 0.274 mol). Aluminum chloride (58 g: 0.425 mol) was added with stirring allowing the temperature to rise to 80-90°C. The mixture was cooled to 60°C and naphthalene (13.2 g; 0.103 mol) was added portion-wise with care at 60-70°C over 5 hours. (Caution: naphthalene has to be added very carefully; the reaction mixture is very viscous and may blow out of the flask because of foaming.) The reaction was held 8 hours at 70°C and then the hot reaction mixture, a reddish black semisolid, was added slowly to 200 mL of water. (Caution; HCl gas is generated violently.) The yellow precipitate was washed thoroughly with water until acid free. It was dried under reduced pressure at 80°C and recrystallized from chlorobenzene; yield 19.50 g (56.3%), tan colored needles, m.p. 210-213 °C, ^{1}H-NMR (200MHz, DMSO-d_6) δ 7.42–7.62 (m, 10H), 7.90 (d, J_2=7.80, 4H), 8.25 (d, J_2=8.20, 2H)

2,3:7,8-Dibenzopyrene-1,6-quinone (6.19a)

To a 250 mL a three neck flask equipped with a mechanical stirrer, a calcium chloride tube and a thermometer, anhydrous aluminum chloride (40 g; 0.3 mol) and sodium chloride (9.63 g; 0.165 mol)) was added and melted by heating up to 180°C. After the mixture was cooled down to 120°C, sodium *m*-nitrobenzenesulfonate (12.56 g; 0.0558 mol) was added. The temperature was increased to 150°C and, 1,5-dibenzoylnaphthalene (9.374 g; 0.0279mol) was added carefully portionwise over 1 hour. The temperature was allowed to rise to 160°C. On completion of the addition, aluminum chloride (22.5g; 0.169 mol) was added. The temperature was held at 160-170°C for 4 hours. The melt was added carefully to 200 mL of water. Hydrochloric acid was then added and the temperature raised to 100°C and held for 30 min. The reaction mixture was cooled and the product was filtered and washed thoroughly until acid free. The product was recrystallized from boiling 1,2,4-trichlorobennzene to give a golden yellow powder. Yield 89% (8.34 g), m.p. 565°C (DSC, decomposition), ^{1}H-NMR (200MHz, D_2SO_4) 7.65 (s, 2H), 7.95 (s, 2H), 8.34 (s, 4H), 8.69 (s, 2H), 8.97 (s, 2H)

1,5-Bis(4-fluorobenzoyl)naphthalene (6.18b)

This material was prepared by the reaction of naphthalene with 4-fluorobenzoyl chloride in the presence of anhydrous aluminum chloride. The procedure was described in Chapter 5.

2,3;7,8,Bis(4-fluorobenzo)pyrene-1,6-quinone (6.19b)

To a three neck round bottom flask equipped with a mechanical stirrer, a water cooled condenser and a calcium chloride tube, were placed 5.58 g (0.015 mol) of 1,5-bis(4-fluorobenzoyl)naphthalene and 32.51 g (0.15 mol) of antimony pentafluoride and the mixture heated to 120°C. The purplish black viscous half solid was stirred for 20 hours. Then it was poured into water to precipitate an orange powder. Recrystallization from 1,2,4-trichlorobenzene gave orange small needles; yield 3.81 g (69 %), m.p. 583 °C (dec.), ^{1}H-NMR (200MHz, D_2SO_4) δ 9.17 (s, 2H), 8.86 (s, 2H), 8.66 (s, 2H), 8.23 (s, 2H), 7.53 (s, 2H), ^{13}C-NMR (200MHz, D_2SO_4) δ 112.79, 113.69, 118.95, 122.65, 124.25, 134.14, 135.16, 139.90, 140.12, 166.50, 171.96, 181.55.

Model reactions

To a 50 mL 3-neck flask equipped with a Dean-Stark trap, a water cooled condenser, a nitrogen inlet and a thermometer were placed 0.1502 g (1.0 mmol) of t-butylphenol, 0.3584 g (1.1 mmol) of cesium carbonate, 3 mL of DMPU, and 5 mL of toluene. The mixture was heated to reflux for 4 hours and then toluene was slowly removed from the Dean-Stark trap. After the reaction mixture was cooled down to room temperature, 0.1842 g (0.5 mmol) of **6.19b**. was added. The temperature was raised to slowly to 100°C. The reaction mixture was stirred at 120°C for 8 hours. The orange slurry gradually turned into dark reddish brown solution. The reaction mixture was cooled to room temperature and poured into 300 mL of water. The crude solid was filtered and recrystallized from NMP to give the product **6.22** (0.262 g; 82%). m.p. 354.1°C (DSC) ^{1}H-NMR (270MHz, DMSO-d_6) δ 7.2 (d, J_2=8.64, 4H), 7.8 (s, 2H), 8.0 (d, J_2=8.64, 4H), 8.21 (s, 2H), 8.61 (s, 2H), 8.98 (s, 2H), 9.11 (s, 2H)

Polymerization

Typical method. Polymerization and copolymerization of BPA capped monomer **6.25** were carried out in the same manner.

To a 50 mL 3- neck flask equipped with a Dean-Stark trap, a water condenser, a nitrogen inlet and a thermometer, was added 0.1142 g (0.50 mol) of bisphenol A, 0.3584 g (1.1 mmol) of anhydrous cesium carbonate, 2.62 g of DMPU and 3 mL of toluene. The mixture was heated to reflux for 4 hours. Toluene was removed from Dean-Stark trap. The mixture was allowed to cool down to room temperature after toluene was completely removed. Then 0.1842 g (0.5 mmol) of **6.19b** was added and the mixture was stirred and temperature was slowly raised to 120°C during a period of 16 hours. The monomer gradually went into solution in 6 hours and reddish black residue came out about 12 hours. The reaction mixture was poured into mixture of 300 mL methanol and 100 mL of water. The dark orange material was filtered and extracted with acetone and dried to give 0.22 g (86 %) of product.

Synthesis of BPA End-capped Monomer (6.25)

To a three neck round bottom flask equipped with a stir bar, a Dean-Stark trap with a water cooled condenser, and a nitrogen inlet, were placed 2.28 g (0.010 mol) of BPA and 3.26 g (0.010 mol) of cesium carbonate in 25 mL of DMPU and 10 mL of toluene. The reaction mixture was refluxed for 6 hours at 120-130°C. Water formed by deprotonation of BPA was removed from the Dean-Stark trap. In the later stage of the reaction toluene was removed from the Dean-

Stark trap. After toluene was completely removed, the reaction mixture was cooled down to room temperature and 0.737 g (0.002 mol) of monomer **6.19b** was added. The temperature was slowly raised to 100°C, and was controlled by a temperature controller. The reaction mixture, a dark orange slurry, turned gradually into homogeneous reddish black solution. After stirring for 6 hours at 120°C, it was poured into 400 mL of water to precipitate a red brown powder. Recrystallization from DMF-water gave an orange powder; yield 1.41 g (89 %). m.p.>400°C, ^{1}H-NMR (200MHz, DMSO-d_6) d 1.55 (s, 12H), 6.69 (d, J_2=8.42, 4H), 6.96 (br, 2H) 7.07 (d, J_2=8.42, 8H), 7.31 (d, J_2=7.91, 4H), 7.85 (br, 2H), 8.02 (br, 2H), 8.13 (br, 2H), 8.32 (br, 2H), 9.22 (s, 2H)

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Chapter 7

Chemistry of Acridone

7-1 Introduction

7-1-1 Fluorescent Polymers

The field of polymer light emitting diodes (LEDs) has attracted much attention since Cambridge's researchers reported that poly(*p*-phenylenevinylene)(PPV) sandwiched in an ITO/PPV/metal device emits visible light under an applied bias in 1990[1)]. Polymer LEDs have several advantages over inorganic materials or low molecular weight fluorescent compounds[2]. Polymeric materials can easily be processed into large-area thin films using simple and inexpensive technology. The polymers are light-weight and flexible and many of their properties can be adjusted to suit specific needs. Common organic LEDs consist of an electron transport layer (ET), emitter and hole transport layer sandwiched between two electrode (Figure 7-1).

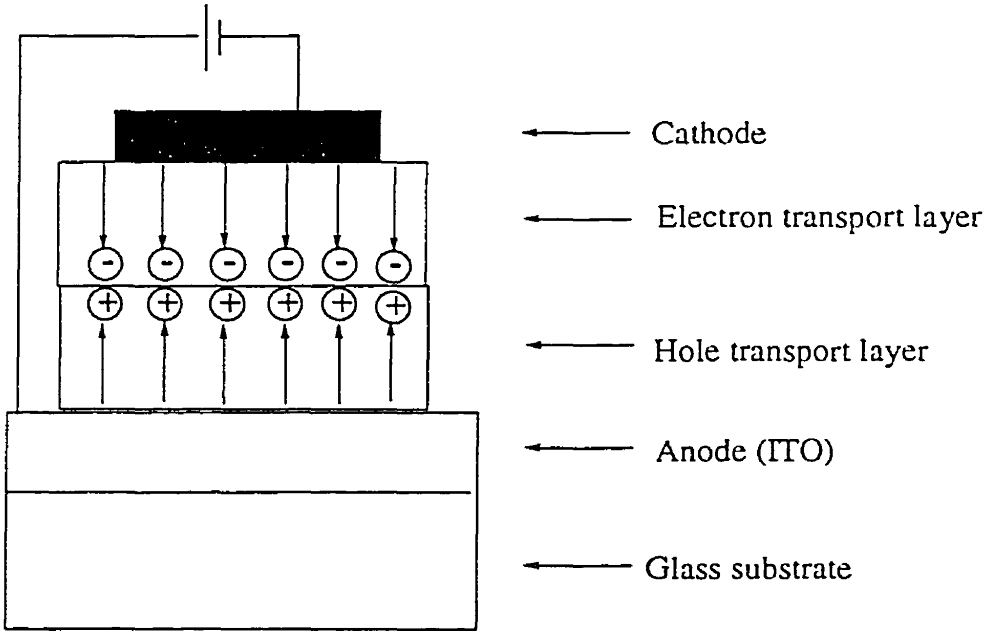


Figure 7-1 Double-layer Type LED Cell

Positive holes are injected from ITO, while electrons are injected from the cathode (Mg, Al etc.) into the organic layer. Excited singlets of the organic molecules are generated by combination of positive holes and electrons in the organic layer. The luminescence is emitted from the singlet organic molecule. The hole transport layer blocks holes so that the carriers are confined to the organic layer, thus maximizing the recombination efficiency.

Recently many fluorescent polymers have been reported. They are classified into two groups: fully conjugated polymers (Figure 7-2) and partially conjugated polymers (Figure 7-3). Conjugated polymers have been more widely studied. The fluorescent properties of PPV have been chemically modified. Interruption of conjugation by partial elimination of precursor leaving groups[3] or attachment of alkoxy groups[4], change the emission colour. Besides PPVs, poly(cyanoterephthalylidine)s[5], poly(9,9-dialkylfluorene)s[6], poly(p-phenylene)s[7], poly(thiophene)s[8], poly(naphthalene vinylene)s[9] and poly(quinoxaline)s[10] have been synthesized and their fluorescent properties have been studied.

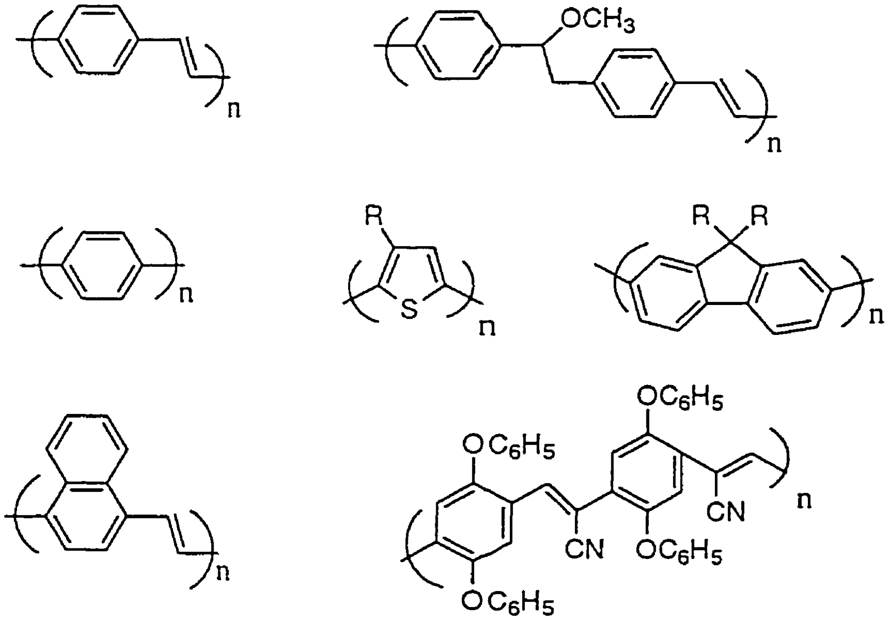


Figure 7-2 Conjugated Polymers for LEDs

Polymers which have fluorescent groups in the main chain or side chain are relatively few because of the difficulty of the synthesis. Poly(n-vinylcarbazole)[11], poly(stilbenyl-*p*-methoxystyrene)[12], poly(methyl methacrylate)[13] or poly(vinyl ether) containing azo-chromophoric groups[14] and polystyrene with tetraphenyldiaminobiphenyl[15] groups and poly(arylene ether)s with a fluorescent group from phenolphthalein[16] have been synthesized.

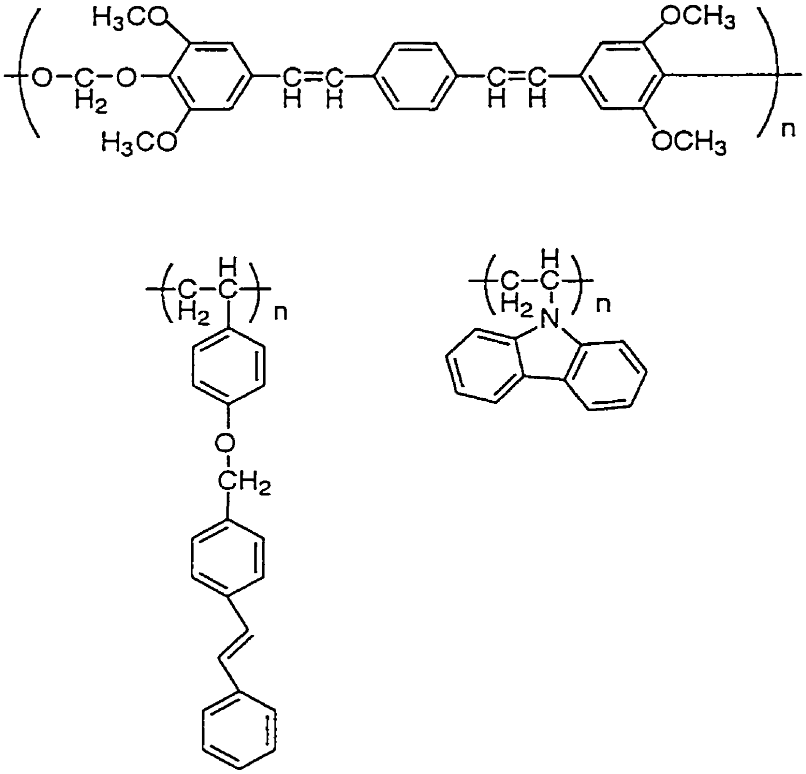


Figure 7-3 Non-conjugated Fluorescent Polymers

7-1-2 Chemistry of Acridone[17]

9-Acridanone, commonly known as "acridone" is a very stable compound as indicated by the high melting point without decomposition. Acridone derivatives are dyestuffs, pharmaceuticals, and alkaloids. Acridone is one of the most fluorescent substances known, showing a blue-violet fluorescence in water or alcohol that changes to green on the addition of alkali.

An acridone derivative, quinacridone, which was developed as a dye in 1950s in Germany, is receiving great attention because of its stability and high fluorescent ability. Quinacridones have been used as emitters in LED's fabricated by chemical vapour deposition of the organic components[18]. Quinacridone with solubilizing branched alkoxy groups is soluble in organic solvent §§and forms stable hydrogen bonded aggregates. The aggregates emit intense orange-red photoluminesence (Figure 7-4)[19].

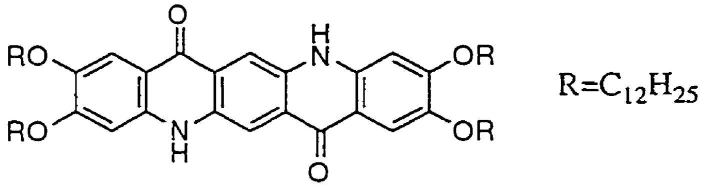
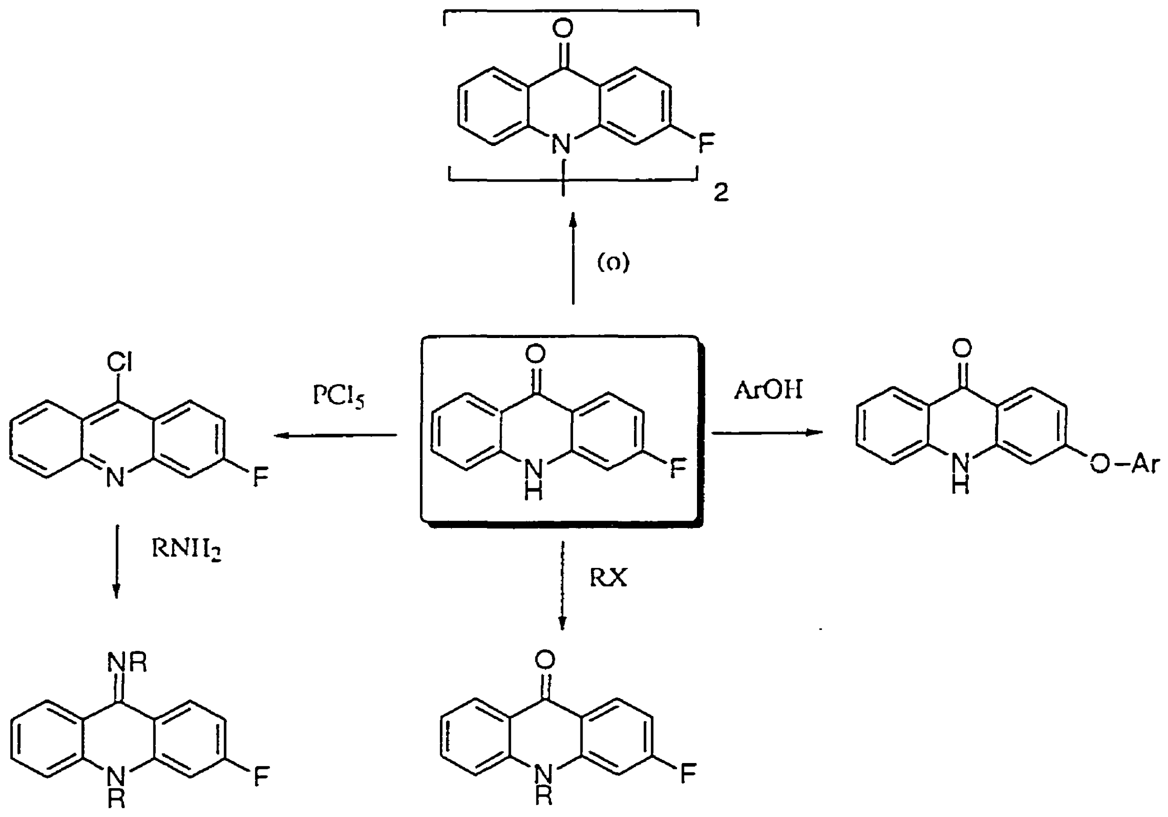


Figure 7-4 Quinacridone with Long Side Chains

7-2 Strategy and Goals

The objective of this chapter is the synthesis of novel fluorescent acridone containing polymers for LEDs. An acridone containing polymer is potentially an interesting material. It should be highly fluorescent and have processability. To incorporate the acridone moiety into polymer chains, chemical reactions on acridone were studied and the possibilities for a polymer forming reaction were explored. Despite its stability, many chemical reactions of acridone are known because it has amine and carbonyl functionalities (Scheme 7-1). Many reactions of acridone were studied in the beginning of 1900's and some of the compounds synthesized were not well-characterized. Model acridone compounds were synthesized to study the reactivity by model reactions. The most effective monomer structures were then designed. The monomers were subjected to nucleophilic aromatic displacement reactions to obtain high molecular weight acridone containing polymers.

Scheme 7-1



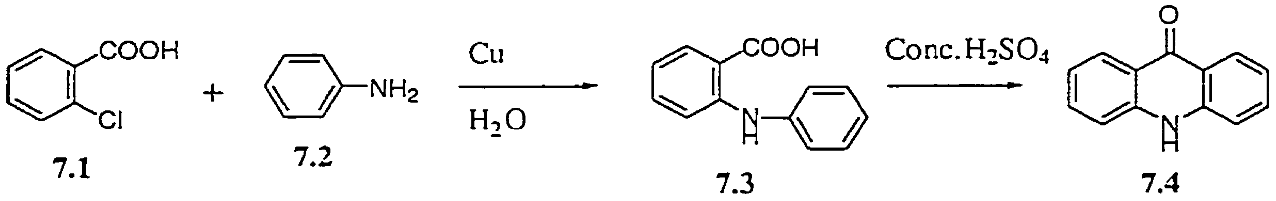
7-3 Preparation of Acridone Monomers

The most common method to prepare acridone compounds is cyclization of diphenylamine-2-carboxylic acids. Other methods are the Lehmstedt-Tanasescu (L-T method) route via phenylanthranils, cyclization of 2-amino-2'-fluorobenzphenones and the oxidation routes from acridines. Among them, §§°“‘§ß L-T method was chosen for the halogenated acridone because of starting material availability and synthetic ease.

7-3-1 The Cyclization of Diphenylamine-2-carboxylic Acid

Acridone derivatives are most commonly prepared by the cyclization of diphenylamine-2-carboxylic acids (Scheme 7-2). In the first step, diphenylamine-2-carboxylic acid **7.3** was synthesized by an Ulmann coupling reaction[20,21]. Chapman rearrangement of imino ethers has also been used but it is much less common[22]. The Ulmann condensation is the reaction of aryl halogenated compounds with phenols or aromatic amines using copper salts or other metals as catalysts[23]. *o*-Chlorobenzoic acid **7.1** was reacted with excess of aniline **7.2** in water in the presence of copper powder catalyst affording **7.3** in 70% yield. **7.3** was cyclized to acridone **7.4** by heating a solution of phenylanthranic acid **7.3** in concentrated sulfuric acid at 85°C for one-half hour[24]. Prolonged heating causes sulfonylation and reduction of the yield.

Scheme 7-2

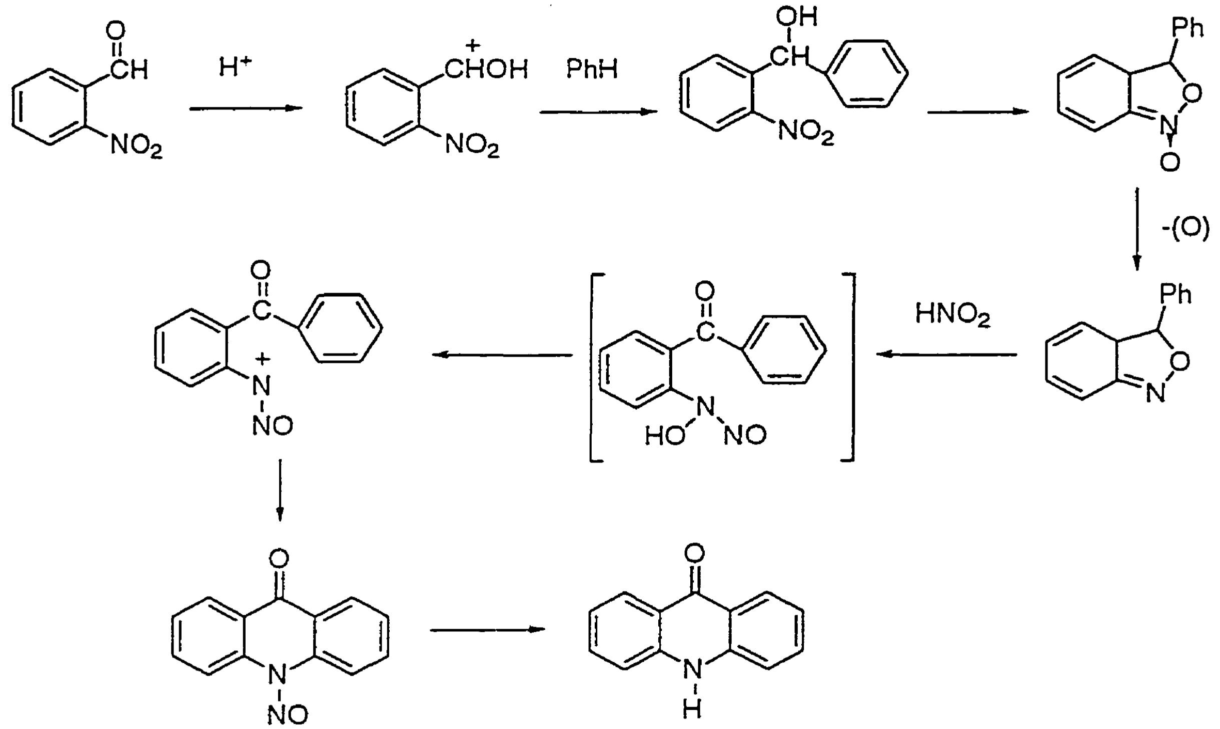


We attempted the synthesis of a substituted acridone (3-fluoroacridone) from 3-fluoroaniline and **7.1**, however, the yield on the first step was less than 10 % and two isomers, 2-fluoroacridone and 3-fluoroacridone were formed by the cyclization of the diphenylamine carboxylic acid.

7-3-2 Rearrangement of Phenylanthranils to Acridone (the Lehmstedt-Tanasescu Reaction)

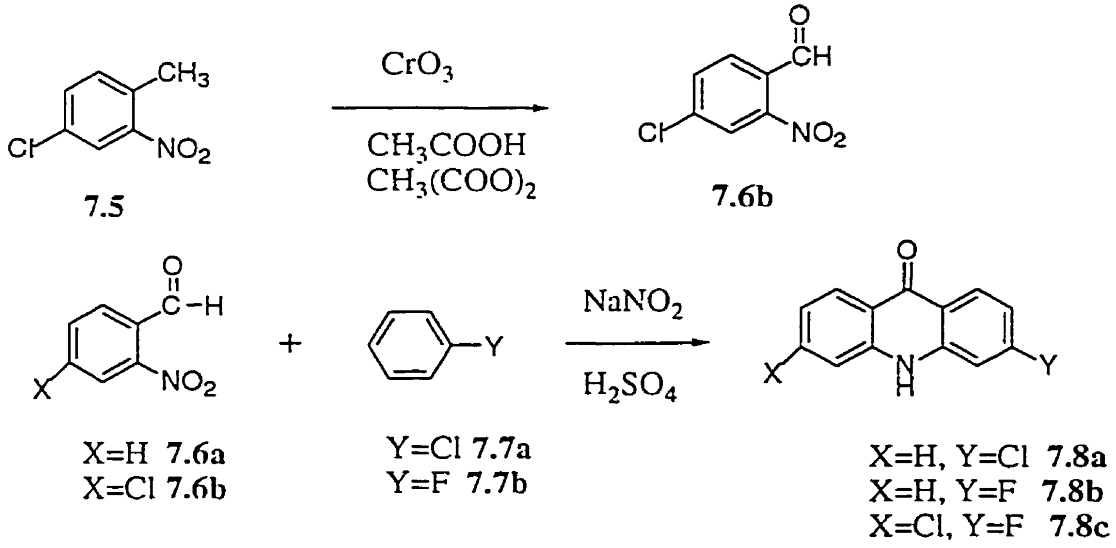
Acridone can be obtained from 2-nitrodiphenylmethane, 2-nitrobenzophenone, phenylanthranil, or 2-nitrobenzaldehyde[25]. Reactions of o-nitrobenzaldehydes with benzene and concentrated sulfuric acid give 3-phenylanthranyls[26]. On strong heating or treatment with nitrous acid at room temperature they rearrange to acridones. A mechanism for the reaction is shown in Scheme 7-3. It starts with a protonation of the aldehyde followed by an electrophilic attack on benzene derivatives to form a benzhydrol which cyclizes to the phenylanthranyl. Phenylanthranyl rearranges to N-nitrosoacridone in the presence of nitrous acid which is formed from sodium nitrite. Loss of the N-nitroso group by acid gives acridone.

Scheme 7-3



Three halogen substituted acridones 3-fluoro, 3-chloro- and 3-chloro-6-fluoroacridone were synthesized by the L-T reaction in 56-69 % yield[27] (Scheme 7-4).

Scheme 7-4



7.5

7.6b

X=H 7.6a
X=Cl 7.6b

Y=Cl 7.7a
Y=F 7.7b

X=H, Y=Cl 7.8a
X=H, Y=F 7.8b
X=Cl, Y=F 7.8c

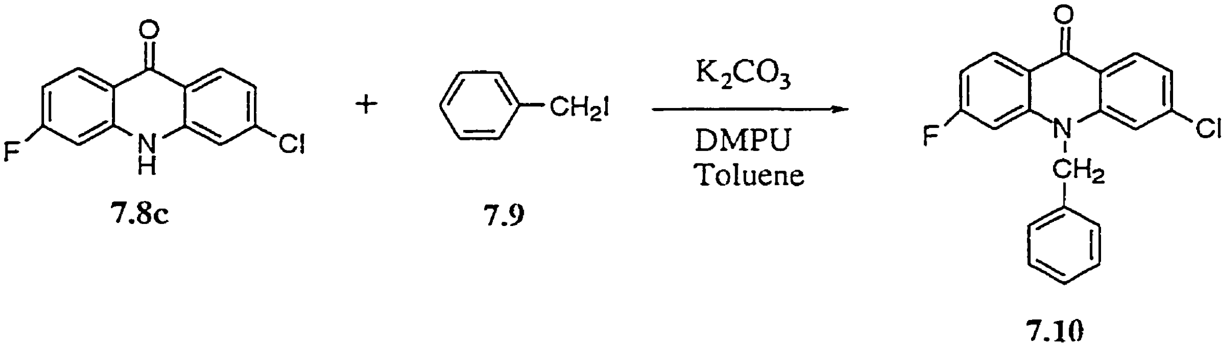
A typical synthesis follows. 2-Nitrobenzaldehyde **7.6a** was reacted with fluorobenzene **7.7b** in concentrated sulfuric acid overnight at 40°C in the presence of a catalytic amount of sodium nitrite. The viscous black liquid formed was poured into excess water. The resulting red brown powder was digested in benzene. Several recrystallizations did not remove the brown color. Sublimation removed the brown color to form a light yellow powder of 3-fluoroacridone **7.8b**.

7-3-3 N-Alkylation of Acridone

Several conditions for N-alkylation of acridone have been reported. For example, potassium hydroxide in DMF[28] or potassium hydroxide with a phase transfer catalyst in two phase water-toluene system[29] have been reported. Under these conditions, yields are not high and long reaction times or high temperatures are needed. We studied N-alkylation of acridone to find an effective N-protection and a possible polymerization reaction.

HMO calculations suggest that the 3-chloro group on NH protected acridone may be reactive in nucleophilic aromatic displacement reactions (Section 7-4-1). In the N-alkylation of acridone, methylation and benzylation proceed in good yield. HMO calculations suggest that the chlorine on the 3-position of N-benzylacridone is more reactive than that on N-methylacridone (Table 7-1). We therefore attempted to synthesize N-benzyl-3-chloro-6-fluoroacridone **7.10**. Commercially available 4-chloro-2-nitrotoluene **7.5** was oxidized to 4-chloro-2-nitrobenzaldehyde **7.6b** by chromic anhydride in a mixture of glacial acetic acid and acetic anhydride in 56% yield. **7.6b** was cyclized to 3-chloro-6-fluoroacridone **7.8c** in concentrated sulfuric acid in the presence of sodium nitrite at 40°C for six days in 58% yield (Scheme 7-4). Crude **7.8c** was deprotoated by anhydrous potassium carbonate in DMPU and formed water was removed by azeotropic distillation with toluene. Then the acridone salt was reacted with benzyl iodide **7.9**, which was made from benzyl chloride by a halogen exchange reaction, at 120°C for 30 minutes affording N-benzyl-3-chloro-6-fluoroacridone **7.10** in 75% (Scheme 7-5). It is important to use benzyl iodide to obtain **7.10** in high yield.

Scheme 7-5

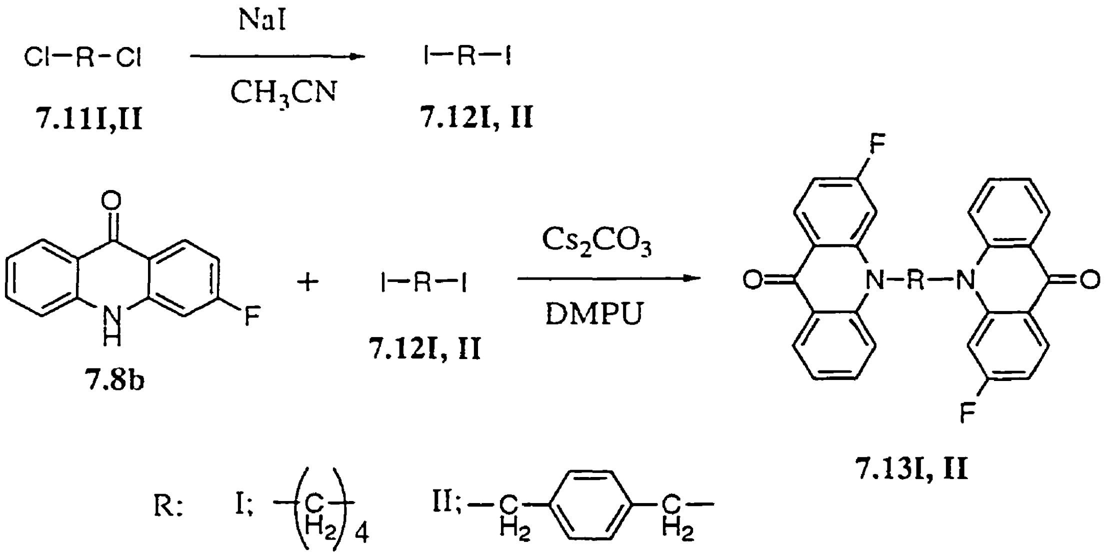


7.8c 7.9 7.10

7-3-4 1,4-Bis(3-fluoroacridonyl)butane and α,α'-bis(3-fluoroacridonyl)-*p*-xylene

To make a monomer containing the acridone moiety, two functionalities should be present in the molecule. A monomer which has two activated aromatic halides for the synthesis of poly(arylene ether)s can be made by linking two 3-fluoroacridone by an alkyl chain. Reactions of acridone potassium salt with diiodoalkanes gave bisacridone compounds in moderate yield under mild conditions[30].

Scheme 7-6



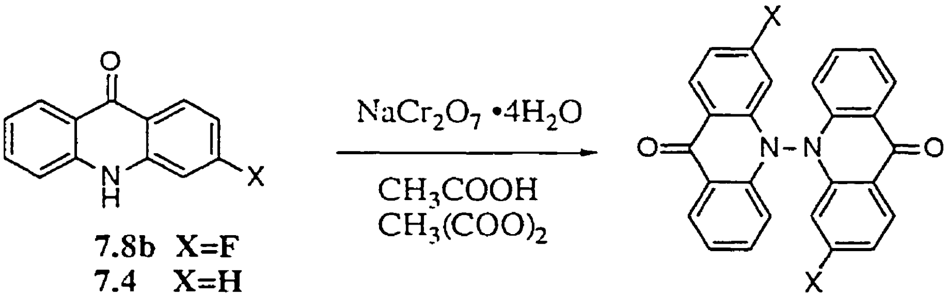
7.11I,II 7.12I, II 7.8b 7.12I, II 7.13I, II

As alkylating reagents, 1,4-diiodobutane and α,α'-diiodo-*p*-xylene were chosen. 3-fFuoroacridone **7.8b** was deprotonated by cesium carbonate in DMPU and the formed water was removed by azeotropic distillation. The acridone cesium salt was reacted with 1,4-diiodobutane **7.12I**, or α,α'-diiodo-*p*-xylene **7.12II**, which were made from dichloro compounds by halogen exchange. Very insoluble bisacridone monomers 1,4-bis(3-fluoroacridonyl)butane **7.13I** and α,α'-bis(3-fluoroacridonyl)-*p*-xylene **7.13II** were obtained in 67% and 92% yield, respectively.

7-3-5 10,10'-Bis(3-fluoroacridan)

10,10'-Bi-9-acridanonyl **7.14a** was obtained from 9- acridanone **7.4** by chromic acid oxidation. It was reported in 1893[31], however the characterization was limited. Derivatives are as yet not known. To introduce two reaction functionalities into the biacridone, the synthesis of 10,10'-bis(3-fluoroacridan) **7.14b** was attempted in the same way, i.e. chromic acid oxidation of 3-fluoroacridone **7.8b**. **7.8b** was oxidized by sodium chromate tetrahydrate in a mixture of glacial acetic acid and acetic anhydride (1:1) at 100 °C for 1 hour to give 10,10'-bis(3-fluoroacridan) **7.14b** as an orange powder which decomposes at 280°C (Scheme 7-7).

Scheme 7-7



7.8b X=F
7.4 X=H

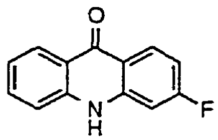
7.14a X=H
7.14b X=F

7-4 Attempted Polymerization of Acridone Monomers

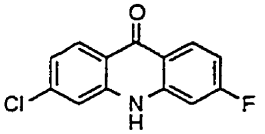
The reactivity of halogens on the 3-position of acridone in a nucleophilic aromatic displacement reaction was evaluated by HMO calculations and ^{19}F-NMR. Three types of monomers to be used the synthesis of poly(arytlene ether)s were then designed. The reactivity of the synthesized monomers were then studied by model reactions.

7-4-1 Nucleophilic Aromatic Displacement of Halogens on the 3-Position of Acridone

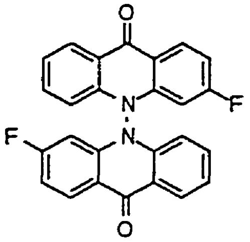
If halogens are placed in a position para to the carbonyl group, the 3- or 6-position of acridone compounds, they should be reactive in a nucleophilic aromatic displacement reaction because the carbonyl group is electron-withdrawing group and can stabilize the intermediate, the Meisenheimer complex. In 1,4-dihalogenoacridones the halogen, chlorine or fluorine, is displaced by anionic reagents under mild conditions[32,33]. As described in Chapter 1, the reactivity of fluorine atoms in nucleophilic aromatic displacement reactions by phenolate anions can be predicted qualitatively by the Huckel molecular orbital (HMO) molecular modeling program. Other workers have utilized ^{19}F-NMR for the evaluation of fluorine reactivity. The results for both methods appear in Table 7-1. 4,4'-Bis(4-fluorophenyl)sulfone **7.16** and 4,4'-bis(4-chlorophenyl)sulfone **7.17** are included for reference. The ^{19}F-NMR chemical shift of the fluorine on the 3-position of acridone appeared slightly upfield of **7.16**. The reactivity of the fluorine is almost as reactive as that of **7.16**. HMO calculations agreed with the ^{19}F-NMR results. The electron density at the 3-position carbon of **7.8b** is slightly less positive than the 4-position carbon of **7.16**. For unprotected acridone compounds, the prediction may be incorrect because the acridone NH proton is deprotonated under the reaction conditions. Benzimidazole which has an acidic NH group can activate fluorobenzene in nucleophilic aromatic displacement reactions[34,35]. The ^{19}F-NMR shift of fluorine at the 3-position of 10,10'-bisaridane **7.14b** is at lower field than that of **7.16** and the charge density of the carbon which has fluorine is less positive than **7.16**. Even though results indicated that there is a discrepancy between ^{19}F-NMR and HMO calculation method, the fluorine should be reactive toward a nucleophilic aromatic displacement reaction.



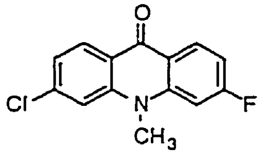
7.8b



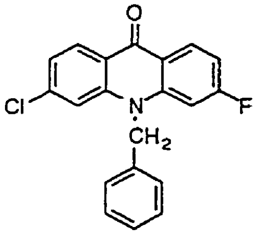
7.8c



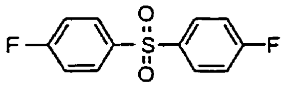
7.14b



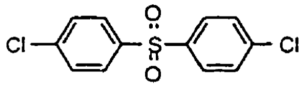
7.15



7.10



7.16



7.17

Table 7-1 ^{19}F-Chemical Shifts and HMO Charge Densities of Halogenated Acridone Derivatives

Compound	^{19}F-Chemical Shift[a] (ppm)	HMO Charge Densities[b]	
7.8b	-104.97	0.033	
7.8c	-104.93	0.033 (F)	0.012 (Cl)
7.14b	-102.22	0.028	
7.15	-	0.029 (F)	0.008 (Cl)
7.10	-104.89	0.028 (F)	0.012(Cl)
7.16	-104.08	0.035	-
7.17	-	-	0.014(Cl)

a) Chemical shifts are are referenced to fluorobenzene (-112.77 ppm)
b) Calculated charge density at the carbon atom adjacent to fluorine.

The charge density of the carbon, which has a chlorine group, attached on the 3-position of acridone (**7.8c**) was the same as that of the 4-position carbon of **7.17**.

If the acridone NH group is protected by an alkyl group, the reactivity of the halogens on aridone decreases. The ^{19}F-NMR chemical shifts shift upfield and the electron density becomes less positive. Compared with methyl protected acridone **7.15**, the electron density of the carbon which has chlorine of benzyl protected acridone **7.10**, is more positive and slightly less positive than that of **7.17**. They should still be reactive in a nucleophilic aromatic displacement reactions.

In summary, ^{19}F-NMR and the HMO calculations predict that the halogens on the 3-position of acridone should be reactive in nucleophilic aromatic displacement reactions. In the case of unprotected acridones, the reactivity is not clear because of deprotonation of NH even though both methods suggest the halogens are highly reactive. In the case of an alkyl protected acridone, the fluorines should be still reactive. However, HMO calculations predict that the reactivity of the chlorine is borderline. To displace chlorine on N-alkylacridones, high temperatures or longer reaction times may be needed.

To clarify the reactivities of halogens on the 3-position of acridone, model reactions were performed on **7.8a, b**. **7.8a,b** were reacted with preformed t-butylphenol alkali metal salt in a dipolar aprotic solvent. The fluorine was displaced quantitatively by potassium t-butylphenolate to form 3-(4-t-butylphenyl ether) acridone **7.19** in 18 hours at 200°C in sulfolane. The chlorine was unreactive in a nucleophilic aromatic displacement reaction by the phenolate anion.

Scheme 7-8

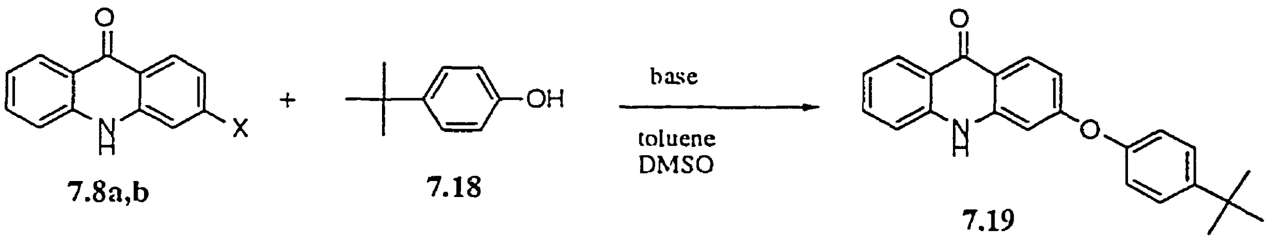


Table 7-2 Nucleophilic Aromatic Displacement on Acridone Derivatives by t-Butylphenolate

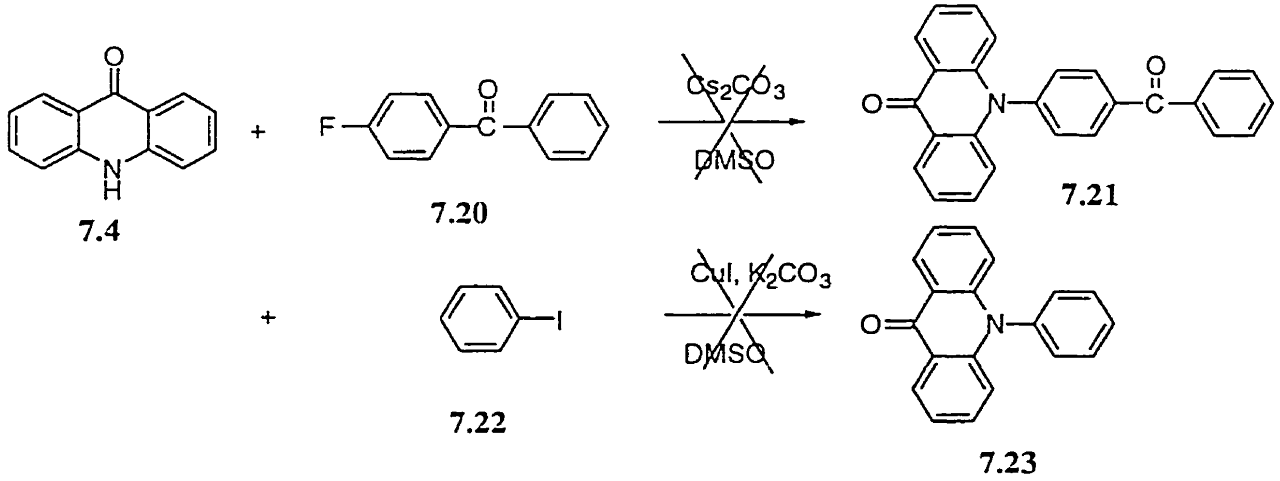
X	base	solvent	temp(°C)	yield (%)
F	K_2CO_3	DMAc	150	34
F	K_2CO_3	sulfolane	200	95
Cl	K_2CO_3	sulfolane	200	0
Cl	Cs_2CO_3	DMPU	250	<10
Cl	Cs_2CO_3	DPS	300	0

When a more reactive anion, cesium t-butylphenolate was reacted with **7.8b** at higher temperature in DPS or DMPU, no reaction took place. To displace the chlorine, the NH group of acridone must be protected.

7-4-2 Attempted N-Arylation of Acridone

The N-arylation of acridone was studied. There have been no reports of N-arylation of acridone in the literature. N-Arylacridone have been synthesized from the corresponding triphenylamine benzoic acid[34]. Acridone 7.4 was reacted with 4-fluorobenzophenone **7.20** in a dipolar aprotic solvent in the presence of a small excess of base (Scheme 7-9).

Scheme 7-9



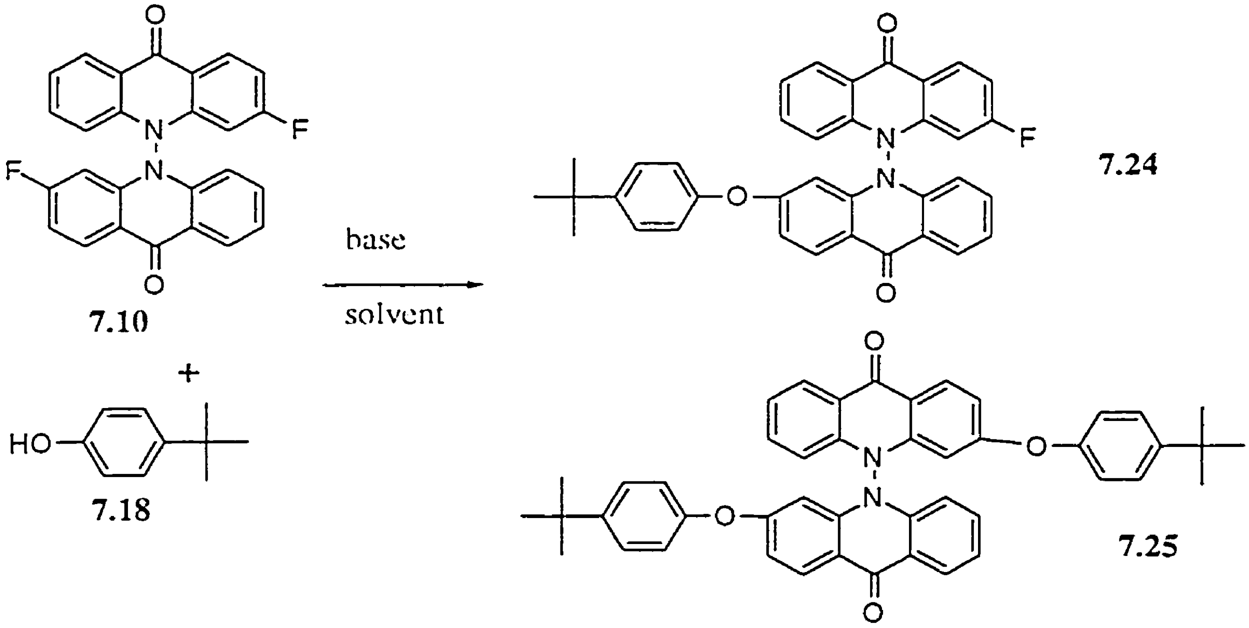
Potassium carbonate or cesium carbonate was used as a base, and DMSO (150°C), or DMPU (250°C) was used as a solvent. No reaction took place even when cesium carbonate, which gives a reactive aza anion, was used.

N-arylation under Ulmann reaction conditions was tried. Acridone was reacted with iodobenzene in the presence of copper catalyst and equimolar potassium carbonate. No reaction took place. The reactivity of the aza anion of acridone is presumably too low.

7-4-3 Nucleophilic Substitution on 10,10'-Bis(3-fluoroacridan)

7.10 was reacted with t-butylphenol **7.18** in a dipolar aprotic solvent in the presence of a base. Potassium carbonate was first used as a base at 150 °C in DMAc (Scheme 7-8).

Sheme 7-8



The reaction was followed by HPLC. The peak for **7.10** disappeared in 5 hours. Beside peaks for monosubstituted bisacridan **7.24** and disubstituted bisacridan **7.25**, decomposition product peaks appeared (Table 7-3).

Table 7-3 Nucleophilic Aromatic Substitution on **7.10** by t-Butylphenolate

Base	Solvent	Temp(°C)	Time (hr)	Conv. (%)[a]		
				7.24	**7.25**	Others
K_2CO_3	DMAc	150	5	34	5	61
Cs_2CO_3	DMSO	100	5	68	22	10
Cs_2CO_3	DMSO	100	18	55	1	44

a) Caluculated from HPLC peak area

To suppress side reactions, anhydrous cesium carbonate was used as a base and the reaction was run at 100°C. Because cesium phenolate is more reactive than potassium phenolate, the displacement took place at 100°C. However, decomposition peaks still appeared in 5 hours. If the reaction mixture was stirred for a longer time, the **7.24** peak decreased. Both **7.10** and **7.24** seemed to be unstable under the reaction condition. Polymerization with bisphenol A in DMSO in the presence of anhydrous cesium carbonate at 100°C was tried. A low molecular weight oligomer, with M_w less than 7000, was obtained. Copolymerization with 4,4'-bis(4-fluorophenyl)sulfone **7.16** under the same condition also formed only low molecular weight oligomer. Even though the reactivity of the fluorine on **7.10** is high, the bisacridan is unstable under the polymerization conditions and high molecular weight polymer could not be obtained.

7-4-4 1,4-Bis(3-fluoroacridonoyl)butane and α,α'-bis(3-fluoroacridonyl)-*p*-xylene

Both 1,4-bis(3-fluoroacridonoyl)butane **7.13I** and α,α'-bis(3-fluoroacridonyl)-*p*-xylene **7.13II** are very insoluble. Ghassemi synthesized high molecular weight polyimides from very insoluble monomers in a reaction that took 7 days[35]. In this polymerization, the product is soluble, and as the reaction proceeds, the reaction mixture gradually became homogeneous. The rate determining step is the dissolution of the monomer.

7.13I was reacted first with bisphenol A in DMAc in the presence of anhydrous potassium carbonate at 150°C. After the water formed by deprotonation of bisphenol A was removed by azeotropic distillation with toluene, **7.13I** was added.

Scheme 7-9

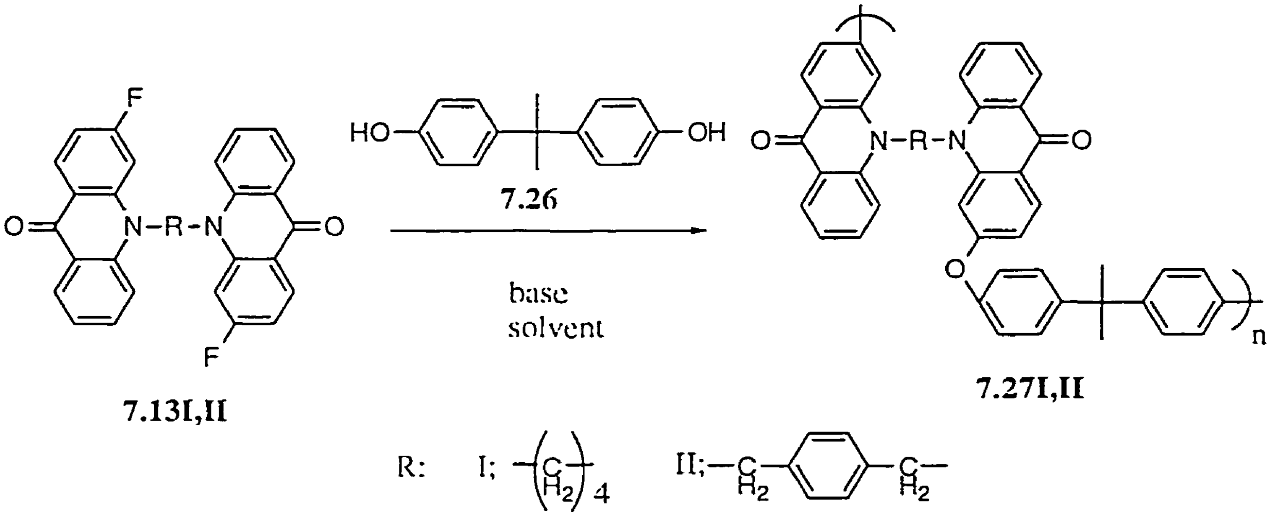


Table 7-4 Polymerization of 7.13I,II

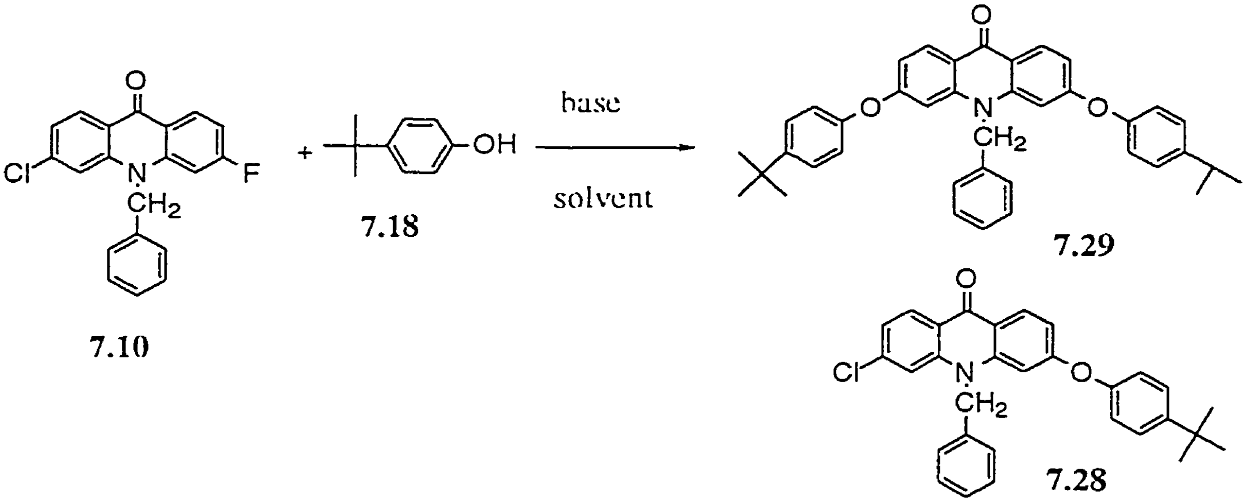
R	base	solvent	temp(°C)	time (hr)	yield (%)	
I	K_2CO_3	DMSO	150	24	-	dec.
I	Cs_2CO_3	DMSO	100	48	-	insoluble
I	Cs_2CO_3	DMSO	120	24	-	dec.
II	Cs_2CO_3	DMSO	120	48	-	insoluble
II	Cs_2CO_3	DMSO	140	48	-	dec.

The reaction mixture was a heterogeneous slurry and became gradually homogeneous in 24 hours. The inherent viscosity of the product in NMP is less than 0.1. The solubility of **7.13I** is so low that reaction did not take place and decomposition dominates over the displacement reaction. Lower temperature polymerization reactions were tried with cesium carbonate at 100°C to avoid the decomposition, but after 4 days no change was observed at this temperature since **7.13I** did not go into solution. After the temperature was increased to 120°C, the reaction mixture became homogeneous in 24 hours but the product obtained was very low molecular weight. **7.13II** was less soluble than **7.13I.** Almost the same results were obtained in the attempted polymerizations (Table 7-4).

7-4-5 N-Methyl-3-chloro-6-fluoroacridone

N-Methyl-3-chloro-6-fluoroacridone **7.13**, was reacted with t-butylphenol **7.24**, in sulfolane in the presence of potassium carbonate at 200°C. The bisubstituted product **7.29** was observed in HPLC. The displacement of chlorine at the 3-position of acridone takes place if the acridone NH group is protected.

Scheme 7-10



However, it reacted very slowly and after 48 hours monosubstituted product **7.28** was still detected by HPLC. In addition, some decomposition product peaks were observed. A more reactive system was therefore tried to shorten the reaction time.

7.10 was reacted with **7.18** in the presence of anhydrous cesium carbonate in DMPU at 200°C. The reaction was fast but **7.28** was still left in the reaction mixture and decomposition could not be avoided after 48 hours.

Table 7-5 Nucleophilic Aromatic Displacement on **7.10** by **7.18**

base	solvent	temp(°C)	time (hr)	conv.[a]		
				7.28	7.29	ohers
K_2CO_3	sulfolane	200	48	40	36	24
Cs_2CO_3	DMPU	200	24	48	18	34
Cs_2CO_3	DPS	250	24	61	31	8
Cs_2CO_3	DPS	250	48	75	8	17
$Cs_2CO_3/CaCO_3$	DPS	250	24	66	34	0
$Cs_2CO_3/CaCO_3$	DPS	250	48	85	7	2

a) Conversion; calculated from HPLC peak area

A mixed metal carbonate cesium carbonate/ calcium carbonate was next used for the nucleophilic aromatic substitution. In this system, calcium carbonate will react with fluoride anion and form calcium fluoride which is insoluble in a dipolar aprotic solvent. Fluoride anion is known to cleave aryl ether linkages at high temperature, so addition of calcium carbonate should remove the fluoride anion from the system and suppress the side reactions. The cesium carbonate/ calcium carbonate system gave an improved yield of **7.29**. After 48 hours a conversion of 85 % was achieved (Table 7-5).

Scheme 7-11

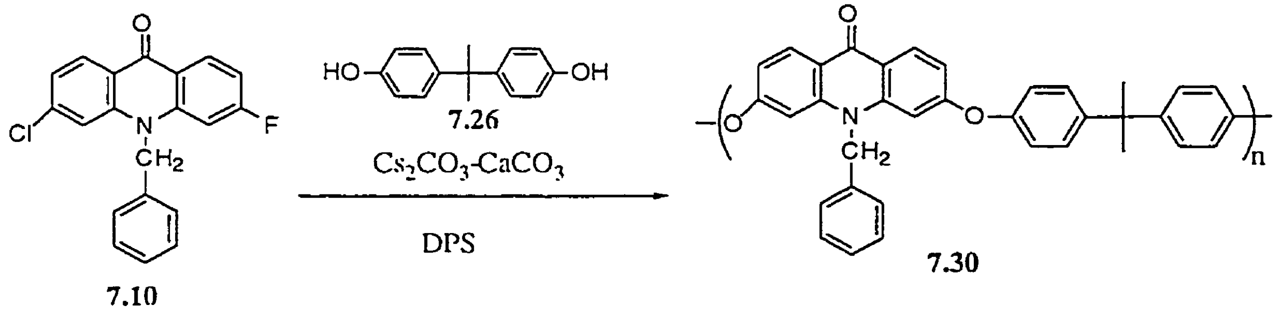


Table 7-6 Polymerization of **7.10**

solvent	temp(°C)	time (hr)	η_{inh}	M_w	M_n	PD
DPS	250	24	0.12	5900	3300	1.78
DPS	250	48	0.15	6800	2500	2.72
DPS	300	8	0.11	6300	2400	2.63

The polymerization with bisphenol A under the same condition was carried out (Scheme 7-11). An oligomer with inherent viscosity 0.15 in NMP was formed (Table 7-6). The reactivity of the chlorine in this molecule is apparently not high enough to form a high molecular weight polymer.

7-5 Conclusions

Novel acridone containing monomers were designed and synthesized. The reactivity of halogens on acridone to be used for nucleophilic aromatic displacement reactions was estimated by HMO calculations and ^{19}F-NMR of model compounds. The reactivity was then evaluated by model reactions. The fluorine on the 3-position of acridone can be displaced quantitatively by phenolate anion in a dipolar aprotic solvent. Chlorine on the 3-position of acridone is unreactive but if the acridone NH group is protected by alkyl group, it can be displaced by the cesium salt of t-butylphenol in high yield.

Three kinds of bis(3-fluoroacridone) monomers were synthesized and subjected to nucleophilic aromatic displacement polymerizations. The monomers and the displaced products are unstable under the polymerization conditions. High molecular weight polymers could not be obtained. N-benzyl-3-chloro-6-fluoroacridone was synthesized and subjected to a nucleophilic aromatic displacement polymerization. The chlorine reactivity was not high enough to form high molecular weight polymers.

7-6 Experimental

General Methods.

Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. The ^{1}H and ^{13}C-NMR spectra were recorded in DMSO-d_6 solutions on a JEOL 270 instrument, and results are reported in ppm from tetramethylsilane on the δ scale. The coupling constants were assigned by assuming first-order specra were obtained. Low-resolution mass spectra were obtained on a VGZAB-HS spectrometer, ion source at 240°C and with 70-eV electron impact, direct inlet: *m/z* (assignment). Elemental analysis were performed by Galbraith Laboratories Inc. IR spectra were performed on a Analet AQS-60 FTIR spectrophotometer. HPLCs were performed on a Milton Roy CM4000 system equipped with a Lichrosphere 5 RP18e reverse phase column and methanol was used as the eluent.

Polymer Characterization

Gel permeation chromatography (GPC) analyses were performed on a Waters 510 HPLC equipped with 4 phenogel columns (1xlinear, 3x500Å). $CHCl_3$ was used as the eluent and the UV detector was set at 254 nm. Inherent viscosities were measured in $CHCl_3$ at 25.0±0.1 °C using an Ubbelhode viscometer.

Materials.

o-Chlorobenzoic acid, 2-nitrobenzaldehyde, sodium nitrite, sodium chromate tetrahydrate, 1,4-dichlorobutane, α,α'-dichloro-*p*-xylene, sodium iodide, t-butylphenol, 4-chloro-2-nitrotoluene were purchased from Aldrich Chemical company and used as received. 1,3-dimethyl-3,4,5,6-tetrahydro-2-(1H)-pyrimidinone (DMPU), dimethylsulfoxide (DMSO) were dried over 4Ä molecular sieves for at least 48 hours prior to use. Diphenyl sulfone (Aldrich) was recrystallized from 95% ethanol.

Synthesis

N-Phenylanthranilic acid. (7.3)

A mixture of 46.95 g of o-chlorobenzoic acid (0.30 mol) and 55.88 g (0.60 mol) of aniline and 1.5 g of copper powder was refluxed in water (180 mL) for 5 hours. The reaction mixture was cooled and made alkaline with 5% aqueous potassium hydroxide solution. The mixture was extracted with diethyl ether and acidified with 16 % hydrochloric acid. The solid was filtered and washed, extracted with boiling water and recrystallized from benzene; yield 44.14 g (69 %). m.p. 182-4°C (Lit. 184°C), ^{1}H-NMR (270MHz, DMSO-d_6) δ 6.77 (m, 1H), 7.09 (m, 1H), 7.20-7.39 (m, 6H), 7.91 (m, 1H), 9.63 (s, 1H)

Acridone. (7.4)

To a 250 mL round bottom three neck flask equipped with a mechanical stirrer and a thermometer, was added 12.06 g (0.566 mol) of N-phenylanthranilic acid and concentrated sulfuric acid (120 g). The reaction mixture was stirred for 45 minutes at 85 °C. It was cooled down to room temperature, then poured into 1L of crushed ice and left over night. The yellow powder was filtered, washed in water thoroughly until acid-free, dried and recrystallized from *m*-cresol; yield 7.75 g (70.1 %). m.p. 363.5°C (DSC), ^{1}H-NMR (270MHz, DMSO-d_6) δ 7.26 (t, J_2=7.91, 4H), 7.54 (d, J_2=8.15, 4H), 7.73 (t-d, J_2=7.68, J_3=1.49, 4H), 8.23 (d-d, J_2=7.55, J_3=1.22, 4H), 11.74 (s, 1H)

3-Fluoroacridone. (7.8b)

In a 500 mL round bottom flask, were placed 15.11g (0.10 mol) of 2-nitrobenzaldehyde and 0.35 g (0.005 mol) of sodium nitrite. Fluorobenzene (67.27 g; 0.70 mol) was added and the reaction mixture was stirred for 10 minutes to dissolve the solid components into fluorobenzene. 37.5 mL of concentrated sulfuric acid was added. The reaction mixture was stirred at 40°C for two days. The mixture was poured onto 500 mL of crushed ice- water. The dark brown solid was filtered and thoroughly washed with water until acid free. After air-drying , the dark brown powder was digested three times with benzene. The resulting brown powder was recrystallized from glacial acetic acid and then sublimed in vacuo; yield 12.45 g (56 %), m.p. 389 °C (DSC); cream color powder, ^{1}H-NMR (270MHz, DMSO-d_6) δ 7.10 (t, J_2=8.40, 1H), 7.22-7.31(m, 2H), 7.52 (d, J_2=8.40, 1H), 7.74 (t, J_2=6.94), 8.20-8.31 (m, 2H); MS (EI) (m/e, relative intensity %): 212.96 (M^+, 100), 184,97 (15.0), 213.96 (14.6); ^{13}C-NMR (270MHz, DMSO-d_6), 102.56, 110.32, 118.21, 121.10, 126.58, 130.05, 134.18, 141.56, 142.90, 163.80, 167.47, 176.56. Analysis calc'd for $C_{13}H_8FNO$: C, 67.99; H, 3.51; N, 6.10; found: C, 67.98 ;H, 3.32 ;N, 5.91

3-Chloroacridone. (7.8a)

This material was prepared by a reaction of chlorobenzene and 2-nitrobenzaldehyde in conc. sulfuric acid in the presence of a catalytic amount of sodium nitrite using the procedure described above for 3-fluoroacridone; yield 59%, yellow powder, m.p. 398.8 °C (DSC), MS (EI) (m/e, relative intensity %): 229.03 (M^+, 100), 184,95 (13.0), 230.06 (11.1); ^{1}H-NMR (270MHz, DMSO-d_6) δ 7.22–7.31 (m, 2H), 7.44-7.60 (m, 2H), 7.74 (m, 1H), 8.19 (m, 2H), 11.79 (s, 1H). Analysis calc'd for $C_{15}H_6ClNO$: C, 68.88; H, 3.78; N, 6.57; found: C, 72.88 ;H, 3.68 ;N, 6.43

4-Chloro-2-nitrobenzaldehyde. (7.6b)

A 2-liter three-necked flask equipped with a mechanical stirrer, a thermometer adapter fixed with a thermometer, and the flask immersed in a bath of ice and salt. These were added 570 mL of glacial acetic acid, 565 mL of acetic anhydride and 61.77 g (0.36 mol) of 4-chloro-2-nitrotoluene in the flask, and then slowly, with stirring, then was added 85 mL of concentrated sulfuric acid. The temperature of the mixture was held between 5 and 10°C while 100 g of chromium trioxide was added slowly over a 3 hour period. The reaction mixture, a viscous black liquid was poured into 8 L of crushed ice-water with stirring. The greenish black liquid was allowed to stand overnight and a white powder separated. The solid was filtered and washed with water until the washings were colorless. The product was suspended in 360 mL of 2% sodium carbonate solution and stirred for 1 hour; filtered and washed with water. The white powder was refluxed in 500 mL of petroleum ether, cooled down, and filtered. The same procedure was then repeated. The resulting white powder was air-dried. The yield of crude 4-chloro-2-nitrobenzaldehyde diacetate was 76.6 g. m.p. 114-117°C (Lit. 116°C). The aldehyde diacetate (42.59 g) was heated to reflux with 320 mL of water, 195 ml of concentrated HCl and 60 mL of ethanol for 5 hours. An orange colored oil separated. The mixture was cooled and the white powder that separated was filtered. The resulting crude aldehyde was recrystallized from diethyl ether and petroleum ether (1:1). yield 36.1g (54 %), m.p. 53-55 °C (lit. 58°C) ^{1}H-NMR (270MHz, DMSO-d_6) δ 7.88-8.08 (m, 2H), 8.49 (d, J_2=8.64, 1H)

3-Chloro-6-fluoroacridone. (7.8c)

Crude 2-nitro-4-chlorobenzaldehyde (18.5 g; 0.10 mol), fluorobenzene (78.7 g; 0.70 mol), 37.5 mL of concentrated sulfuric acid, and sodium nitrite (0.35 g) were stirred at 40 °C for six days. At the end of each two-day period (except the last) 10 mL of concentrated sulfuric acid containing 0.1 g of sodium nitrite was added to the reaction mixture. The mixture was poured into 500 mL of water . The water was decanted and the red brown powder was washed twice with 500 mL of water. The black residue was digested twice with 1L of benzene. The resulting brown powder was sublimed in vacuo; yield 12.45 g (56%), m.p. 389 °C (DSC); ^{1}H-NMR (270MHz, DMSO-d_6) δ 7.10 (t, J_2=8.40, 1H), 7.22-7.31(m, 2H), 7.52 (d, J_2=8.40, 1H), 7.74 (t, J_2=6.94), 8.20-8.31 (m, 2H); MS (EI) (m/e, relative intensity %): 246.92 (M^+, 100), 219.93 (27.9), 183.97 (30.8), 109.46 (29.5); ^{13}C-NMR (270MHz, DMSO-d_6), 102.56, 110.32, 118.21, 121.10, 126.58, 130.05, 134.18, 141.56, 142.90, 163.80, 167.47, 176.56. Analysis calc'd for $C_{13}H_7ClFNO$: C, 63.05; H, 2.85; N, 5.66; found: C, 63.33 ;H, 2.81 ;N, 5.46.

Benzyl iodide. (7.9)

This material was prepared by the reaction of benzylchloride with sodium iodide in acetonitrile at room temperature using the procedure described below for α,α'-diiodo-p-xylene; yield 78%, m.p. 14-18°C, ^{1}H-NMR (270MHz, DMSO-d_6) δ 7.09-7.52 (5H, m), 4.61 (2H, s)

N-Benzyl-3-chloro-6-fluoroacridone. (7.10)

To a 50 mL three neck flask, equipped with a stirbar, a thermometer, a nitrogen inlet, and a water cooled condenser, were added, 0.346 g (0.0025 mol) of anhydrous potassium carbonate, 1.238 g (0.005 mol) of crude 3-chloro-6-fluoro acridone , 6.77g (25 weight %), of DMPU and 10 mL of toluene. The mixture was refluxed at 120-130°C for 4 hours. Toluene was removed from the Dean-Stark trap. The mixture was cooled to room temperature. Benzyl iodide (0.005 mol; 1.109 g) was added and then the temperature was increased to 100°C in 30 minutes. The reaction mixture was stirred for 4 hours. After cooling down to room temperature, it was poured into 300 mL of water with a few drops of glacial acetic acid. The yellow precipitate was collected by filtration and dried. After purification by column chromatography (silca gel, ethylacetate, hexane 3:5) it was recrystallized from methanol; 1.00 g (59 %) of N-benzyl-3-chloro-6-fluoroacridone. m.p. 209-211°C, ^{1}H-NMR (270MHz, DMSO-d_6) δ 5.81 (s, 2H), 7.16 (d, J_2=7.43, 1H), 7.21-7.42 (m, 7H), 7.50 (d, J_2=12.6, 1H), 7.74 (s, 1H), 8.35 (d, J_2=8.64, 1H), 8.41 (t, J_2=7.16, 1H). ^{13}C-NMR (270 MHZ, DMSO-d_6) 49.70, 103.24 (d, $J_{2C\text{-}F}$=111.16), 111.28 (d, $J_{3C\text{-}F}$=92.6), 116.39, 119.53, 121.03, 122.95, 126.41, 127.98, 129.46, 130.74 (d, $J_{3C\text{-}F}$=45.28), 136.17, 139.93, 143.69, 144.63 (d, $J_{3C\text{-}F}$=49.41), 164.68, 168.31, 175.78, Analysis calc'd for $C_{20}H_{15}ClFNO$: C, 71.12; H, 3.88; N, 4.15; found: C, 71.04 ;H, 3.83 ;N, 4.15

1,4-diiodobutane. (7.12I)

1,4-dichlorobutane (12.70 g; 0.10 mol) was reacted with sodium iodide (59.96 g; 0.40 mol) in 300 mL of acetonitrile over night at room temperature. The light yellow slurry was filtered to remove sodium chloride. then the solvent was removed under reduced pressure. The yellow residue was dissolved in chloroform, filtered and washed in water. The organic layer was dried with anhydrous magnesium sulfate and chloroform was removed under reduced pressure. The liquid was vacuum distilled.; yield 24.1 g (78%), b.p. 66-73°C/ 15 mmHg

1,4-Bis(3-fluoroacridonoyl)butane. (7.13I)

To a 500 mL three-neck, round bottom flask, equipped with a Dean-Stark trap with a water cooled condenser, a nitrogen inlet, and a thermometer, were placed, 9.38 g (44 mmol) of 3-fluoroacridone, 8.15 g (25 mmol) of cesium carbonate, 50 mL of DMPU and 100 mL of toluene. The reaction mixture was refluxed for 2 hours. The water formed by deprotonation of the acridone NH was removed from the Dean-Stark trap. Toluene was then removed from Dean-Stark trap and the reaction mixture was cooled down to room temperature. 1,4-diiodobutane (6.198 g) was added. The temperature was raised gradually to 80°C with stirring. The reaction mixture was stirred at this temperature for 16 hours. The viscous dark brown liquid was poured over 800 mL of crushed ice-water. The resulting red brown powder was filtered and washed with water and then cold methanol. Recrystallization from 1,2-dichloroethane gave yellow-brown needles; yield 5.38 g (67 %), m.p. 281-284 °C ; ^{1}H-NMR (270MHz, DMSO-d_6) δ 2.09 (m, 4H), 4.55 (m, 4H), 7.22 (t, J_2=8.67, 2H), 7.39 (t, J_2=6.67, 2H), 7.80-7.97 (m, 6H), 8.37 (d-d, J_2=9.52, J_3=3.21, 2H), 8.42 (t-d, J_2=8.05, J_3=1.73, 2H)

α,α'-diiodo-*p*-xylene. (7.12I)

p-Xylylene dichloride (17.5 g ; 0.10 mol) and sodium iodide (59.96 g; 0.40 mol) were stirred in 200 mL of acetnitrile at room temperature over night. The solvent was removed under reduced pressure. The resulting white powder was washed with water, dried and recrystallized from ethanol; yield 30.8 g (86%), m.p. 180-182 °C, ^{1}H-NMR (270MHz, DMSO-d_6) δ 7.09-7.52 (4H, m), 4.61 (4H, s)

α,α'-Bis(3-fluoroacridonyl)-*p*-xylene. (7.13II)

To a 500 mL three-neck, round bottom flask, equipped with a Dean-Stark trap with a water cooled condenser, a nitrogen inlet, and a thermometer, were placed, 9.38 g (44 mmol) of

3-fluoroacridone, 8.15 g (25 mmol) of cesium carbonate, 50 mL of DMPU and 100 mL of toluene. The reaction mixture was refluxed for 2 hours. The water formed by deprotonation of acridone NH was removed from Dean-Stark trap. Toluene was removed from Dean-Stark trap, and the reaction mixture was cooled down to room temperature. 7.16 g (20 mmol) of α,α'-diiodo-*p*-xylene was added. The temperature was raised gradually to 150°C with stirring. The reaction mixture was stirred at this temperature for 1 hour. The viscous dark brown liquid was poured over 800 mL of methanol. The resulting light yellow powder was filtered and washed with water and dried. Recrystallization from NMP-methanol gave a slightly yellow powder; yield 9.73 g (92 %), m.p. 414 °C (DSC exothermic peak, decomposition); ^{1}H-NMR (270MHz, DMSO-d_6) δ 5.89 (s, 4H), 6.95 (d, J_2=8.89, 2H), 7.26 (m, 4H), 7.62–8.05 (m, 8H), 8.49 (m, 4H)

10,10'-Bis(3-fluoroacridone). (7.14b)

In a 100 mL round bottom flask, were placed 2.13 g (0.01 mol) of 3-fluoroacridone, 2.34 g (0.01 mol) of sodium chromate tetrahydrate, 10 mL of glacial acetic acid and 10 mL of acetic anhydride. The reaction mixture was heated to 90-100°C and stirred for 1 hour. The reaction mixture was cooled down to room temperature and poured into 400 mL of water to precipitate an orange powder. It was filtered and washed with water, and dried. Recrystallization from glacial acetic acid- methanol gave a yellow powder; yield 2.0 g (48%), m.p. 280-282°C (decomposition, exothermic peak in DSC), ^{1}H-NMR (270MHz, DMSO-d_6) δ 6.41 (d, J_2=9.13, 2H), 6.70 (d, J_2=8.40, 2H), 7.09-7.23 (m, 4H), 7.54 (m, 2H), 7.63 (m, 2H), 8.64 (m, 2H)

10, 10'-Biacridone. (7.14a)

This material was prepared by oxidation of acridone by chromic acid in glatial acetic acid using the procedure described above for 10,10'-bi(3-fluoroacridone). Yield 54%. m.p.

262-265 °C . ^{1}H-NMR (270MHz, DMSO-d_6) δ 6.91 (d, J_2=8.40, 4H), 7.44 (t, J_2=7.91, 4H), 7.63 (d-d, J_2=7.85, J_3=1.24, 4H), 8.48 (d-d, J_2=7.29, J_3=1.24, 4H)

3-(4-t-butylphenoxy)acridone. (Nucleophilic Substitution on Halogenated Acridone). (7.19)

To a round bottom three neck flask equipped with a stirbar, Dean-Stark trap with a water cooled condenser, a nitrogen inlet and a thermometer, were added 0.1502 g (1.0 mmol) of t-butyl phenol, and 0.2073 g (1.5 mmol) of anhydrous potassium carbonate in 1.90 g (30 weight %) of sulfolane and 10 mL of chlorobenzene. The mixture was refluxed for 3 hours and the water formed by deprotonation of t-butylphenol was removed by azeotropic distillation from the Dean Stark trap. After toluene was removed from the Dean Stark trap, the reaction mixture was cooled down to room temperature to give a dark brown viscous solution, to which 0.2132 g (1 mmol) of 3-fluoroacridone was added. The mixture was heated up to 230°C and stirred for 4 hours at this temperature. It was cooled down to room temperature, and then poured into 300 mL of methanol containing 2 drops of glacial acetic acid; yield 0.32 g (96 %), m.p. 293-298°C, ^{1}H-NMR (270MHz, DMSO-d_6) δ 1.31 (s, 9H), 6.78 (d, J_3=2.24, 1H), 6.94 (d-d, J_2=8.13, J_3=2.24, 1H), 7.16 (d, J_2=8.40, 2H), 7.23 (t, J_2=7.91, 1H), 7.41 (d, J_2=8.42, 1H), 7.52 (d, J_2=8.40, 2H), 7.68 (t, J_2=7.18, 1H), 8.20 (t, J_2=8.67, 2H), 11.59 (s, 1H)

Model Reaction on 10,10'-Bi(3-fluoroacridone).

To a round bottom three neck flask equipped with a stirbar, a Dean-Stark trap with a water cooled condenser, a nitrogen inlet and a thermometer, were added 0.1502 g (1.0 mmol) of t-butylphenol, and 0.1629 g (0.5 mmol) of anhydrous cesium carbonate in 2.35 g (30 weight %) of DMPU and 10 mL of toluene. The mixture was refluxed for 3 hours and the water formed by deprotonation of t-butylphenol was removed by azeotropic distillation from the Dean Stark trap. After toluene was removed from the Dean Stark trap, the reaction mixture was cooled down to room temperature to give a dark brown viscous solution, to which 0.2121 g (1 mmol) of 10,10'-bis(3-fluoroacridone) was added. The mixture was heated up to 100°C and stirred for 8 hours at this temperature. It was cooled down to room temperature, and then poured to 300 mL of methanol containing 2 drops of glacial acetic acid; yield 0.22 g (65 %)

Model Reaction on N-benzyl-3-chloro-6-fluoroacridone.

To a round bottom three neck flask equipped with a water cooling condenser, a nitrogen inlet, a thermometer, were added 0.300 g (0.002 mol) of t-butylphenol, 0.3378 g (0.001 mol) of 3-chloro-6-fluoroacridone, 0.3258 g (0.001 mol) of anhydrous cesium carbonate, and 0.200 g (0.002 mol) of calcium carbonate in 5.24 g (20 weight %) of diphenyl sulfone. The reaction mixture was heated up to 200°C and stirred at that temperature. The reaction was followed by HPLC. After 30 hours, the acridone peak disappeared. The reaction mixture was poured into 250 mL of methanol. The white powder obtained was recrystallized from DMF-water; yield 89% (0.518 g). m.p. 255-267°C, ^{1}H-NMR (270MHz, DMSO-d_6) δ 6.85 (d, J_2=8.89, 2H), 6.99 (d, J_2=8.63, 4H), 7.28 (m, 2H), 7.36 (s, 2H), 7.39 (d, J_2=8.89, 2H), 7.63 (s, 5H), 8.32 (d, J_2=8.63, 2H)

Polymer Synthesis.

A typical example is given as follows: To a 50 mL three-neck round bottom flask equipped with a magnetic syirrer bar and a nitrogen inlet, a water cooled condenser, were charged, 0.3371 g (0.001 mol) of N-benzyl-3-chloro-6-fluoroacridone, 0.3362 g (0.001 mol) of 2,2'-bis(4-hydroxyphenyl)hexafluoropropane, 0.1629 g (0.0005 mol) of cesium carbonate, 0.1001 g (0.0010 g) of calcium carbonate, and 3.75 g of diphenyl sulfone. The reaction mixture was heated to 200°C and stirred for 2 hours at this temperature. Then, the temperature was increased to 250°C and kept at that temperature for another 2 hours. The mixture was cooled down to about 60°C and 10 mL of chloroform was added. The chloroform solution was poured into 250 mL of acetone to precipitate the polymer, which was collected by filtration. The polymer was dissolved in 8 mL of chloroform and filtered through a thin layer of celite and reprecipitated by pouring into 250 mL of methanol. The polymer was collected by filtration and dried at 100°C under reduced pressure for 20 hours.

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Contributions to Original knowledge and Future Work

Heterocyclic polymers are well-known for their excellent thermooxidative stabilities and good mechanical properties. In addition, functional heterocyclic polymers, such as conductive polymers, fluorescent polymers, have received a great deal of attention. The objective of this research was the development of new heterocyclic monomers and their polymerizations to form high molecular weight novel heterocyclic polymers.

In chapter 2, the synthesis of novel phthalazinone monomers to be used for nucleophlic aromatic displacement polymerization reactions is described. A series of monomers, such as oxy-7-bis[1,2-dihydro-4-phenylphthalazinone], were synthesized from readily available compounds in three steps. The monomers were polymerized with activated aromatic dihalides, such as 4,4'-bis(4-fluorophenyl)sulfone in the presence of anhydrous potassium carbonate in a dipolar aprotic solvent. High molecular weight poly(phthalazinone)s with inherent viscosities of over 0.3 were obtained. The phthalazinone aza-nitrogen anions, which were formed via deprotonation by potassium carbonate, attack the activated aryl halides with elimination of fluoride to form N-C bonds. An AB-type phthalazinone monomer, 1,2-dihydro-4[4-(4-fluorophenylsulfonyl)phenyl]-1-oxo(2H)phthalazine was successfully copolymerized with bisphenol A to form high molecular weight random copolymers. This suggests that the reactivity of phthalazinone aza nitrogen anion is comparable to that of bisphenol A. The polyphthalazinones had high glass transition temperatures and excellent thermostabilities. Most of them were soluble in organic solvents.

In chapter 3, the synthesis of a series of new bisphenols and aryl halides containing the quinazolinone moiety is described. They were synthesized from inexpensive isatoic anhydride in three steps in good yield. They decomposed under the polymerization conditions and could not form high molecular weight polymers.

In chapter 4, the synthesis of three new quinazolinone diamines is described. They were synthesized from readily available compounds in good yield. Oxy-bis(1,4-

phenylene)bis[3-(4-aminophenyl)-1-oxo-quinazolin-2-yl] was unstable in solution and could not be purified to monomer grade. 2-(4-aminophenyl)-3-amino-4-quinazolinone did not form high molecular weight because of low reactivity of the 3-amino group and instability of the 2,3-diimide substituted quinazolinone. A series of high molecular weight polyimides containing the quinazolinone moiety were synthesized from 2-(4-aminophenyl)-6-amino-4-quinazolinone by either a one-step solution polymerization in *m*-cresol or *p*-chlorophenol in the presence of isoquinoline or a two-step procedure involving ring-opening polyaddition and subsequent thermal cyclodehydration. Polyimides with inherent viscosities of over 0.5 with very high glass transition temperatures and excellent thermal stabilities were synthesized. Films made from the polyimides had high moduli, 2.34-4.89 GPa, and maintained the high moduli to high temperatures.

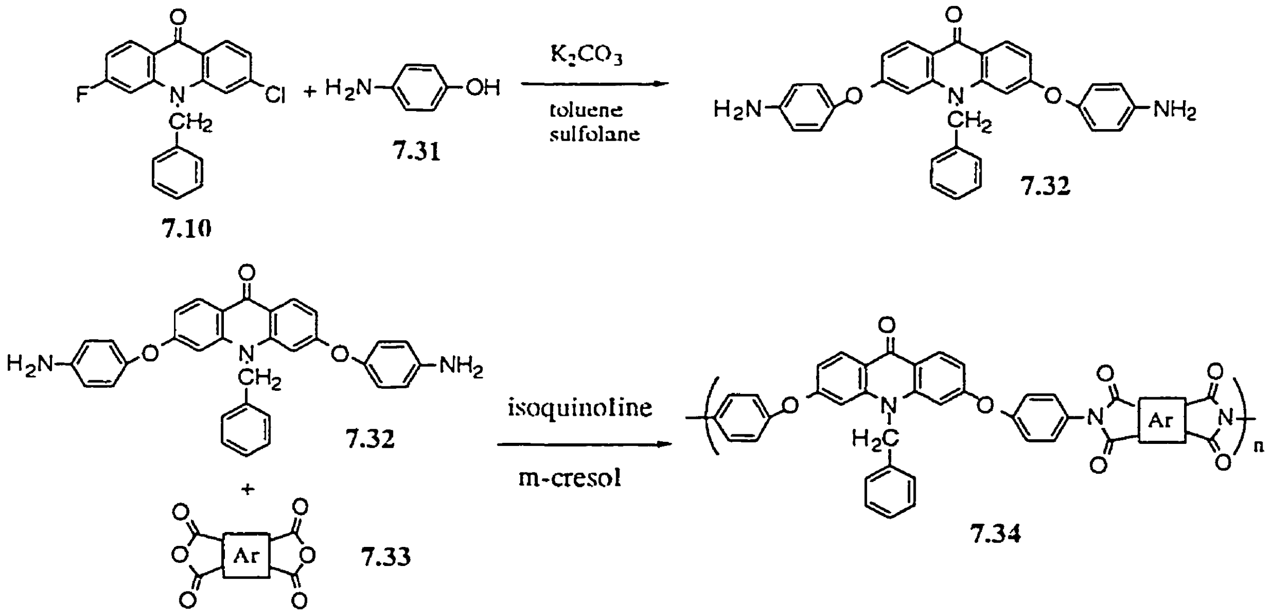
A new monomer 1,5-bis(4-fluorobenzoyl)naphthalene, which was synthesized from naphthalene and 4-fluorobenzoyl chloride by a Friedel-Crafts reaction, was polymerized with a series of bisphenols to form high molecular weight poly(arylene ether)s containing the 1,5-dibenzoyl unit. The poly(arylene ether)s had high glass transition temperatures and high thermostabilities. Some of the polymers were soluble in chlorinated solvents, such as chloroform because of the crank shaft like conformation of the 1,5-benzoyl unit.. Films made from the polymers had high moduli, 1.78-2.18 GPa, and maintained the high moduli to high temperatures.

The synthesis of dye containing polymers is of interest. A new dye monomer, 2,3;7,8-bis(4-fluorobenzo)pyrene-1,6-quinone, was synthesized by a Scholl reaction of 1,5-bis(4-fluorobenzoyl)naphthalene in antimony pentafluoride. It was subjected to a nucleophilic displacement polymerization reaction. Because of side reactions, only insoluble products formed.

In chapter 7, an attempted synthesis of fluorescent acridone containing polymers is described. A series of acridone model compounds and monomers were synthesized. Model reactions on acridone compounds were performed to find a high yield reaction which could be a polymer forming reaction. Fluorine on the 3-position of acridone was displaced by a phenolate anion quantitatively. Bifunctional acridone containing monomers, α,α'-bis(3-fluoroacridonyl)-*p*-xylene, 1,4-bis(3-fluoroacridonyl)butane, 10,10'-bis(3-fluoroacridone), N-benzyl-3-chloro-6-fluoroacridone, were synthesized. They were subjected to a nucleophilic aromatic substitution polymerization reaction by reactions with bisphenoxides. Because of the instability or low reactivity of the monomers, high molecular weight polymers could not be obtained.

Using the nucleophilic aromatic displacement of halogens on the 3-position of acridone, incorporation of an acridone moiety into polymer should be possible. **7.10** could be reacted with *p*-aminophenol **7.31** to form diamino compounds **7.32**, which could be polymerized with a series of dianhydrides 7.33 to form polyimides 7.34 (Scheme A).

Scheme A



Another possibility is the synthesis of side chain acridone polymers. 3-Fluoroacridone could be reacted with *p*-aminophenol to form **7.35**, which could be reacted with bisphenol anhydride **7.36** to form **7.37**. **7.37** could be reacted with activated arylhalides to give poly(arylene ether)s with the acridone side chain **7.38** (Scheme B).

Scheme B

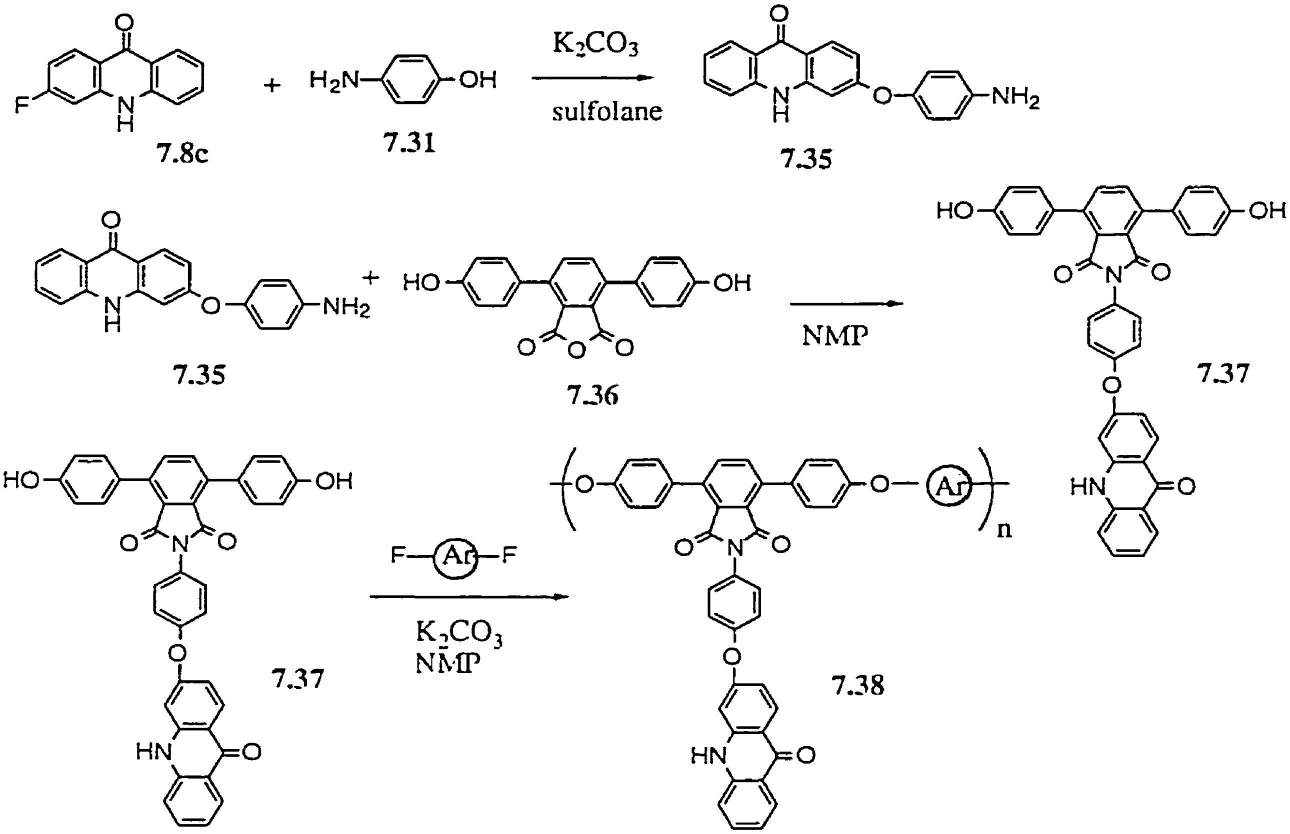
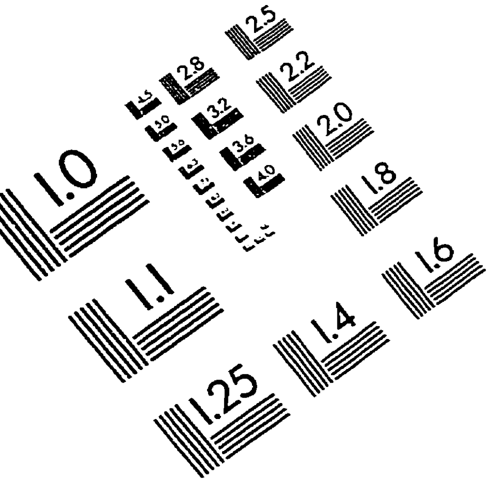
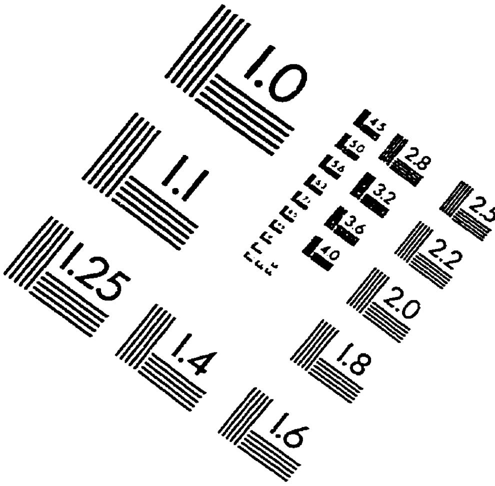
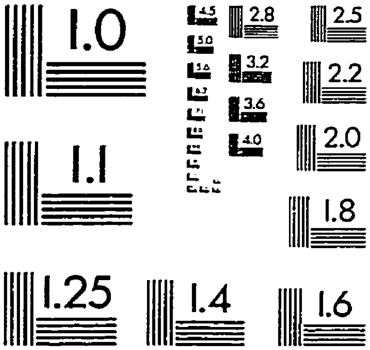
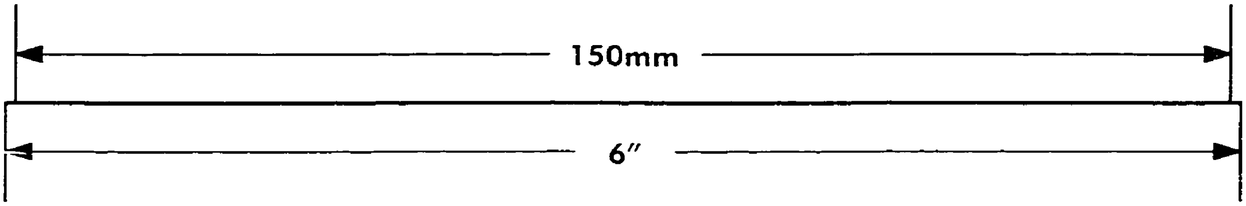
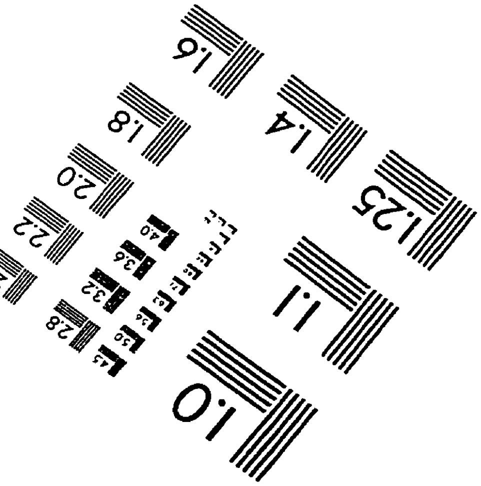
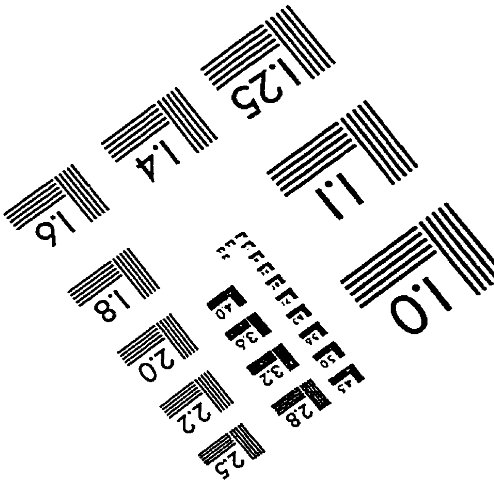


IMAGE EVALUATION
TEST TARGET (QA-3)



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