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# Preparation of polyimides from bisimide monomers via phase transfer catalysis

Sarifah Bt Rejab  
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**Preparation of polyimides from bisimide monomers *via* phase  
transfer catalysis**

Rejab, Sarifah Bt., M.S.

San Jose State University, 1989

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PREPARATION OF POLYIMIDES FROM BISIMIDE MONOMERS  
VIA PHASE TRANSFER CATALYSIS

A Thesis

Presented to

The Faculty of the Department of Chemistry  
San Jose State University

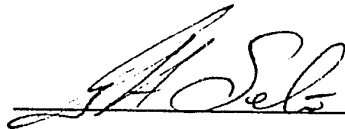
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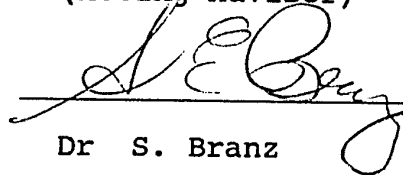
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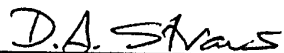
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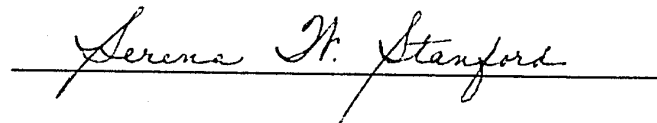


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## TABLE OF CONTENTS

ABSTRACT.....	ii
ACKNOWLEDGMENT.....	iii
LIST OF TABLES.....	vi
LIST OF FIGURES.....	vii
1. INTRODUCTION.....	1
2. HISTORICAL AND BACKGROUND.....	5
A. Phase Transfer Catalysis.....	5
B. Condensation Polymers.....	18
C. Polyimides.....	26
3. RESULTS AND DISCUSSION.....	33
A. Model Compounds and Monomers.....	38
B. Model Reactions.....	41
C. Attempted Polymerizations.....	58
4. EXPERIMENTAL.....	65
A. Materials.....	65
B. Equipment.....	66
C. Procedures.....	67
3-(Thiophenoxy)maleimide (40).....	67
3-p-( <u>t</u> -[Butyl]thiophenoxy)maleimide (43).....	68
3,3'-(1,5-Dimercaptopentane)bismaleimide (42a)....	68
3,3'-(1,6-Dimercaptohexane)bismaleimide (42b).....	68
3,3'-(1,8-Dimercaptooctane)bismaleimide (42c).....	69
3,3'-(1,10-Dimercaptodecane)bismaleimide (42d)....	69

Solvent studies for attempted preparation of $\alpha,\alpha'$ -bis(3-p-[t-butyl]thiophenoxymaleimide)- <u>m</u> -xylene (45).....	70
$\alpha,\alpha'$ -Bis(phthalimide)- <u>m</u> -xylene (50).....	72
Solvent studies for attempted preparation of 4,4'-bis(3-[thiophenoxy]maleimide)-perfluorobenzene (54).....	73
Attempted preparation of 4,4'-bis(3-p-[t-butyl]-thiophenoxymaleimide)perfluorobiphenyl (56).....	74
4,4'-Bis(succinimide)perfluorobiphenyl (52).....	75
$\alpha,\alpha'$ -Bis(3-[thiophenoxy]maleimide)- <u>m</u> -xylene (59)...	76
Attempted preparation of 4,4'-bis(3-p-[t-butyl]-thiophenoxymaleimide)perfluorobiphenyl (56) by using sodium salt.....	77
Attempted polymerization of 3,3'-(1,8-dimercapto-octane)bismaleimide with $\alpha,\alpha'$ -dibromo- <u>m</u> -xylene (68c).....	78
Attempted polymerization of 3,3'-(1,8-dimercapto-octane)bismaleimide with decafluorobiphenyl (65)...	78
Polymerization of sodium 3,3'-(1,6-dimercaptohexane)-bismaleimide with $\alpha,\alpha'$ -dibromo- <u>m</u> -xylene (68b).....	79
Polymerization of sodium 3,3'-(1,8-dimercaptooctane)-bismaleimide with $\alpha,\alpha'$ -dibromo- <u>m</u> -xylene (68c).....	80
Polymerization of sodium 3,3'-(1,10-dimercapto-decane)bismaleimide with $\alpha,\alpha'$ -dibromo- <u>m</u> -xylene (68d).....	80
Attempted polymerization of sodium 3,3'-(1,8-dimercaptooctane)bismaleimide with decafluorobiphenyl (65).....	81
5. REFERENCES.....	82

## LIST OF TABLES

### Table

1. Stability constants of crown-ether ion complexes in methanol at 25 °C.....11
2. The effect of water in polymerization reactions via PTC.....14
3. Polymerization reactions of bisimides with perfluoroaryl substrates under PTC conditions.....36
4. Bisimide monomers (42) synthesized via the Michael addition reaction.....40
5. Polymerization of sodium bisimides (67) with  $\alpha,\alpha'$ -dibromo-m-xylene (44).....60

## LIST OF FIGURES

### Figure

1. The effect of water on preparation of 6 in DMAC/toluene.....15
2. The effect of water on preparation of 8 in acetone.....15
3. Differential scanning calorimetry (DSC) scan showing a characteristic polymer glass transition temperature ( $T_g$ ) and crystalline melt temperature ( $T_m$ ).....25

## 1. INTRODUCTION

Nucleophilic aromatic substitution is an important and useful reaction in synthetic organic chemistry. Often these reactions involve ionic compounds and water-insoluble organic substrates. However, such reactions are slow, requiring high reaction temperatures and extended reaction times if they are to occur at all. The usual procedure involves dissolving the reactants in a reaction medium. If a hydroxylic solvent is used, the reaction may be slow because of extensive solvation of the nucleophilic anion. Polar aprotic solvents can alleviate this problem to some extent, but these solvents are usually expensive, hard to purify, and difficult to remove and recover.

These problems, and others, such as side reactions and product decomposition, can be avoided by using "phase transfer catalysis", (PTC).<sup>1-3</sup> This procedure involves two immiscible phases; one containing an ionic, nucleophilic salt (aqueous or solid state), and the other the organic (liquid organic phase) substrate. PTC permits or accelerates reaction between ionic compounds and organic, water-insoluble substrates in solvents of low polarity. A phase transfer catalyst is used to transport the nucleophilic anion into the organic phase in the form of an ion pair, thus allowing reaction to occur. PTC

offers the advantages of improved yields, faster reaction rates, lower reaction temperatures, increased selectivity and access to a reaction pathway that is not normally available under non-phase transfer catalyzed conditions.

Since its discovery, PTC has been used not only for nucleophilic displacement but also for addition, insertion, dehydration, alkylation, oxidation and reduction reactions as well as in polycondensation reactions.<sup>4</sup>

This work will focus on the application of PTC to polymer chemistry. The first reported work on PTC in polymer chemistry was in anionic addition polymerization.<sup>1</sup> Only recently has there been a focus on condensation polymers. The condensation polymerization of bisphenol-A with phosgene to form polycarbonate is one of the most important industrial applications of PTC.<sup>5</sup>

Kellman and co-workers at the University of Texas, San Antonio have shown that high molecular weight polymer can be prepared under mild solid-liquid PTC conditions. Until their research, the use of solid-liquid PTC for polymerization had received little attention. They began a broad investigation on solid-liquid PTC by examining nucleophilic aromatic substitution. Model studies were

performed in order to determine the optimum conditions for polycondensation. They successfully synthesized fluorinated polyaryl ether sulfones<sup>6,7</sup>, fluorinated polyarylsulfides and polyarylethers.<sup>7,8</sup>

The research reported herein investigates further the condensation polymerization of fluorinated substrates (hexafluorobenzene, decafluorobiphenyl) with bithioalkyl maleimides (of different chain length) as nucleophiles by PTC aromatic substitution. Our goal is to prepare polyimides, an important class of condensation polymers known for high strength and high temperature resistance. However, the most common problem associated with polyimides is insolubility. Various efforts are being made to overcome this problem.<sup>9-11</sup> Our approach is to modify the polymer structure by introducing flexibility into the monomer unit, which should improve polymer solubility. Model studies are conducted to determine the feasibility of our approach. Using the optimized conditions determined from model studies, we anticipate synthesizing polyimides which might have better solubility properties.

In both model reactions and the polymerization reactions, the products and their substitution patterns provide insight into the synthetic utility of the PTC reaction. This research has demonstrated the use of PTC

in polycondensation reactions in which novel polymers of theoretical and practical interest have been successfully synthesized and characterized.

We wish to report here some results of our ongoing investigations.



## 2. HISTORICAL AND BACKGROUND

### 2.A. Phase Transfer Catalysis

The first examples of the application of phase transfer catalysis (PTC) were described by Jarrouse in 1951.<sup>12</sup> PTC, as we know it today, was originated from the independent and simultaneous work of three workers. In 1965 Makosza developed many fundamental aspects of PTC technology.<sup>13</sup> Starks characterized the mechanism and coined a name for it, <sup>14,15</sup> while Brandstrom studied the use of stoichiometric amounts of quaternary ammonium salts "and aprotic solvents," in ion-pair extraction.<sup>16</sup>

Phase transfer catalysis facilitates the transport of an organic and inorganic salt from a solid or aqueous phase into an organic liquid phase where reaction with an organic-soluble substrate occurs.<sup>17</sup> It permits or accelerates reaction between ionic compounds and organic, water insoluble substrates in solvents of low polarity.<sup>3</sup>

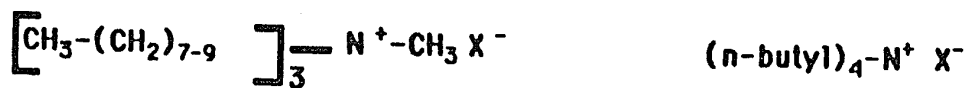
PTC involves two immiscible phases. One of these phases, often aqueous, contains a reservoir of the salt expected to function as either a base or nucleophile. The second phase is an organic phase and contains the substrate which is expected to react with the salt. In the absence of interfacial phenomena, no reaction is observed. A phase transfer catalyst is added to this system in a



metathesize with the nucleophile salt  $M^+Nu^-$ , thus completing the cycle.

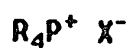
In general, the solvents used in this system should be immiscible with water. Otherwise, highly hydrated, "shielded" ion pairs of low reactivity are present. Solvents such as hydrocarbons and chlorinated hydrocarbons are used to avoid hydrogen bonding to the ion-pair anion. Therefore, the solvent chosen should be aprotic. As with any other reactions, in PTC side reactions involving the solvent have to be taken into consideration. For instance, in reactions involving acids and bases or strong nucleophiles, chloroform is readily deprotonated to yield either trichloromethide anion or dichlorocarbene,<sup>13</sup> while dichloromethane often suffers nucleophilic displacement.<sup>18-20</sup> However, most PTC reactions are so fast that reaction with solvent is not a problem.

For liquid-liquid PTC, the most commonly used onium ions are quaternary ammonium salts (1, 2) and a wide variety of phosphonium salts (3).<sup>18</sup>



1

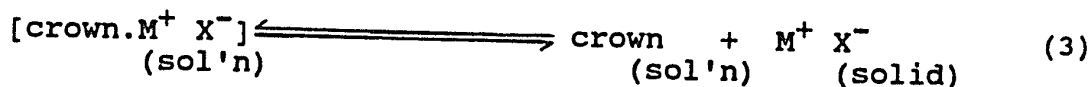
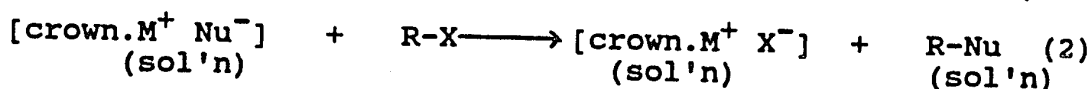
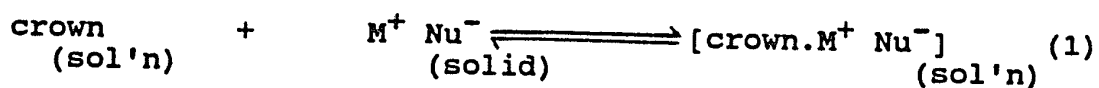
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3

In the case where the second phase is a solid, the system is referred to as solid-liquid PTC. In this system, an organic substrate is dissolved in an organic solvent, and this solution is placed in contact with a solid reagent. The phase transfer catalyst used for this system is usually a crown ether that will form a soluble cationic complex with the solid salt (Eq. 1). This cation-complexed ion pair then becomes soluble in the organic phase where the reaction with the substrate takes place (Eq. 2). After this occurs, the crown-cation complex picks up exchange anion ( $X^-$ ) and returns it to the solid phase, repeating this function catalytically (Eq. 3). The whole process is illustrated in Scheme II.

## SCHEME II



The success of solid-liquid PTC depends on several factors.<sup>21</sup> First, the catalyst chosen must be capable of forming a complex with the solid reagent. Second, the complexed salt must be soluble in the reaction medium.

Finally, the equilibrium between the crown-cation complex and the anionic leaving group must be such that anions can be readily exchanged (Eq. 3). The activity of the anionic nucleophile depends on the choice of solvent, when factors such as the nature of catalyst, the substrate, the nucleophile, and the leaving group are kept constant. In general, reactions are faster in solvents of greater dielectric constant,<sup>22</sup> in which the reactive ion pairs are more readily separated.

The effectiveness of crown ethers or macrocyclic polyethers as PTC catalysts lies in their ability to complex with a wide variety of cationic substrates such as alkali metal cations, alkaline earth cations and ammonium ions.<sup>23</sup> Therefore in PTC, once the salt is in the organic phase, the anion is shielded from the positive charge of the cation. This cation-complexation leads to solvent-separated or free ion pairs.<sup>24</sup> As a result, the anions generated in phase transfer catalysis are highly nucleophilic compared to those solubilized in aqueous media.

Generally it was thought that the catalyst's ability to complex a particular cation was dependent on "hole size relationship" properties. For example, 15-crown-5 was thought to be selective for  $\text{Na}^+$  over cations since its hole size is similar to sodium's cation diameter. 18-Crown-6 was believed to be more selective toward

potassium cation for the same reason. Gokel et al.,<sup>25</sup> in their studies on the cation-binding properties of crown ethers (Eq. 4), discovered that 18-crown-6 is the best cation binder among the five ligands studied and that all of the five ligands bind  $K^+$  more strongly than any of the cations studied. This study showed that the cavity size of the macrocyclic polyethers doesn't effect the cation selectivity. The results obtained from their studies are shown in Table 1.



$M^+$  = metal cation

L = ligand

The equilibrium constant for the above process (Eq. 4),  $K_s$ , is called the stability or binding constant. The results from Table 1 show that  $K_s$  for 15-crown-5. $Na^+$  is 3.24 compared with 3.43 for 15-crown-5. $K^+$ .

Even though crown ethers have generally been shown to be the best catalysts for solid-liquid PTC, there are cases where quaternary ammonium salts prove to be more efficient than 18-crown-6. The argument given for the effectiveness of 18-crown-6 as a catalyst for solid-liquid PTC is that crown behaves as a two-dimensional system with multiple polar sites which can approach a crystal lattice

TABLE 1

Stability constants of crown ether-ion complexes in methanol at 25°C.

Crown	Na <sup>+</sup>	Log K <sub>s</sub> in MeOH		
		K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Ca <sup>2+</sup>
12-cr-4	1.7	1.74	1.3	----
15-cr-5	3.24	3.43	3.03	2.36
18-cr-6	4.35	6.08	4.14	3.90
21-cr-7	2.54	4.35	3.27	2.80
24-cr-8	2.35	3.53	2.63	2.66

so closely that the required movement of the cation from the lattice to the ligand is small.<sup>21</sup> Quaternary ammonium salts, on the other hand, have a sterically shielded positive central atom, and therefore cannot approach the lattice closely.

There is no satisfactory explanation given as to why quaternary salts behave more efficiently in some cases than 18-crown-6. However, the catalytic process that takes place for both quaternary ions and crown-complexes is similar; that is, the dissolved ion pair simply exchanges anions on the surface of the crystal lattice.

Previous work in solid-liquid systems showed that a trace amount of water is actually necessary for nucleophilic displacement to occur. An investigation on the effect of water in polymerization via phase transfer catalysis has been performed by Kellman and co-workers.<sup>26</sup> A series of polymerizations catalyzed (18-crown-6; 27.7 mole-%) and uncatalyzed were conducted in which the water content was increased incrementally (Eq. 5, 6).

The results obtained from both studies showed that the optimal water content is critical for producing highly viscous polymer (see Table 2). Figure 1 and 2 show plots of polymer viscosity versus mole ratio of water to catalyst in the formation of 6 and 8 via PTC. A maximum in viscosity of polymer 6 was observed at a mole ratio of





TABLE 2

The effect of water in polymerization reactions via PTC

Polymers	Polymerization Solvent	Mole Ratio H <sub>2</sub> O/cat	$\eta_{inh}$ (%yield)
6	DMAc/Toluene	0.20	0.27 (85.6)
	DMAc	0.75	0.20 (98.2)
	Acetone	2.53	oligomeric
8	Acetone	2.40	0.58 (88.2)
	DMAc	0.75	0.40 (90.4)

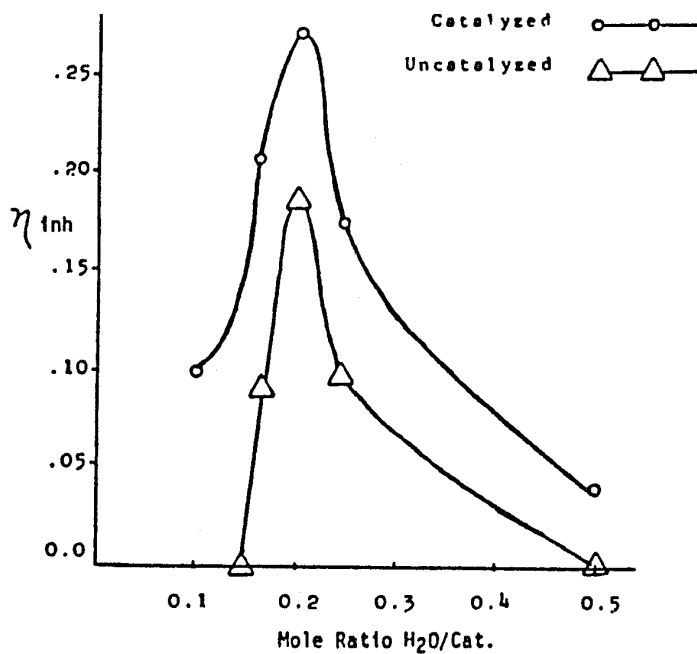


Fig. 1 Effect of water on preparation of 6 in DMAC/toluene.

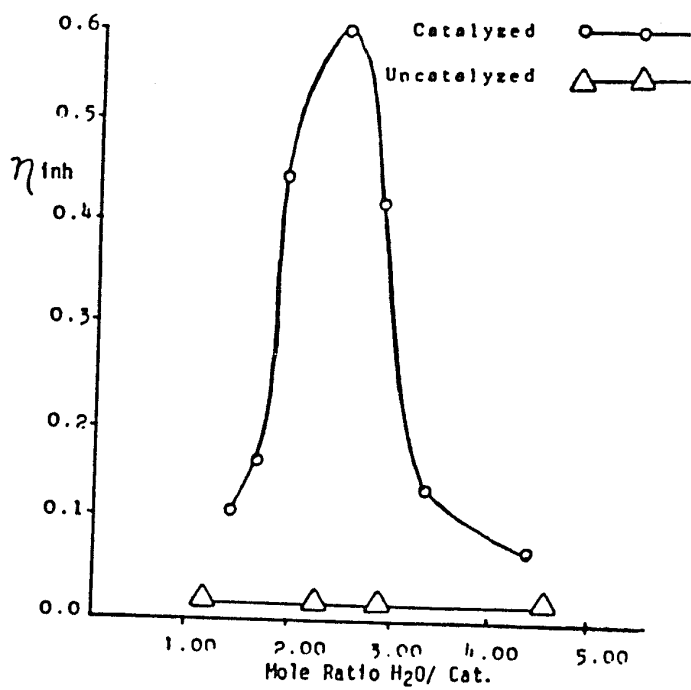


Fig. 2 Effect of water on preparation of 8 in acetone.

These results demonstrate that the water content is critical and that optimal water concentrations vary from one reaction to another. The trace amount of water required depends on the catalyst, the cation, the anion, and the salts formed and their concentrations (solubility in reaction medium). A trace amount of water present is believed to operate at the potassium carbonate solid-liquid interface which facilitates ionization and crown-complexation of the solid base. No polymer is formed in either "bone dry" or "wet" solvents.

Studies conducted by Liotta and co-workers<sup>27</sup> on the rates of reaction of benzyl bromide and benzyl chloride with potassium cyanide in toluene solution as a function of added water, support the premise that the presence of small amount of water in the reaction medium has a marked effect on the rate of reaction. In the absence of added water, the rate of benzyl halide disappearance is observed to be zero-order, whereas in the presence of added water, the rate is observed to be first-order in benzyl halide. In the zero-order process, the rate-controlling step is believed to be the complexation of the crown in the organic phase with the salt in the solid phase. In the first-order process, the displacement step is rate-determining since water enhances the interaction between the crown and the salt by forming an "omega

phase," where the reaction occurs. The omega phase forms when water coats the surface of the salt. It is this aqueous salt coating that extracts crown from the organic phase. This newly defined region is still undergoing investigation and is the subject of some controversy.

## 2.B. Condensation Polymers

Polymers are macromolecules built of multiple units which are joined together by covalent bonds. Polymers were originally classified by Carothers<sup>28</sup> in 1929 into condensation and addition polymers on the basis of compositional difference between the polymer and the monomer(s) from which it was derived. Condensation polymers were those polymers that were formed from polyfunctional monomers by the various condensation reactions of organic chemistry with the elimination of some small molecule such as water. Addition polymers are formed by the addition reactions of olefins or carbonyl compounds.<sup>29,30</sup> They contain a repeating unit which is identical to the starting material (monomer).

In addition to the above classification, there is another classification system which is based on the mechanism of the growth reaction in a polymerization rather than the composition or structure of the polymer. This classification is known as chain-growth polymerization and step-growth polymerization. Chain-growth polymerization involves a reaction in which each polymer chain is formed by the rapid addition of olefin molecules to a growing chain end. Step-growth polymerization, on the other hand, involves a reaction in which each polymer chain grows at a relatively slow rate over a much longer

period of time compared to an addition polymerization reaction. It occurs in a stepwise manner, in which two monomer molecules react to form a dimer, and the dimer can then react with another monomer to form a trimer, or with another dimer to form a tetramer, and so on.

Polymers have also been classified from a consideration of the chemical structure of the groups present in the polymer chains. Thus, a condensation polymer is classified as a polymer which contains heteroatoms in the backbone. Addition polymers do not contain such atoms in the polymer backbone but heteroatoms may be present as pendant substituents along the polymer chain.

The degree of polymerization,  $\overline{DP}$ , of a condensation polymer is defined as the average number of structural units per chain. If  $p$  is defined as the extent of reaction, with 0 being no reaction and 1 being 100% reaction, then  $\overline{DP}$  can be defined as

$$\overline{DP} = \frac{1}{1-p} \quad (7)$$

The properties of polymers are highly dependent on their molecular weight. Molecular weight of a polymer is usually given in terms of either a number-average molecular weight,  $\overline{M}_n$  or weight-average molecular weight,

$\overline{M}_w$ . The number-average molecular weight,  $\overline{M}_n$ , is defined as the total weight of all the molecules in a polymer sample divided by the total number of moles present and is strongly influenced by the number of polymer chains present (Eq. 8). The weight-average molecular weight,  $\overline{M}_w$ , is defined as the summation of the weight fractions of molecules times their molecular weights, and is strongly influenced by the size of the polymer chain present (Eq. 9). The weight-average molecular weight is always greater than the number-average molecular weight in polydisperse systems. Polydisperse is defined as a mixture containing polymer molecules of different molecular weights. The ratio of  $\overline{M}_w / \overline{M}_n$  can be used to determine the polydispersity in a polymer sample.

$$\overline{M}_n = \frac{\sum_x N_x M_x}{\sum_x N_x} \quad (8)$$

$N_x$  = number of moles whose weight is  $M_x$

$$\overline{M}_w = \sum_x w_x M_x \quad (9)$$

$w_x$  = weight fraction of molecules whose weight is  $M_x$

In condensation reactions in particular, high molecular weight polymer is only obtained when the



reaction is allowed to proceed to a very high degree of conversion. It is important to maintain an equal concentration of reactive functional groups at all the times during the reaction process. For this to occur, the stoichiometric equivalence of the starting materials must be exact. Reactant monomers must be free of impurities and side reactions that might selectively consume functional groups cannot be tolerated. Consider the polymerization of two homodifunctional monomers with functional groups A and B. If the stoichiometric imbalance  $r$  (Eq. 10) is defined as the ratio of the number of functional groups present initially (defined such that  $r \leq 1$ ), then the maximum average degree of polymerization is given by Eq. 11

$$r = \frac{N_A}{N_B} \leq 1 \quad (10)$$

$N_A$  = moles of functional groups of the A-A monomer

$N_B$  = moles of functional groups of the B-B monomer

$$\overline{DP}_{\max} = \frac{1 + r}{2r(1-p) + 1-r} \quad (11)$$

where  $p$  is the extent of reaction. When the reaction is

complete (i.e., when  $p=1$ ) equation 11 reduces to

$$\overline{(DP)}_{\max} = \frac{1 + r}{1 - r} \quad (12)$$

Equation 12 clearly illustrates the importance of using very pure reagents, and exact stoichiometric ratios of functional groups (starting materials).<sup>29,30</sup>

Once the polymer has been synthesized, it is important to determine its molecular weight, which can be done either by an absolute or secondary method.<sup>31</sup> An absolute method would give direct values of the  $\overline{M}_w$  and  $\overline{M}_n$ , whereas a secondary method would give only a relative measure of the polymer's molecular weight. The absolute methods are well established both theoretically and experimentally, but they are difficult to carry out, time consuming, and often require expensive apparatus. Due to these factors, molecular weight determinations are performed by much faster and simpler secondary methods, usually solution viscosity or gel permeation chromatography. These give satisfactory results providing that calibration has been performed.

The method chosen to determine the relative molecular weight of polymer synthesized in our lab is viscometry. The presence of even a low concentration of a dissolved polymer dramatically increases the viscosity of a solution

relative to that of pure solvent. This increase in viscosity is caused principally by the unusual size and shape of the dissolved polymer. The relative viscosity ( $\eta_{rel}$ ) of a polymer is given as the ratio of the viscosity of a polymer solution to that of the solvent (Eq. 13).

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0} \quad (13)$$

$\eta$  = viscosity of the solution,

$\eta_0$  = the viscosity of pure solvent, and

$t$  = the flow time for the polymer solution

$t_0$  = the flow time for the pure solvent.

The relative viscosity is always greater than unity because the presence of the polymeric solute always increases the viscosity. The magnitude of  $\eta_{rel}$  depends on the concentration of the polymer in solution and increases with an increase in concentration. Use of the inherent viscosity,  $\eta_{inh}$ , is an attempt to eliminate concentration effects, and is given by

$$\eta_{inh} = \frac{\ln \eta_{rel}}{c} \quad (14)$$

$c$  = grams/100 mL

Inherent viscosities are commonly used as a general means of comparing molecular weights of various polymers.

A  $\eta_{inh}$  value greater than unity reveals that the polymer in solution is of high molecular weight.

The properties of the polymer synthesized are greatly affected by the glass transition temperatures,  $T_g$ , and the crystalline melting temperature,  $T_m$ . The glass transition temperature is defined as the temperature where the linear, polymer changes from a glassy to a rubbery or flexible thermoplastic states. It is dependent on the types of skeletal atoms present, side groups, and even on the spatial disposition of the side groups. The crystalline melting temperature,  $T_m$ , is defined as the temperature where the crystalline polymer melts and becomes a rubber, which is the liquid state for high polymer. At this point the microcrystallites of the polymers are thermally disrupted.

The practical utility of polymers and their different properties depend heavily on their glass transition temperatures. For example, polystyrene with a  $T_g$  of  $100^\circ\text{C}$  is used at room temperature in applications as a hard glassy material. Ethylene propylene copolymer with a  $T_g$  of about  $-60^\circ\text{C}$  is used as a rubber at room temperature.

The most popular technique for measurements of glass transition temperature is differential scanning calorimetry (DSC). A typical diagram obtained from such a measurement made is shown in Fig. 3.

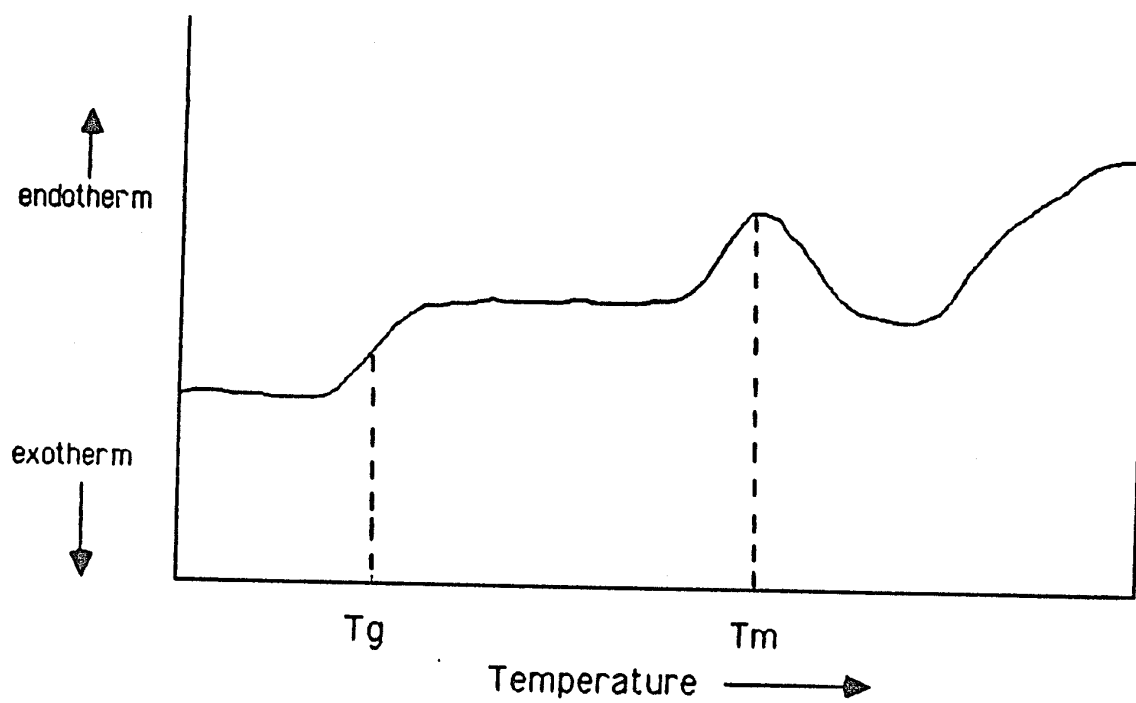


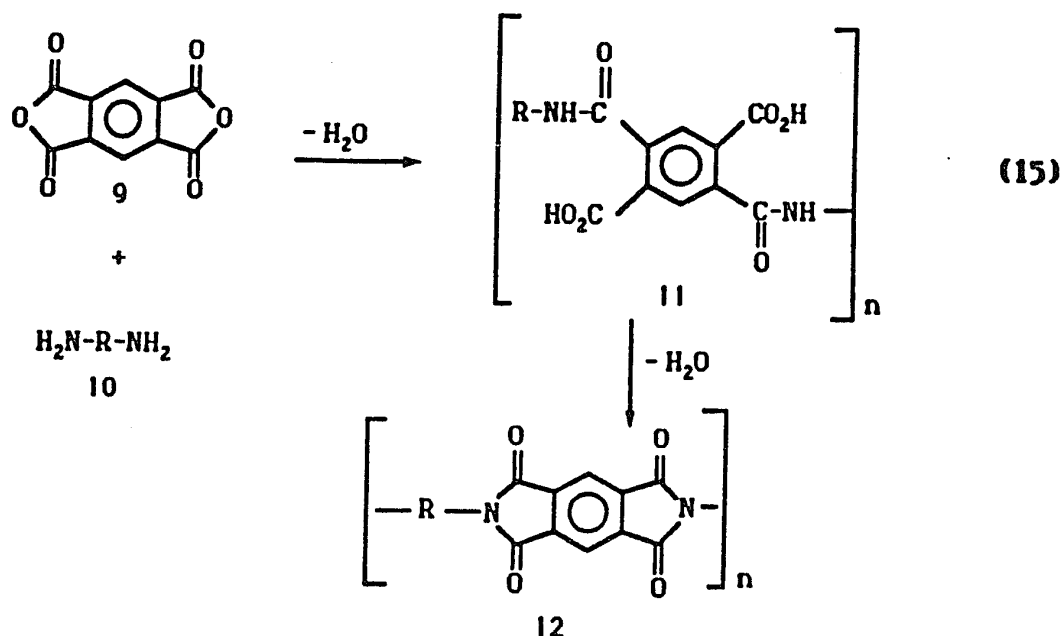
Fig. 3. Differential scanning calorimetry (DSC) scan showing a characteristic polymer glass transition temperature ( $T_g$ ) and crystalline melt temperature ( $T_m$ ).

## 2.C. Polyimides

Among the earliest types of thermally stable polymers, and now among the most common commercial materials, are polyimides which were initially synthesized by DuPont and marketed as a yellow film under the name H-Film<sup>R</sup> and later Kapton<sup>R</sup>. Polyimides are best known for their high strength and high temperature resistance. They are used in aerospace and electrical-electronic applications (aircraft engine parts, printed circuit boards, high speed-high load bearings, insulation in electric motors, wire, and cable). However, their uses have been limited. This is primarily due to their insolubility, combined with their high transition temperatures, which makes them extremely difficult to fabricate.<sup>32</sup> Polyimides are usually processed in the form of their soluble, fusible poly(amic) acid precursors which are then thermally or chemically converted to the imide structure.

The general method of polyimide (12) synthesis involves a two-step condensation polymerization of a dianhydride such as pyromellitic anhydride (9) with a diamine (10), (Eq. 15). The first stage is an amidation reaction performed in polar solvents to give high molecular weight poly(amic acid) (11). This form is soluble and processable, and it is at this point that

the final product conformation is developed (film, fiber, etc). The second stage is the cyclization of poly(amic acid) into polyimides, which is usually done at temperatures above 150 °C.



As with other synthetic polymers, the physical properties of polyimides depend on their molecular structure, mainly on the polymer backbone. Aromatic polyimides contain a rigid backbone and therefore possess a high  $T_g$  and  $T_m$  and low solubility. They generally exhibit poor solubility in common organic solvents, which made the processing of polyimides difficult or impossible. Polyimides show some solubility only in concentrated sulfuric and fuming nitric acid.

Therefore, a compromise had to be made with the polyimides; some desirable properties must be sacrificed in order to gain practicability. For example, a decrease in thermal stability might be accepted in order to achieve processability, acceptable cost, flexibility, solubility, etc.

Many efforts have been made to overcome the solubility problems. Harris and coworkers<sup>33</sup> in their review on structure-solubility relationships in aromatic polyimides claimed that the solubility of aromatic polyimides can be increased by structural modification. This can be done by (1) the introduction of large polar (phthalide, phthalimide) or non-polar (phenyl, fluorene) substituents along the polymer backbone, (2) the incorporation of flexible (ether, perfluoroalkylene) or kinked (m-phenylene, o-phenylene) thermally stable linkages in the backbone, and (3) the disruption of symmetry and recurrent regularity through copolymerization employing two dianhydrides or two diamines.

It has been reported that incorporation of flexible groups such as the bipyridyl<sup>11</sup> unit (with sulfur, sulfoxide and sulfone linkages), ether, sulfone, and alkylene<sup>9</sup> or a block of these functional groups into the polymer backbone did enhance the solubility of polyimides in common organic solvents such as m-cresol and N,N-

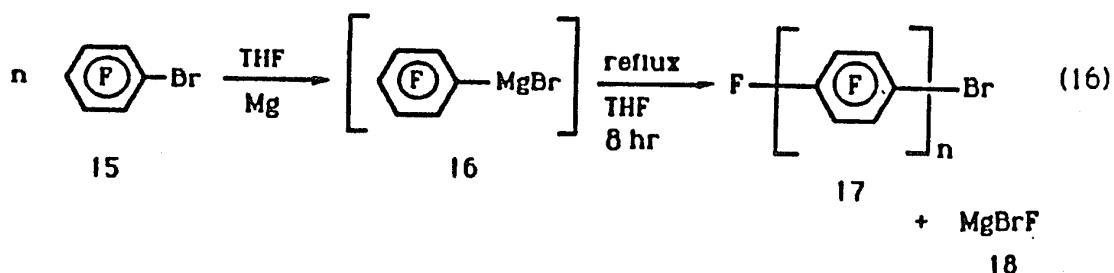




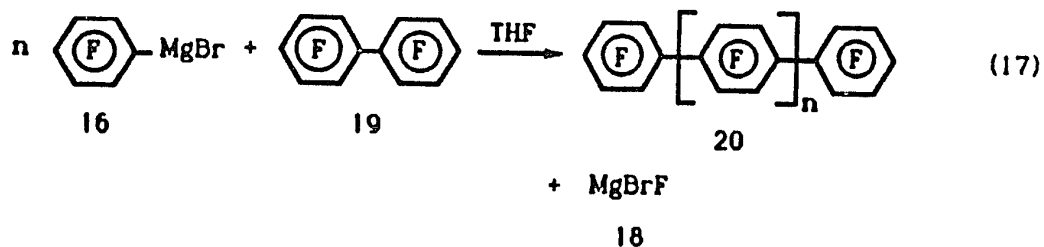
bases and strong nucleophiles in solution. The strong inductive effect of the electronegative fluorine atoms leads to highly positive ring carbon atoms which are susceptible to nucleophilic attack. Hexafluorobenzene has been used in reactions involving metal hydroxides, phenolates, amines and organolithium compounds.<sup>37</sup>

Tatlow, at the University of Birmingham, studied the orientation pattern of the product isolated from nucleophilic aromatic substitution of hexafluorobenzene.<sup>37</sup> The disubstituted products were shown to be predominantly para but some ortho and meta substitution also was observed.

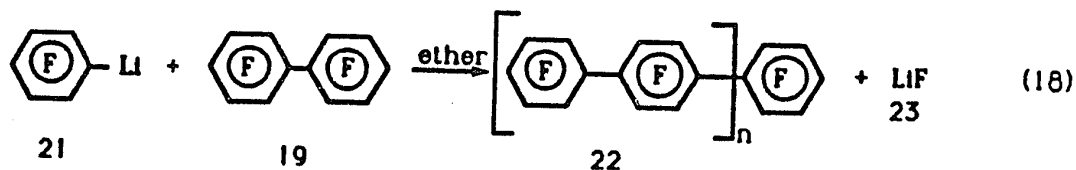
Hexafluorobenzene and its derivatives have been used as monomers for the preparation of high molecular weight perfluoropolyphenylenes via the Grignard reaction (Eq. 16).<sup>38</sup>



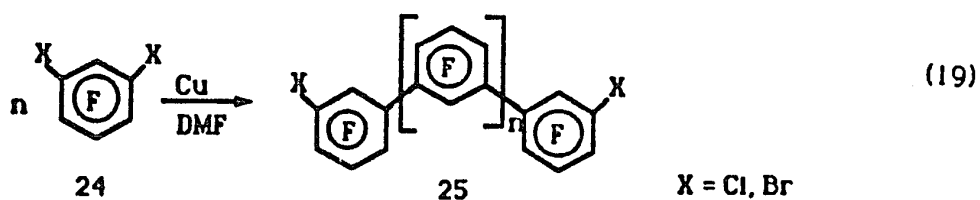
Low molecular weight polyphenylenes were synthesized when pentafluorophenyl magnesium bromide and decafluorobiphenyl was subjected to reaction at room temperature (Eq. 17).<sup>38</sup>



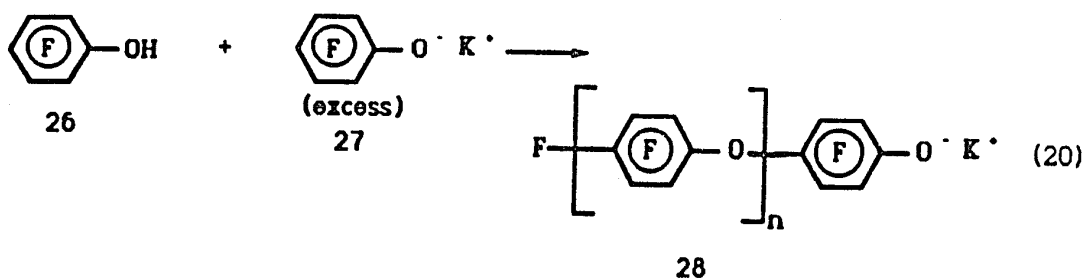
Reaction of pentafluorophenyl lithium with decafluorobiphenyl in ether also yielded low molecular weight perfluoropolyphenylenes (Eq. 18).<sup>39</sup>



An Ullman reaction (bulk or in refluxing dimethylformamide) of 1,3-dichloro- or dibromotetrafluorobenzenes and copper powder yielded pure meta-linked perfluoropolyphenylenes (Eq. 19).<sup>1,4,24</sup>



Relatively high molecular weight perfluoropolyphenylene ethers can be prepared directly from excess potassium pentafluorophenoxide and pentafluorophenol (Eq. 20).<sup>23</sup>



Hexafluorobenzene and decafluorobiphenyl also have been used in the polycondensation reaction PTC. Kellman and co-workers<sup>40</sup> have used hexafluorobenzene and decafluorobiphenyl as the monomer with bisphenol-A in the polycondensation PTC reaction and were able to produce high molecular weight polymers with high  $T_g$  and  $T_m$ .

This research uses a series of fluorinated aromatic compounds as monomer units to make fluorinated polyimides via the solid-liquid PTC approach. The polymers synthesized are characterized by spectral and elemental analysis.

### 3. RESULTS AND DISCUSSION

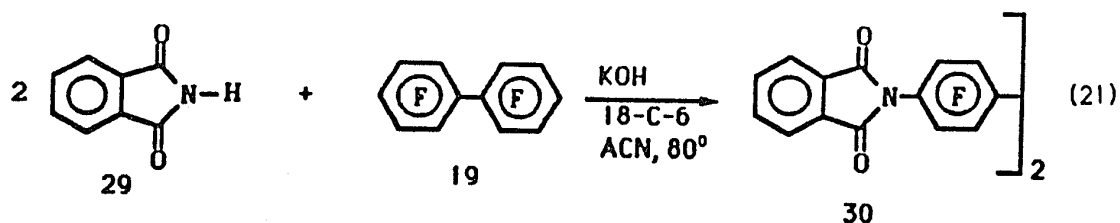
As stated earlier, one of the major problems associated with polyimides is their general lack of solubility in common organic solvents, which has undoubtedly limited the utilization or application of this particular class of polymers. It is well established that the introduction of a suitable heteroatom such as nitrogen into an aromatic nucleus usually produces a significant change in the solubility pattern of the organic species.<sup>33</sup> Similar solubility effects can be produced by the introduction of various aliphatic links or bridges within these aromatic systems.

The present study has sought to address this question by examining the incorporation of various lengths of linear alkane bisulfide units within the polymer backbone. This should yield a new class of polymer with rigid and flexible segments in its backbone; the flexible segments resulting from the methylene and sulfide linkages, and the rigid segments due to the perfluoroaromatic units. By manipulating the proportion of flexible to rigid segments, a series of novel polymers having a wide variation in their physical properties is expected.

Our interest in the preparation of new highly soluble polyimides arose through a study of nucleophilic aromatic

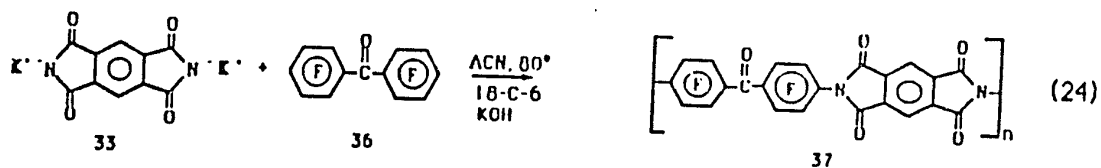
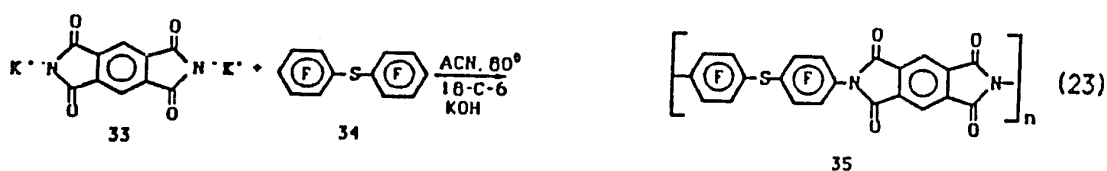
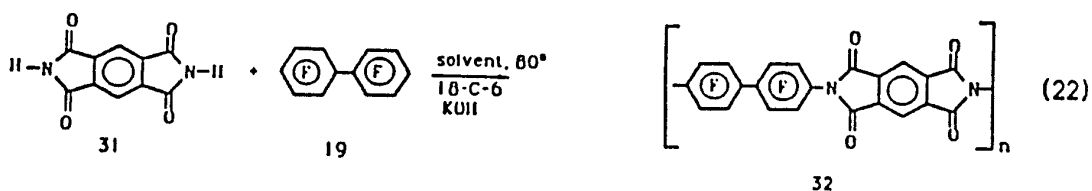
substitution of perfluoroaryl compounds with arylimides via PTC.

Previous studies<sup>41</sup> show that when two equivalents of phthalimide (29) and one equivalent of decafluorobiphenyl (19) are allowed to react in acetonitrile at 80°, 4,4'-bis(phthalimide)perfluorobiphenyl (30) is isolated in 45% yield (Eq. 21). This heterogenous system employs 18-crown-6 as a phase transfer catalyst and potassium hydroxide as a solid phase base. This reaction represents a model for the polycondensation reaction of difunctional imides and perfluorodiaryl substrates.



Based on the results of model studies above, a series of polymerizations (Eq. 22, 23, 24) of difunctional imides (31, 33) with perfluorodiaryl substrates (19, 34, 36) were performed under the same conditions as above.<sup>41</sup> The inherent viscosity of the resulting polymers was determined by using a capillary viscometer at 30 °C and the glass transition temperatures ( $T_g$ ) and crystalline melting temperatures ( $T_m$ ) were determined using DSC. The results

obtained from each polymerization are summarized in Table 3.



Under the conditions used, the imide nucleophile showed an overwhelming preference for 4,4' substitution (100% para) of the perfluoroaryl substrate. Low yields obtained are due to premature precipitation of the rigid rod polymers from solution, preventing chain growth to high molecular weight.

In an attempt to prepare highly soluble polyimides, we began by synthesizing a series of bisthiol monomers

TABLE 3  
Polymerization reactions of bisimides with perfluoroaryl  
substrates under PTC conditions.

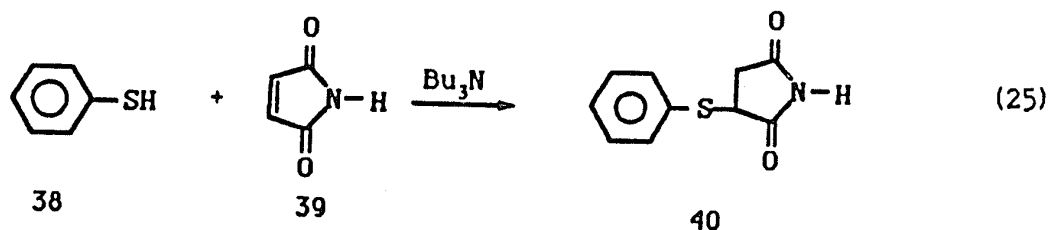
reaction	%yield	$\eta_{inh}$ (dL/g)	$T_g$ , °C	$T_m$ , °C
22	64	0.20	80	260
23	60	0.15	71	205
24	56	0.15	-	170



with different methylene  $[(-\text{CH}_2-)_x; x = 5, 6, 8, 10]$  chain segments. Such alkane linkages should introduce flexibility in the polymer backbone and thereby enhance the polymer solubility. Another factor that should also increase the solubility is the introduction of a heteroatom in these monomers. The sulfur linkage, which has a low energy barrier to rotation, should contribute to chain flexibility along with the methylene units. These two factors will undoubtedly increase the solubility of polymer synthesized. The more soluble the polymers, the more likely it is to obtain high molecular weight polymers, as premature precipitation at low DP is not likely to occur.

### 3.A. Model Compounds And Monomers

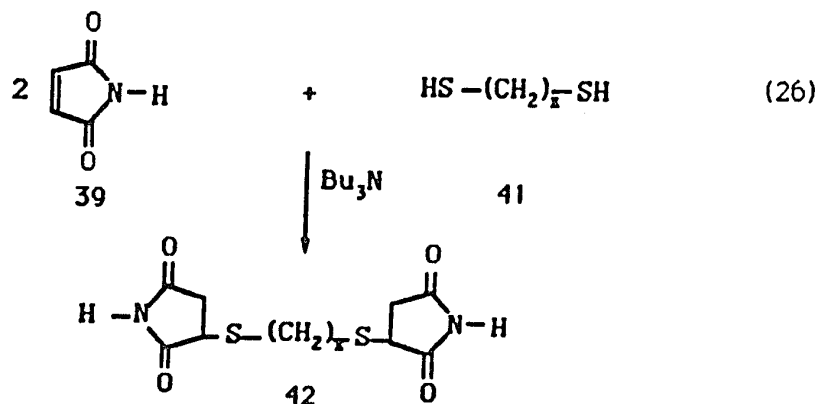
Model compounds (40, 43) and difunctional monomers (42) were synthesized according to the procedure reported by Crivello and coworkers.<sup>42</sup> This was accomplished by adding thiophenol (38) to maleimide (39) in m-cresol. A trace amount of tributylamine was used as a catalyst to initiate the formation of thiolate anion ( $\text{Ar-S}^-$ ) that attacks the maleimide double bond to give the corresponding product (40).



When thiophenol (38) was allowed to react with maleimide (39) an 84% yield of white crystalline product (40) (mp 92-94 °C) was obtained (Eq. 25). The structure of the product isolated was verified by spectral and elemental analysis. Along with the complete loss of the weak S-H absorption at  $2560\text{ cm}^{-1}$  present in the IR spectrum of starting thiol (38), the spectrum of 3-(thiophenoxy)maleimide (40) exhibited the expected imide carbonyl stretching bands at 1783 (weak) and 1705-1720  $\text{cm}^{-1}$ , and C-S-C stretching vibrations at 1165-1180  $\text{cm}^{-1}$ . The proton NMR spectrum of 40 displays a

doublet of doublets ( $J = 9.0, 4.5$  Hz) near  $\delta$  4.35, due to absorption of the ring methine proton adjacent to sulfur, along with two sets of doublet of doublet resonances at  $\delta$  3.23 ( $J = 18.5, 9.0$  Hz) and  $\delta$  2.61 ( $J = 18.4, 4.6$  Hz) corresponding to the two nonequivalent ring methylene protons. Other signals in the nmr spectrum of model compound (40) are consistent with the structure shown. Elemental analysis agreed well with the composition calculated for 3-(thiophenoxy)maleimide (40).

A series of "flexible" monomers (42) was obtained when bisthiols (41) with different number of methylene units were allowed to react with two moles of maleimide (39) under the same conditions as above (Eq. 26). Monomers isolated were white, powdery materials. Structural verification by spectral and elemental analysis was carried out. The results obtained from monomers synthesized are summarized in Table 4.



$$x = 5, 6, 8, 10$$

TABLE 4

Bisimide monomers (42) synthesized via the Michael addition reaction.

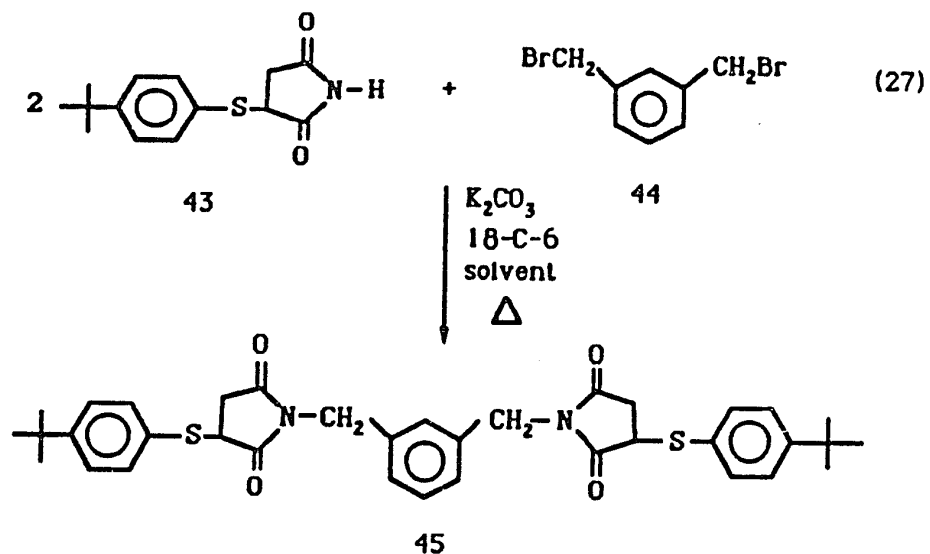
42	x	mp ( $^{\circ}$ C)	%yield
a	5	105-108	84
b	6	106-109	84
c	8	108-110	78
d	10	112-115	85

### 3.B. Model Reactions

A series of model reactions was conducted under a variety of conditions to determine the feasibility of the polymerizations of interest. If the reaction proved to be feasible, the polymerization reaction would be performed. This study was undertaken with a view toward determining the optimum conditions under which the polymerization should be conducted, and the presence or absence of competing substitution side reactions in PTC. Several factors such as monomer purity, stoichiometric ratio, solvent, reaction time, temperature and catalyst affect the formation of high molecular weight polymer. These are best examined in simple models.

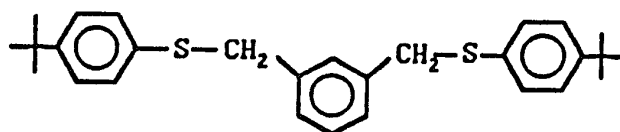
We initiated our work by examining nucleophilic substitution of 3-(p-[t-butyl]thiophenoxy)maleimide (43) with  $\alpha,\alpha'$ -dibromo-m-xylene (44) in tetrahydrofuran (THF), pyridine or toluene. These heterogenous systems employed 18-crown-6 ether as the catalyst and potassium carbonate as the solid phase and base. The anticipated reaction is shown in Equation 27.

The reactions were monitored by tlc to determine the time required for complete reactions. The reactions were stopped after 26 hr when the starting material, 3-(p-[t-butyl]thiophenoxy)maleimide (43) was no longer



detected on tlc plates. The results obtained were surprising, since neither the starting material nor the expected product was recovered. Crude product was obtained in yields ranging from 48-63%. The IR and NMR spectra of the crude product (mp 91-102 °C with decomposition) were not in complete agreement with each other. The NMR showed narrow absorbances from aromatic ring at  $\delta$  7.43 (s, 6H), as well as resonances at  $\delta$  4.10 (s, 2H, -CH<sub>2</sub>-) and at  $\delta$  1.30 (s, 9H, *t*-butyl group). There was no indication from NMR data that the maleimide ring was present in the product isolated. The IR spectrum on the other hand showed the expected imide carbonyl stretching at 1707-1720 (strong) cm<sup>-1</sup>, which suggested that the maleimide ring is present in the product isolated. When a portion of the product was recrystallized, light yellow needles of a compound with

mp 103-105 °C were obtained in 63% recovery. The NMR of the recrystallized product showed consistent results with that obtained from the corresponding crude product. However, the IR of the recrystallized product did not show the expected imide carbonyl stretching absorption in the 1707-1720  $\text{cm}^{-1}$ . This led us to conclude that the isolated product was  $\alpha, \alpha'$ -bis(p-[t-butyl]thiophenoxy)-m-xylene (46) rather than the expected  $\alpha, \alpha'$ -bis(3-p-[t-butyl]-thiophenoxy)maleimide)-m-xylene (45). The carbonyl stretching observed earlier in the crude product is believed to be from imide salt residue.



46

Based on the results obtained from this reaction, it can be concluded that reverse Michael addition reaction competes with aromatic substitution (Scheme III). The process that takes place during the reaction could be explained as follows; the potassium carbonate reversibly removes the imide proton to form the salt (47) of 3-(p-[t-butyl]thiophenoxy)maleimide (Eq. 28). The potassium salt thus formed can undergo substitution with  $\alpha, \alpha'$ -dibromo-m-xylene (44) in a slow step (Eq. 29) or

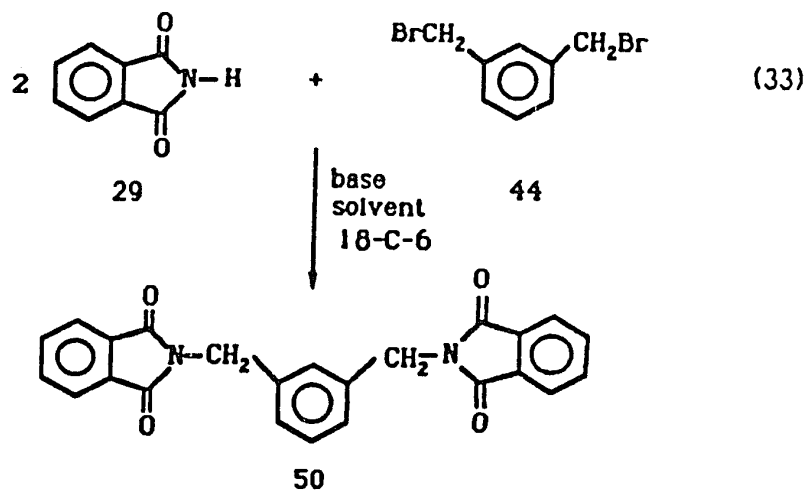




give base-promoted elimination (reverse Michael addition) by way of enolate (Eq. 30). Enolate (48) once formed, may, in a fast step, lose arylthiolate anion (49) to give maleimide (39) (Eq. 31). The arylthiolate anion, being a stronger nucleophile than nitrogen anion, reacts with  $\alpha, \alpha'$ -dibromo-m-xylene (44), to give bis(p-[t-butyl]-thiophenoxy)-m-xylene (46) rather than the expected bis(p-[t-butyl]thiophenoxy)maleimide-m-xylene (45) (Eq. 46). There is no evidence from IR and NMR data to indicate even a trace of the expected product.

The failure of this reaction (Eq. 27) to produce the expected product (45) led us to reinvestigate the reaction between phthalimide (29) and  $\alpha, \alpha'$ -dibromo-m-xylene (44) that was carried out by Henry<sup>47</sup> in 1980 (Eq. 33). In his reaction, potassium hydroxide was used as a solid base, 18-crown-6 as a phase transfer, and *N,N*-dimethylacetamide as a solvent. The product (50) was isolated in 95% yield (mp 260-263 °C). Mass spectroscopy (*m/e* 396.4) and elemental analysis showed that the product isolated was  $\alpha, \alpha'$ -bis(phthalimide)-m-xylene (50).

Thus we performed a similar reaction to see whether nucleophilic aromatic substitution of arylimides with  $\alpha, \alpha'$ -dibromo-m-xylene does take place under our solid-liquid phase transfer conditions (Eq. 33). A slight modification was made in our reaction where potassium



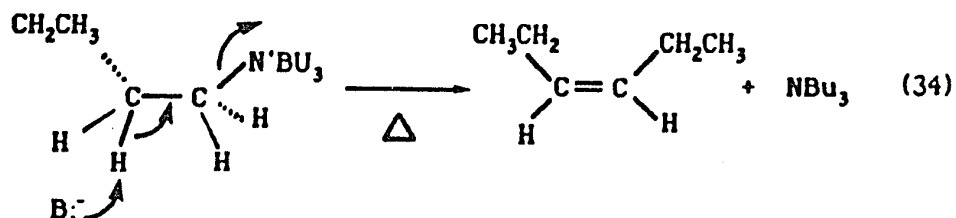
carbonate was used as a solid phase base instead of potassium hydroxide and toluene as a solvent instead of *N,N*-dimethylacetamide. The product (50) isolated was a white powder obtained in 75% yield (mp 261-262 °C). The spectral results agreed well with the results reported previously.

The low yield of product (50) isolated can be explained in terms of inadequate solubility of potassium phthalimide crown-complex in toluene. As mentioned earlier, an important requirement for the success of PTC is the solubility of the crown complexes in the reaction solvent. If the crown-cation-nucleophile complex is not soluble in the organic phase, the nucleophilic substitution reaction would be inhibited or retarded and only the insoluble salt would be isolated. In this case,

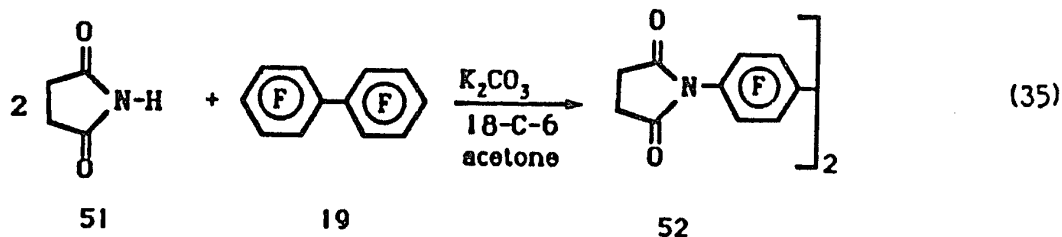
only a small amount of potassium phthalimide nucleophile soluble in the reaction medium; therefore, the product isolated is of low yield.

Studies conducted by Godz and co-workers<sup>43</sup> on the preparation of N-alkylphthalimides via solid-liquid PTC showed that if a mixed catalyst was used, an increased in yield is observed. He reported that the reaction of phthalimide with primary halides under solid-liquid PTC conditions required the use of two phase transfer catalysts for reaction to occur. One catalyst, 18-crown-6 was used to solubilize the solid phase base (KOH) and the other catalyst, a quaternary ammonium salt, was used to solubilize the phthalimide nucleophile. Each catalyst was used in a 0.5 molar equivalent.

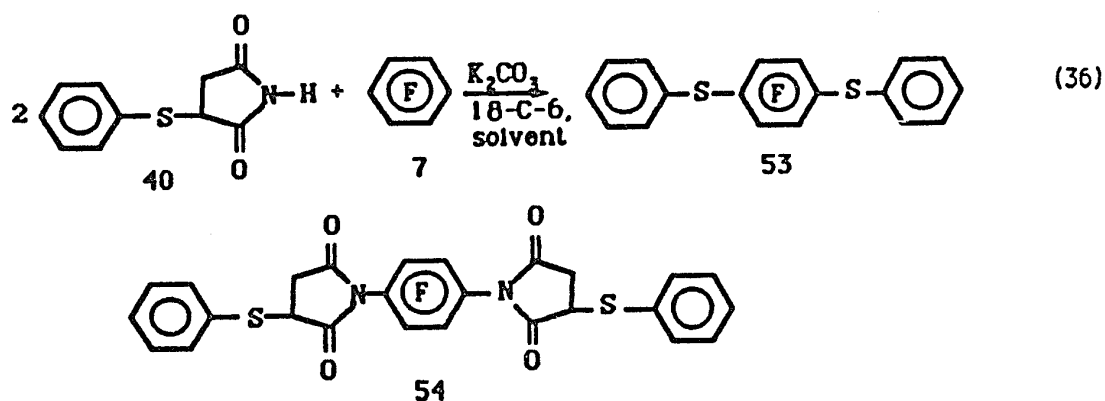
This led us to perform a similar model reaction (Eq. 33) under the same conditions Godz used, employing two phase transfer catalysts. The amount of product increased to 80% from 75% yield. Even though "mixed" catalyst has proved to increase the yield of product isolated, this system is, however, not suitable for our solid-liquid phase transfer reactions. This is because the quaternary ammonium salt has a tendency to undergo Hoffman elimination in the presence of base at temperatures above 80° (Eq. 34). Therefore, we decided to use only 18-crown-6 as our catalyst for the remaining reactions.



When two equivalents of succinimide (51) were allowed to react with decafluorobiphenyl (19) in acetone, 4,4'-bis(succinimide)perfluorobiphenyl (52) was isolated in 84% yield (mp 125-127 °C) (Eq. 35). The infrared spectrum of the product isolated showed the expected carbonyl stretching at 1735  $\text{cm}^{-1}$ , and C-F stretching at 1505  $\text{cm}^{-1}$ . Proton NMR showed the disappearance of the N-H absorption at  $\delta$  8.6 and showed an absorption for methylene protons ( $\text{CH}_2$ ) at  $\delta$  3.86. Fluorine NMR showed para disubstituted ring absorptions at  $\delta$  188 and  $\delta$  184. Therefore, this model demonstrates the feasibility of PTC nucleophilic aromatic substitution by imide nucleophiles on perfluoroaryl substrates.



Reaction of 3-(thiophenoxy)maleimide (40) with hexafluorobenzene (7) in tetrahydrofuran, pyridine or toluene yielded a white crystalline material (mp 111-112 °C), (Eq. 36). Spectral analysis of the product showed that the compound isolated was not the expected product (54). The infrared spectrum exhibited no evidence for the presence of imide carbonyl stretching bands in the 1783-1720 region, but a strong C-F stretch was observed at 1580  $\text{cm}^{-1}$ . The proton NMR spectrum displayed only one aromatic ring absorbance at  $\delta$  6.81; no absorbances from protons attached to the maleimide ring were observed. Fluorine NMR showed an absorption at  $\delta$  -132.97 ( $\text{CFCl}_3$  as an internal standard) and GC/MS showed a molecular ion at  $m/e$  366. These data led us to conclude that the product obtained has the structure shown below (53). The results obtained from elemental analysis agreed well with the composition calculated for 4,4'-bis(thiophenoxy)-perfluorobenzene (53).



When 3-(p-[t-butyl]thiophenoxy)maleimide (43) was allowed to react with decafluorobiphenyl (19) under the same conditions as above, the same behavior was observed. A crystalline product (mp 115-116 °C) was isolated in 71% yield. Elemental analysis agreed well with composition calculated for 4,4'-bis(p-[t-butyl]thiophenoxy)-perfluorobiphenyl (55).

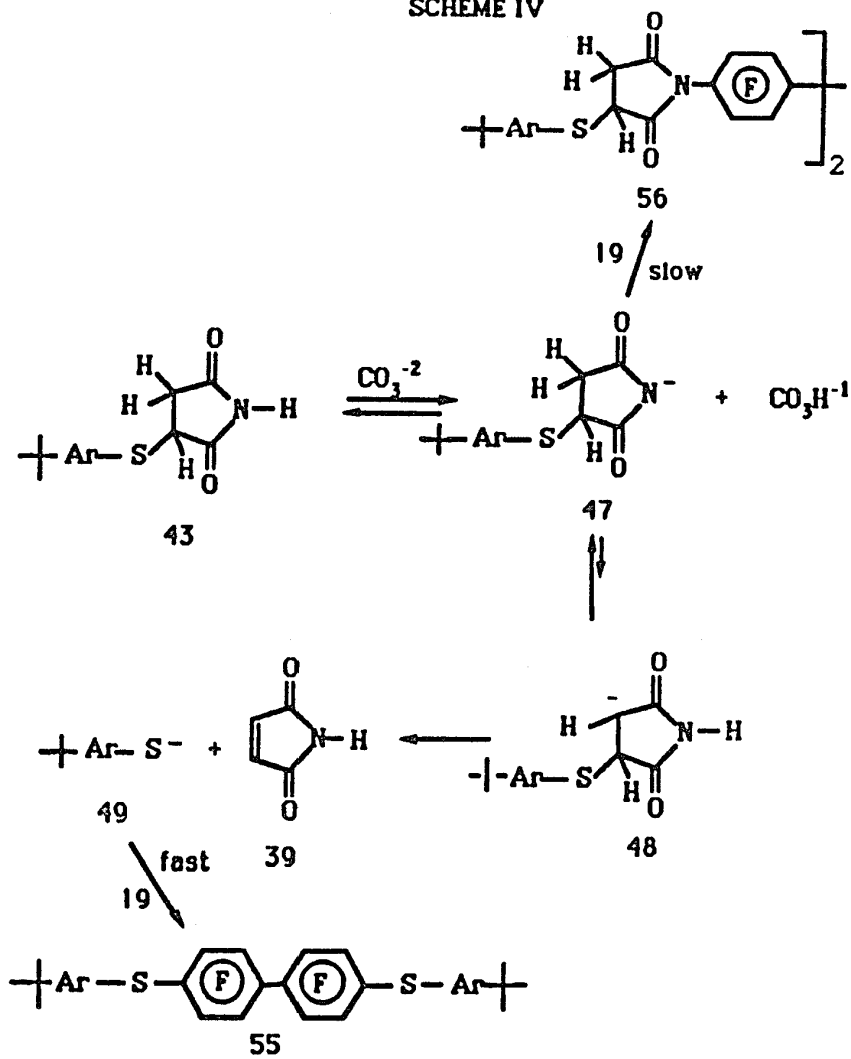


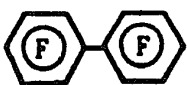
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Based on the results obtained from these two reactions, we concluded that the reverse Michael addition reaction competes with aromatic substitution (Scheme IV). The mechanism that operates in these reactions (Eq. 36 and 37) is believed to be the same as that discussed previously (see scheme III and Eq. 27).

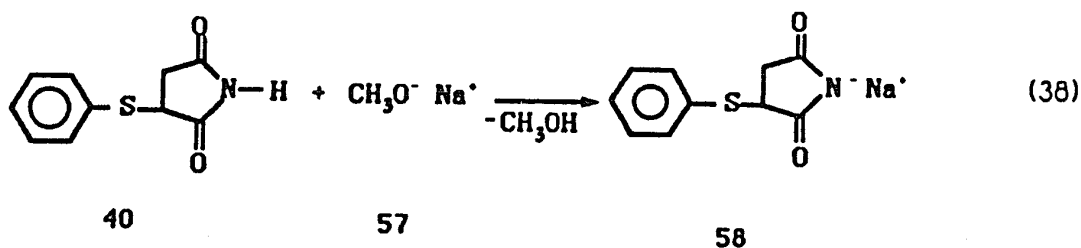
These model studies led us to an alternate method of synthesizing the product of interest. Our next approach was to use the sodium salt of the imide compound as our starting material rather than using the neutral imide. Sodium 3-(thiophenoxy)maleimide (58) can be obtained by mixing an equimolar amount of sodium methoxide (57) solvent with 3-(thiophenoxy)maleimide (40) at room

SCHEME IV



where 19 = 

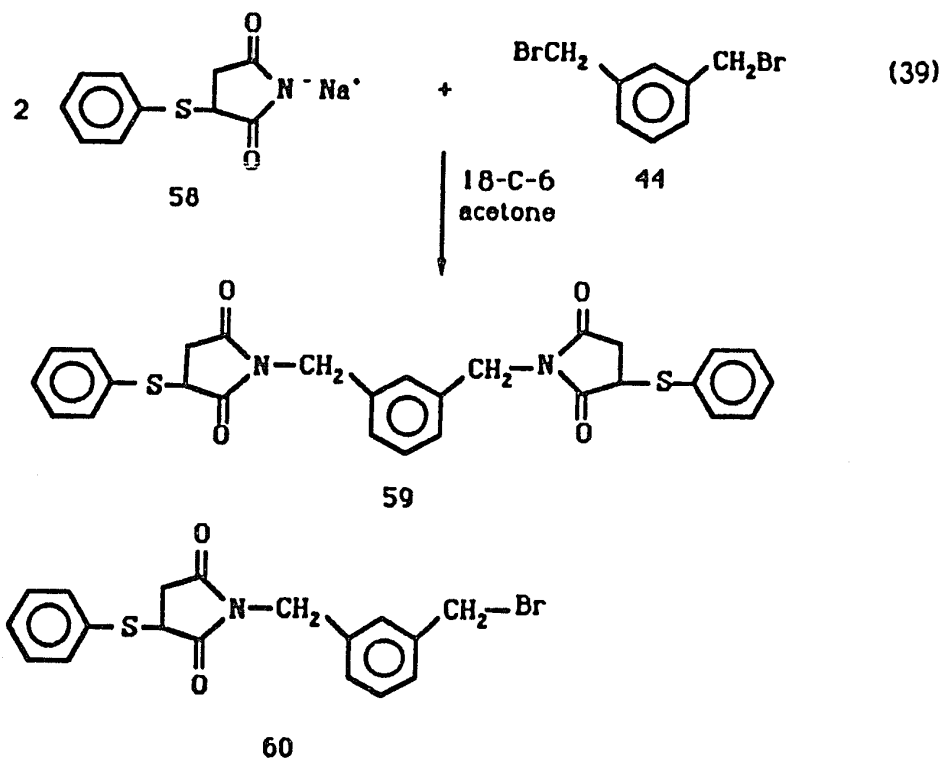
temperature (Eq. 38). Concentration of the reaction mixture through rotary evaporation yielded 58 as a white crystalline hygroscopic material which was not further characterized.



The salt (58) was then allowed to react with  $\alpha,\alpha'$ -dibromo-m-xylene (44) for 16 hr in acetone at reflux with 18-crown-6 as phase transfer catalyst (Eq. 39). The product collected was a 60% yield of a white crystalline compound (mp 120-123 °C). The low yield obtained is probably due to the short time period allowed for the reaction performed. This means that the reaction was stopped before its completion as was evident from column chromatographic separation. Four different products were isolated from column chromatographic separation, 18-crown-6, followed by  $\alpha,\alpha'$ -dibromo-m-xylene and the reaction products (mono [60] and disubstituted [59] product). The starting material, sodium 3-(thiophenoxy)maleimide (58) did not pass through the column (it stayed on the base line on tlc plates). When the same reaction was performed for a longer period of



time (24 hr), the product isolated increased by 24% (84% yield) and the spectral results are identical. The infrared spectrum exhibited the expected imide carbonyl stretching bands at 1779 (weak) and 1700-1719  $\text{cm}^{-1}$ . The proton NMR spectrum displayed the expected doublet of doublets near  $\delta$  4.63, 4.25, and 2.50. Elemental analysis of the product isolated agreed well with composition calculated for  $\alpha,\alpha'$ -bis(3-[thiophenoxy]maleimide)-m-xylene (59).



Based on this study, we conclude that imidate salts might be better than neutral imides in the desired polymerization reactions.

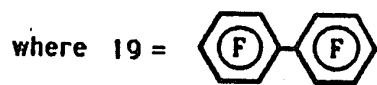
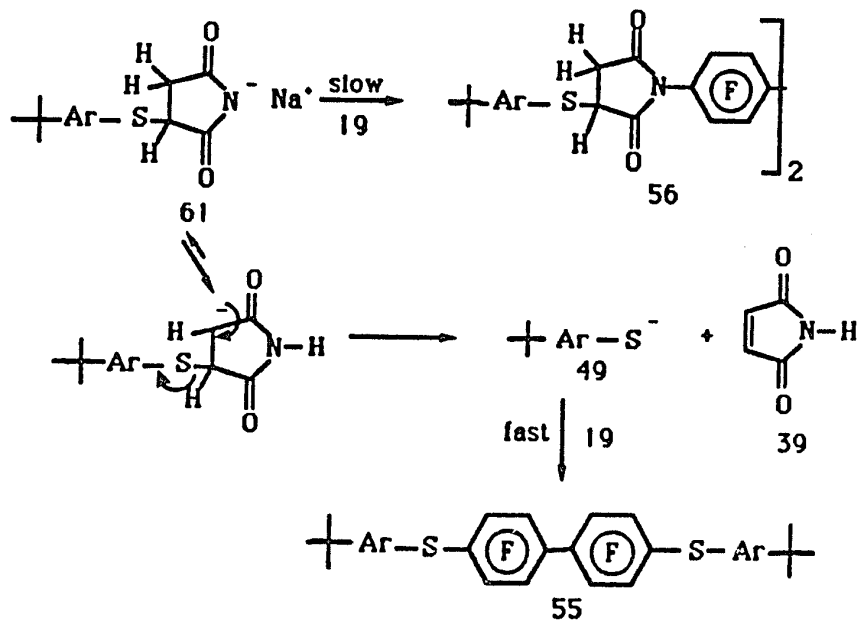
We addressed the question of the difference in behavior observed for the reactions between neutral imide (43) and sodium imide (58). When neutral imide was used as a nucleophile in the reaction performed (Eq. 27), reverse Michael addition competed with nucleophilic substitution by imide nucleophile on  $\alpha,\alpha'$ -dibromo-m-xylene. However, when sodium imide was used instead of neutral imide, nucleophilic substitution is observed rather than reverse Michael addition (Eq. 39). We thought that a difference in solvent polarity could have an effect on the type of reaction that obtains, since we used a moderately polar solvent (acetone) for reaction between sodium imide (58) and  $\alpha,\alpha'$ -dibromo-m-xylene (Eq. 39). However, when neutral imide (43) was allowed to react with  $\alpha,\alpha'$ -dibromo-m-xylene in acetone, employing 18-crown-6 and potassium carbonate as a phase transfer catalyst and solid phase base respectively, reverse Michael addition product (46) was isolated instead of the expected product (45). Therefore, solvent polarity does not account for the behavior observed. Other factors such as the cation (sodium in [Eq. 39] vs potassium in [Eq. 36]) might have an effect on the outcome of the reactions. Also, heterogenous (Eq. 36) vs homogeneous (Eq. 39) conditions may also contribute to these differences. In short, the reasons why nucleophilic substitution by

neutral imide does not occur, and nucleophilic substitution by the imide salt does take place in these reactions is not fully known.

Having established suitable reaction conditions for displacement of benzylic bromides, we turned our attention to aromatic substitution. When sodium imide (61) was subjected to reaction with decafluorobiphenyl (19) in acetone, employing 18-crown-6 as catalyst, the reverse Michael addition competes with aromatic substitution. That is, 4,4'-bis(p-[t-butyl]thiophenoxy)perfluorobiphenyl (55) was isolated in 82% yield. The mechanism that might take place during the reaction process is shown in Scheme V.

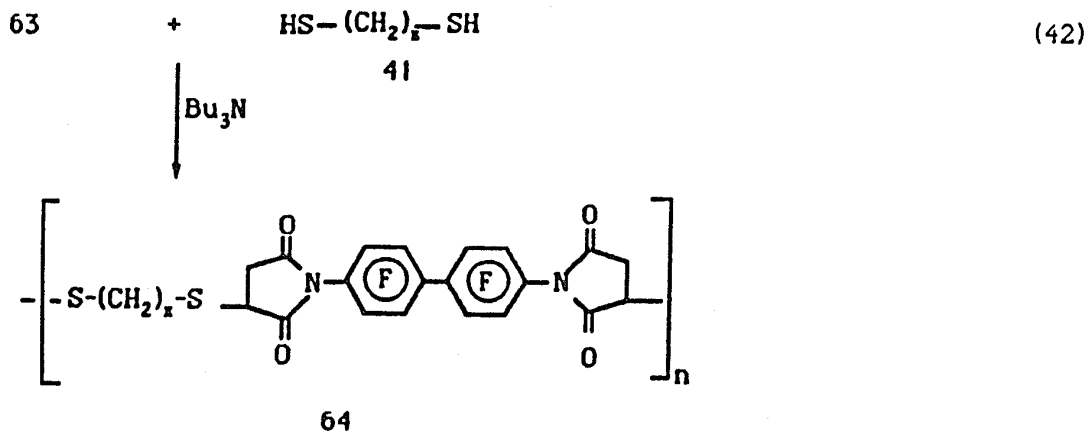
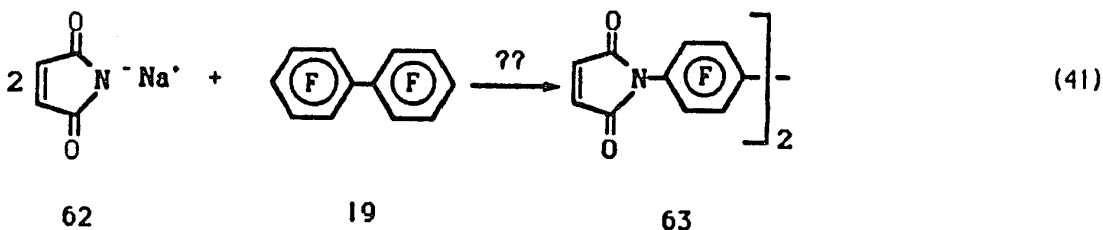
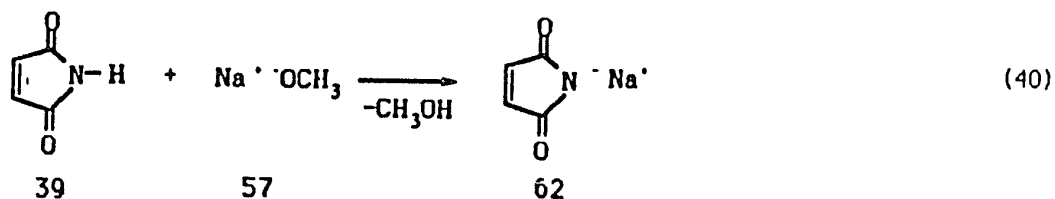
In conclusion, it can be said that even with the use of sodium imide (61) as a starting material, reverse Michael reaction competes against nucleophilic aromatic substitution of aryl imides with perfluoroaryl substrates. However, in the case reaction of  $\alpha,\alpha'$ -dibromo-m-xylene with aryl imides, reverse Michael reaction is observed only if neutral imide was used but not with the imide salt. This behavior is expected, since the rate of attack by a nitrogen nucleophile on a primary, benzylic bromide is so fast that the reverse Michael reaction does not have enough time to compete during the reaction process. On the other hand, the rate of attack by the nitrogen

## SCHEME V



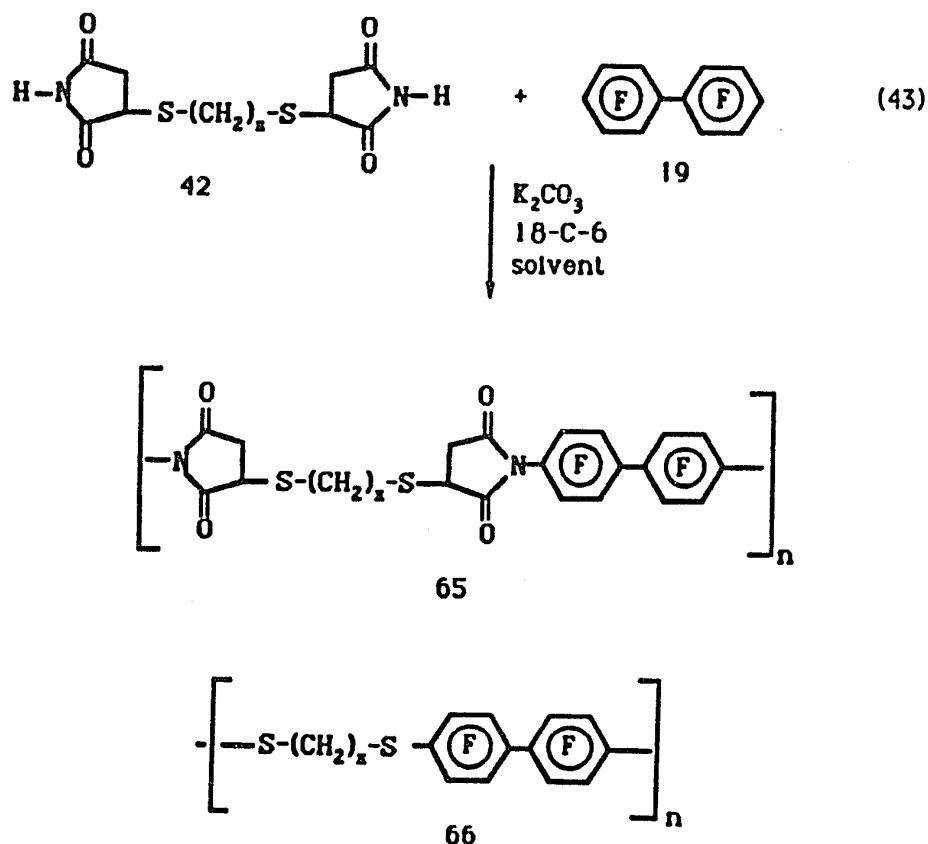
nucleophile on perfluoroaryl substrates is so slow that the reverse Michael reaction has enough time to compete. This behavior has prevented the synthesis of high molecular weight flexible fluorinated-polyimides by direct solid-liquid PTC using flexible bisimides linked by sulfide bonds.

However, another approach as a future project for the formation of perfluoroaryl polyimides via PTC could use the following sequence (Eq. 40, 41, 42).



### 3.C. Attempted Polymerization

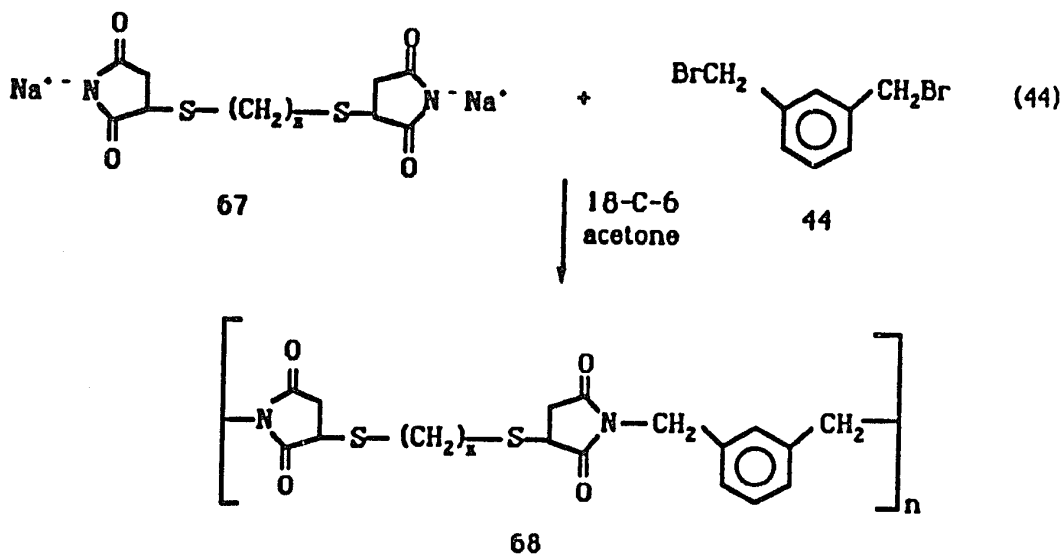
Model studies indicated to us that the perfluoroaryl polyimides (65) proposed cannot be prepared under PTC conditions from the monomers synthesized (the desired reaction is shown in [Eq. 43]). This is due to the fact that reverse Michael addition competes with substitution during the reaction process. As a result, the reaction product isolated would be of a different class of polymer (66).



Model reactions of sodium 3-(thiophenoxy)maleimide (58) with  $\alpha,\alpha'$ -dibromo-m-xylene (44) showed that imide

nucleophilic substitution reaction does take place under PTC conditions. This opens a door to polymerization reaction of  $\alpha, \alpha'$ -dibromo-m-xylene with the series of monomers synthesized.

Several polymerizations (Eq. 44) were conducted by using sodium bisimide (67) as a starting material. The infrared spectra showed the expected imide carbonyl stretching at  $1710 \text{ cm}^{-1}$ . Proton NMR, however, showed mostly broad peaks which is typical behavior for polymer compounds. Inherent viscosity of the product was determined using an Ubbelohde viscometer at  $30 \text{ }^\circ\text{C}$ . Results obtained from each bisimide polymerization are summarized in Table 5.



The low values of inherent viscosity shows that the

TABLE 5  
Polymerization of sodium bisimides (67) with  
 $\alpha,\alpha'$ -dibromo-m-xylene (44).

68	x	%yield	$\eta_{inh}$ (dL/g)	mp ( $^{\circ}$ C)
b	6	64	0.15	178-182
c	8	65	0.20	163-172
d	10	68	0.31	160-165



polymers synthesized are of low molecular weight. Several factors could contribute to the failure to produce high molecular weight polymers. First, the starting material used, sodium bisimide, was subjected to reaction without any purification. Some impurities may have been present in the starting material which would affect the polymerization reaction. Secondly, the reaction time was perhaps not long enough for completion of the reactions, since polycondensation requires long reaction times to reach high percent conversion. Finally, the trace amounts of water used probably were not optimized for the formation of high molecular weight polymers. An optimal level of trace water is essential to formation of high polymer by solid-liquid phase transfer catalysis as shown by Kellman and Liotta.<sup>26,27</sup>

From the results shown in Table 5 above, an increase in inherent viscosity was observed as the length of alkane chain linkage (-CH<sub>2</sub>-) was increased. These results are in agreement with the literature<sup>37</sup> and our expectations that an increase in solubility (and thus molecular weight) would be observed as flexibility is introduced in the polymer chain. The polymers isolated showed solubility in solvents such as dimethyl sulfoxide, dimethyl formamide, dimethyl acetamide, m-cresol, chloroform, and slight solubility in acetone. A decrease in melting point is also

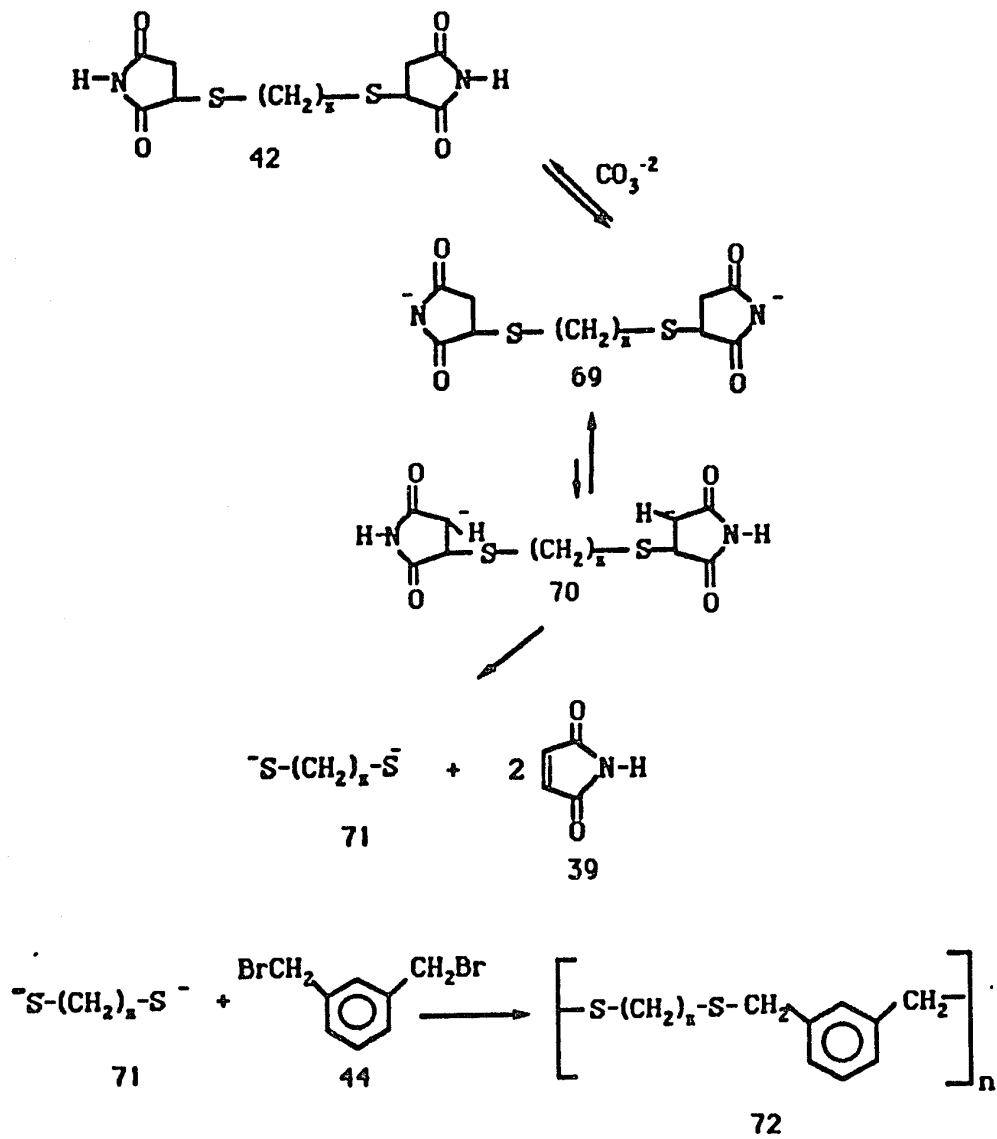
in agreement with increased aliphathic segment lengths in the polymers.

Even though model studies have shown that reverse Michael addition will compete if neutral imide is used under PTC conditions, several attempted polymerizations of neutral bisimides via PTC were performed. Attempted polymerization of  $\alpha,\alpha'$ -dibromo-m-xylene (44) and decafluorobiphenyl (19) with monomer synthesized (42) was conducted in acetone with potassium carbonate as a solid phase and base, and 18-crown-6 as a phase transfer agent.

Spectral analysis of the product isolated shows no imide compound present. This is expected since model studies have already proved that reverse Michael reaction will compete in the reaction performed. However, polymerization would still take place due to the existence of bithiolate nucleophile (71) that will react with  $\alpha,\alpha'$ -dibromo-m-xylene. The polymer (72) isolated, however, would be of low molecular weight since the stoichiometric ratio of thiolate anion generated is probably not equal to that of  $\alpha,\alpha'$ -dibromo-m-xylene. The mechanism believed to prevail is shown in Scheme VI.

Attempted polymerization of sodium bisimides (67) with decafluorobiphenyl (19) "under PTC conditions" was also performed (Eq. 45). The spectral analysis showed

## SCHEME VI





#### 4. EXPERIMENTAL

##### 4.A. Materials

Solvents were degassed by the "freeze-pump-thaw" technique and used directly for each reaction. m-Cresol from Aldrich was distilled under reduced pressure (0.5 mm; bp 60-62 °C). Pyridine was first distilled from potassium hydroxide pellets followed by final distillation from barium oxide under nitrogen. Tetrahydrofuran (THF) was distilled from lithium aluminium hydride under nitrogen. Toluene was dried over MCB Type F-1 (30-40 mesh) activated alumina. Acetone was dried over anhydrous calcium sulphate at room temperature followed by distillation from phosphorous pentoxide under nitrogen.

Tetrabutylammonium bromide,  $\alpha,\alpha'$ -dibromo-m-xylene, and decafluorobiphenyl (purchased from Aldrich Chemical Co.) were recrystallized from toluene, hexane and benzene, respectively. 18-Crown-6 (Aldrich) was purified by complexation using the technique reported.<sup>44</sup> Hexafluorobenzene (Aldrich), and the thiols; p(t-butyl)thiophenol, 1,5-dimercaptopentane, 1,6-dimercaptohexane, 1,8-dimercaptoheptane and 1,10-dimercaptooctane (Parish) were used as received. Phthalimide (Parish) was used without further purification. Potassium carbonate (anhydrous) was oven dried (130 °C) overnight before use.

#### 4.B. Equipment

Gas chromatographic analyses were performed on a Hewlett Packard 5880 (DB5 x 30 meter capillary column). A Finnigan 1020B GC/MS/DS (DB5 x 30 meter column) was used to separate and identify model products. Infrared spectra were recorded either as liquid films or KBr pellets on a Perkin-Elmer Model 1800 FT spectrophotometer.  $^1\text{H}$  NMR data were obtained either from Varian T-60A nuclear magnetic resonance spectrophotometer or from an IBM NR-80 nuclear magnetic resonance spectrometer.  $^{19}\text{F}$ -NMR spectra were obtained on the IBM NR-80. Hexafluorobenzene and tetramethylsiloxane were used as an internal standard for fluorine and proton nmr respectively. Melting points were determined on a Mel-Temp<sup>R</sup> Laboratory device and are uncorrected. The water content in the reaction solvents was determined by using the Karl Fischer titration method using a Metrohm AG CH-9100 automated electronic titrator. Dilute solution viscosity measurements were done at 30 °C by using an Ubbelohde capillary viscometer. Elemental analyses were determined by Microtech Laboratories of Skokie, Illinois and Midwest Microlab, Inc. Indianapolis, Indiana.

#### 4.C. Procedures<sup>42</sup>

##### 3-(Thiophenoxy)maleimide (40)

Thiophenol (0.735 g, 6.67 mmole) and maleimide (0.647 g, 6.67 mmole) were stirred in m-cresol (20 mL) at 80 °C under nitrogen. When all of the starting material dissolved, 2 mL of tributylamine solution (2-3 drops in 5 mL m-cresol [0.021 mole]) was added dropwise to the reaction mixture over a period of 3 minutes. After 4 hr, the cooled reaction mixture was poured into 8% glacial acetic acid (125 mL) and extracted with ether (3 x 40 mL). The ether layer was washed with saturated sodium chloride solution (40 mL) and dried (MgSO<sub>4</sub>). The solvent was removed by rotary evaporation (ether portion) and vacuum distillation (m-cresol; 77-80 °C; 0.2-0.4 mm; 13 mL). The oily product was recrystallized twice from methanol/water (80/20) giving white needles: 1.09 g (87%); mp 92-94 °C; IR (KBr) 3270, 2913, 1783, 1711, 1470, 1346, 1273, 1180, 772 cm<sup>-1</sup>; <sup>1</sup>H (acetone-d<sub>6</sub>) δ 10.01 (s, 1H), 7.40 (m, 5H), 4.35 (dd, 1H, J = 9.0, 4.5 Hz), 3.23 (dd, 1H, J = 18.5, 9.0 Hz), 2.61 (dd, 1H, J = 18.5, 4.7 Hz). Anal. Calcd for C<sub>10</sub>H<sub>9</sub>N<sub>1</sub>O<sub>2</sub>S<sub>1</sub>: C, 57.96; H, 4.38; N, 6.76; S, 15.47. Found: C, 58.15; H, 4.37; N, 6.87; S, 15.92.

**3-(p-t-Butyl)thiophenoxymaleimide (43)**

p-(t-Butyl)thiophenol (1.11 g, 6.67 mmole) and maleimide (0.647 g, 6.67 mmole) were treated following the same procedures as described above to give 43 as white needles: 1.29 g (86%); mp 113-114 °C; IR (KBr) 3302, 2953, 1787, 1707, 1464, 1352, 1270, 1180, 774 cm<sup>-1</sup>; <sup>1</sup>H NMR (acetone-d<sub>6</sub>) δ 10.01 (bs, 1H), 7.46 (s, 4H), 4.34 (q, 1H), 3.01 (q, 1H), 2.70 (q, 1H), 1.32 (s, 9H). Anal. Calcd for C<sub>14</sub>H<sub>17</sub>N<sub>1</sub>O<sub>2</sub>S<sub>1</sub>: C, 53.98; H, 7.05; N, 6.99; S, 16.01. Found: C, 53.78; H, 7.33; N, 6.64; S, 15.70

**3,3'-(1,5-Dimercaptopentane)bismaleimide (42a)**

1,5-Dimercaptopentane (1.53 g, 11.2 mmole) and maleimide (2.17 g, 22.4 mmole) were treated following the same procedures as described above to give 42a as a white powder: 3.12 g (84%); mp 105-108 °C; IR (KBr) 3199, 2821, 1779, 1715, 1350, 1270, 1180, 690 cm<sup>-1</sup>; <sup>1</sup>H NMR (acetone-d<sub>6</sub>) δ 8.01 (bs, 2H), 3.92 (dd, 2H, J = 9.0, 4.0 Hz), 3.32 (dd, 2H, J = 18.4, 9.0 Hz), 2.85 (m, 4H), 2.4 (dd, 2H, J = 18.4, 4.0 Hz), 1.64 (m, 6H).

**3,3'-(1,6-Dimercaptohexane)bismaleimide (42b)**

1,6-Dimercaptohexane (1.68 g, 11.2 mmole) and maleimide (2.17 g, 22.4 mmole) were treated following the same procedures as described above to give 42c as a white



powder: 3.25 g (84%); IR (KBr) 3235, 2982, 2847, 1779, 1712, 1353, 1188, 800, 677  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ )  $\delta$  11.33 (bs, 2H), 3.90 (dd, 2H,  $J = 9.0, 4.1$  Hz), 3.15 (dd, 2H,  $J = 18.3, 9.0$  Hz), 2.65 (dd, 2H,  $J = 12.4, 6.0$  Hz), 2.29 (d, 4H), 1.45 (s, 8H). Anal. Calcd for  $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_4\text{S}_2$ : C, 48.82; H, 5.85; N, 8.13; S, 18.62. Found: C, 48.64; H, 5.95; N, 8.10; S, 18.82.

**3,3'-(1,8-Dimercaptooctane)bismaleimide (42c)**

1,8-Dimercaptooctane (1.20 g, 11.2 mmole) and maleimide (2.17 g, 22.4 mmole) were treated following the same procedures as described above to give 42c as a white powder: 2.41 g (78%); IR (KBr) 3159, 3080, 2921, 2842, 1779, 1707, 1347, 1267, 1164, 697  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ )  $\delta$  11.33 (bs, 2H), 3.88 (dd, 2H,  $J = 8.8, 4.0$  Hz), 3.20 (dd, 2H,  $J = 18.3, 8.8$  Hz), 2.60 (dd, 2H,  $J = 12.8, 6.2$  Hz), 2.28 (d, 4H), 1.50 (bs, 12H). Anal. Calcd for  $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_4\text{S}_2$ : C, 51.54; H, 6.50; N, 7.52; S, 17.21. Found: C, 51.09; H, 6.50; N, 7.37; S, 17.35.

**3,3'-(1,10-Dimercaptodecane)bismaleimide (42d)**

1,10-Dimercaptodecane (2.31 g, 11.2 mmole) and maleimide (2.17 g, 22.4 mmole) were treated following the same procedures as described above to give 42d as a white powder: 2.55 g (85%); IR (KBr) 3164, 2911, 2840, 1779,

1718, 1346, 1269, 1159, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ )  
 $\delta$  11.31 (bs, 2H), 3.85 (dd, 2H,  $J = 8.9, 4.2$  Hz), 3.15 (dd, 2H,  $J = 18.4, 8.8$  Hz), 2.45 (dd, 2H,  $J = 18.3, 4.24$  Hz), 2.20 (d, 4H), 1.60 (s, 16H). Anal. Calcd for  $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_4\text{S}_2$ : C, 53.98; H, 7.05; N, 6.99; S, 16.01. Found: C, 53.78; H, 7.33; N, 6.64; S, 15.70.

Solvent studies for attempted preparation of  $\alpha, \alpha'$ -bis(3-[p-t-butyl]thiophenoxymaleimide)-m-xylene (45)

General procedure in THF as a solvent

To a mixture of anhydrous  $\text{K}_2\text{CO}_3$  (0.720 g, 5.20 mmole) and 18-crown-6 (0.0881 g, 0.334 mmole) in solvent (20 mL) was added 3-(p-t-butyl)thiophenoxymaleimide (0.635 g, 2.41 mmole). The magnetically stirred reaction mixture was allowed to reflux under nitrogen in an oil bath for 3 hr. To the cooled reaction mixture was added  $\alpha, \alpha'$ -dibromo-m-xylene (0.318 g, 1.21 mmole). The reaction mixture was brought to reflux for 26 hr (complete by TLC). The solvent was evaporated in vacuo and the residue was washed with 10% HCl (40 mL) and distilled water (2 x 50 mL) to yield 0.545 g (63%) of crude product. Recrystallization from acetone/water (60/40) gave  $\alpha, \alpha'$ -bis(p-[t-butyl]thiophenoxy)-m-xylene (46) as white needles: 0.220 g (55%); mp 83-84  $^\circ\text{C}$ ; IR (KBr) 2953, 1707, 1485, 1394, 1267,

1006, 823  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (acetone- $\text{d}_6$ )  $\delta$  7.43 (s, 12H), 4.10 (s, 4H), 1.30 (s, 18H). Anal. Calcd. for  $\text{C}_{28}\text{H}_{34}\text{S}_2$ : C, 77.35; H, 7.82; S, 14.75. Found: C, 77.73, H, 7.56; S, 14.30.

#### Toluene as a solvent

Following the above general procedure but substituting toluene for THF, the product was obtained as a crude yellow solid, 0.340 g (48%); mp 78-81  $^{\circ}\text{C}$ .

Recrystallization (0.25 g crude) from acetone/water (70/30) afforded 46 as a light yellow needle; 0.153 g (61%); mp 83-85  $^{\circ}\text{C}$ ; IR (KBr) 2949, 1707, 1486, 1390, 1260, 1109, 1006, 823  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (acetone- $\text{d}_6$ )  $\delta$  7.48 (s, 12H), 4.21 (s, 4H), 1.23 (s, 18H).

#### Pyridine as a solvent

Following the above general procedure but substituting pyridine for THF, the crude product was obtained as a light brown compound, 0.456 g (57%); mp 79-82  $^{\circ}\text{C}$ .

Recrystallization (0.350 g crude) from acetone/water (60/40) afforded 46 as a light yellow needle: 0.203 g (58%); mp 82-84  $^{\circ}\text{C}$ ; IR (KBr) 2949, 1707, 1486, 1390, 1260, 1109, 1006, 823  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (acetone- $\text{d}_6$ )  $\delta$  7.48 (s, 12H), 4.19 (s, 4H), 1.23 (s, 18H).

**$\alpha,\alpha'$ -Bis(phthalimide)-m-xylene (50)****Use of 18-crown-6**

To a solution of  $K_2CO_3$  (0.802 g, 5.90 mmole) and 18-crown-6 (0.100 g, 0.380 mmole) in toluene (20 mL) was added phthalimide (0.400 g, 2.73 mmole). The magnetically stirred reaction mixture was maintained at 80 °C under nitrogen in an oil bath for 3 hr. To the cooled reaction mixture was added  $\alpha,\alpha'$ -dibromo-m-xylene (0.361 g, 1.37 mmole). The reaction was brought to 80°C for 2 hr. The solvent was evaporated in vacuo and the residue was washed with 10% HCl (40 mL) and distilled water (2 x 80 mL), to give 50 as a white powder: 0.407 g (75%); mp 260-263 °C; IR (KBr) 1763, 1707, 1612, 1462, 1430, 1390, 1077, 950, 728, 530  $cm^{-1}$ ;  $^1H$  NMR (DMSO- $d_6$ )  $\delta$  7.87 (m, 12H), 4.84 (bs, 4H).

**Use of 18-crown-6 and tetrabutylammonium bromide (TBAB)**

The experimental procedure is essentially as described above. The catalysts used were 18-crown-6 (0.132 g, 0.500 mmole) and TBAB (0.161 g, 0.500 mmole). The product (50) isolated was as a white powder: 0.434 g (80%); mp 260-262 °C; IR (KBr) 1763, 1707, 1612, 1462, 1430, 1390, 1077, 950, 728, 530  $cm^{-1}$ ;  $^1H$  NMR (DMSO- $d_6$ )  $\delta$  7.87 (m, 12H), 4.84 (bs, 4H).

Solvent studies for attempted preparation of  
4,4'-bis(3-[thiophenoxy]maleimide)perfluorobenzene (54)

General procedure in THF as a solvent

To a solution of anhydrous  $K_2CO_3$  (0.642 g, 4.64 mmole) and 18-crown-6 (0.0790 g, 0.298 mmole) in tetrahydrofuran (20 mL) was added 3-(thiophenoxy)maleimide (0.446 g, 2.15 mmole). The magnetically stirred reaction mixture was allowed to reflux under nitrogen for 3 hr in an oil bath. To the cooled reaction mixture was added hexafluorobenzene (0.200 g, 1.71 mmole). The reaction was brought to reflux for 24 hr. The reaction mixture was concentrated (rotary evaporation) and washed with 10% HCl (40 mL) and distilled water (2 x 50 mL), yield 0.357 g (42%) as a light yellow powder (mp 110-113 °C). Recrystallization of the crude product from acetone/water (70/30) afforded 4,4'-bis(thiophenoxy)perfluorobenzene (53) as light yellow needles: 0.228 g (81%); mp 111-112 °C; IR (KBr) 2930, 1580, 1462, 1236, 992, 812, 745, 697, 689  $cm^{-1}$ ;  $^1H$  NMR (acetone- $d_6$ )  $\delta$  6.81 (s, 10H);  $^{19}F$  NMR  $\delta$  -132.97 (s, 4F); GC/MS m/z 366. Anal. Calcd for  $C_{18}F_4H_{10}S_2$ : C, 59.01; F, 20.74; S, 2.75; Found: C, 58.60; F, 20.22; H, 2.46; S, 17.21.

**Toluene as a solvent**

Following the above general procedure but substituting toluene for THF, the crude product was obtained as a yellow solid, 0.255 g (42%); mp 97-101 °C.

Recrystallization (0.200 g crude) from acetone/water (70/30) afforded 53 as a light yellow needle: 0.156 g (78%); mp 110-112 °C; IR (KBr) 2929, 1158, 1462, 1240, 1022, 953, 813, 746, 689  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (acetone- $\text{d}_6$ )  $\delta$  6.86 (s, 10H);  $^{19}\text{F}$  NMR  $\delta$  -130.23 (s, 4F).

**Pyridine as a solvent**

Following the above general procedure but substituting pyridine for THF, the crude product was obtained as a yellow solid, 0.362 g (72%); mp 100-106 °C.

Recrystallization of the product from acetone/water (70/30) afforded 53 as a light yellow needle: 0.241 g (80%); mp 110-112 °C; IR (KBr) 2926, 1578, 1462, 1236, 988, 954, 817, 745, 697, 686  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (acetone- $\text{d}_6$ )  $\delta$  6.79 (s, 10H);  $^{19}\text{F}$  NMR  $\delta$  -131.95 (s, 4F).

**Attempted preparation of 4,4'-bis(3-[p-t-butyl]thiophenoxy-maleimide)perfluorobiphenyl (56)**

To a solution of anhydrous  $\text{K}_2\text{CO}_3$  (0.892 g, 6.45 mmole) and 18-crown-6 (0.0790 g, 0.296 mmole) in acetone (20 mL)

was added 3-(p-t-butyl)thiophenoxymaleimide (0.446 g, 2.16 mmole). The magnetically stirred reaction mixture was allowed to reflux under nitrogen in an oil bath for 3 hr. To the cooled reaction mixture was added decafluorobiphenyl (0.359 g, 1.08 mmole). The reaction was brought to reflux for 24 hr. The cooled reaction mixture was poured into 10% HCl (100 mL) giving a yellow precipitation, yield 0.499 g (71%), mp 96-107 °C. Recrystallization of the crude product (0.350 g) from acetone/water (80/20) afforded 4,4'-bis(p-[t-butyl]-thiophenoxy)perfluorobiphenyl (55) as white crystals: 0.270 g (77%); mp 115-116 °C; IR (KBr) 2953, 1715, 1628, 1580, 1462, 1236, 954  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (acetone- $\text{d}_6$ )  $\delta$  7.30 (s, 8H), 1.35 (s, 18H);  $^{19}\text{F}$  NMR  $\delta$  193 (s, 4F), 188 (s, 4F). Anal. Calcd for  $\text{C}_{32}\text{H}_{26}\text{F}_8\text{S}_2$ : C, 59.79; H, 4.34; F, 25.22; S, 10.64. Found: C, 61.09; H, 4.19; F, 25.71; S, 10.79.

#### 4,4'-Bis(succinimide)perfluorobiphenyl (52)

To a solution of anhydrous  $\text{K}_2\text{CO}_3$  (0.892 g, 6.45 mmole) and 18-crown-6 (0.100 g, 0.368 mmole) in acetone (20 mL) was added succinimide (0.271 g, 2.74 mmole). The magnetically stirred reaction mixture was allowed to reflux under nitrogen in an oil bath for 3 hr. To the cooled reaction mixture was added decafluorobiphenyl

(0.456 g, 1.37 mmole). The reaction was brought to reflux for 24 hr. The cooled reaction mixture was poured into 10% HCl (100 mL) giving a precipitation, yield 0.594 g (84%) as a light yellow powder, mp 122-128 °C.

Recrystallization of the product from acetone/water (80/20) afforded 52 as a white crystal: 0.39 g (78%); mp 125-127 °C; IR (KBr) 1731, 1668, 1505, 1366, 1263, 1176, 1085, 966, 720  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  3.86 (m, 8H);  $^{19}\text{F}$  NMR  $\delta$  188 (s, 4F), 184 (s, 4F).

$\alpha,\alpha'$ -Bis(3-[thiophenoxy]maleimide)-m-xylene (59)

To a solution of sodium 3-(thiophenoxy)maleimide (0.626 g, 2.74 mmole) in acetone (20 mL) was added 18-crown-6 (0.100 g, 0.378 mmole). The magnetically stirred reaction mixture was heated under nitrogen in an oil bath at 80 °C for 15 minutes. To the cooled reaction mixture was added  $\alpha,\alpha'$ -dibromo-m-xylene (0.361 g, 1.37 mmole). The reaction was brought to 80 °C for 24 hr. The cooled solution was poured into 10% HCl (250 mL) giving a white precipitate. Recrystallization of the product from acetone/water (80/20) afforded 59 as a crystalline material: 0.42 g (84%); mp 120-123 °C; IR (KBr) 2937, 1771, 1699, 1584, 1473, 1434, 1394, 1331, 1164, 736  $\text{cm}^{-1}$ ;



$^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  7.32 (m, 14H), 4.30 (bs, 4H), 4.25 (dd, 2H,  $J = 8.3, 4.1$  Hz), 3.23 (dd, 2H,  $J = 16.0, 7.5$  Hz), 2.50 (dd, 2H,  $J = 15.8, 4.1$ ). Anal. Calcd for  $\text{C}_{28}\text{H}_{24}\text{S}_2\text{O}_4\text{N}_2$ : C, 65.10; H, 4.73; S, 12.41; N, 5.42. Found: C, 65.21; H, 4.68; S, 11.85; N, 5.47.

**Attempted preparation of 4,4'-bis(3-[p-t-butyl]thiophenoxymaleimide)perfluorobiphenyl (56) by using sodium salt**

To a solution of sodium 3-(p-t-butyl)thiophenoxymaleimide (0.780 g, 2.74 mmole) in acetone (20 mL) was added 18-crown-6 (0.100 g, 0.378 mmole). The magnetically stirred reaction mixture was heated under nitrogen in an oil bath at 80 °C for 15 minutes. To the cooled reaction mixture was added decafluorobiphenyl (0.456 g, 1.37 mmole) and the reaction was continued for 24 hr at 80 °C. The cooled solution was poured into 10% HCl (250 mL) giving a white precipitate, 0.518 g (82%). Recrystallization of the crude product from acetone/water (80/20) afforded 55 as white crystals: 0.27 g (60%); mp 115-117 °C; IR (KBr) 1466, 1236, 968, 946, 827, 716, 550  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  7.40 (s, 8H), 1.30 (s, 18H);  $^{19}\text{F}$  NMR  $\delta$  193 (s, 4F), 188 (s, 4F). Anal. Calcd for  $\text{C}_{32}\text{H}_{26}\text{F}_8\text{S}_2$ : C, 59.79; H, 4.34; F, 25.22; S, 10.64. Found: C, 60.72; H, 4.07; F, 24.69; S, 10.57.

**Attempted polymerization of 3,3'-(1,8-Dimercaptooctane)-bismaleimide with  $\alpha,\alpha'$ -dibromo-m-xylene (68c)**

To a solution of anhydrous  $K_2CO_3$  (0.8153 g, 5.899 mmole) and 18-crown-6 (0.1000 g, 0.378 mmole) in acetone (20 mL) was added 3,3'-(1,8-dimercaptooctane)bismaleimide (0.509 g, 1.366 mmole). The magnetically stirred reaction mixture was heated under nitrogen at 80 °C for 15 minutes. To the cooled reaction mixture was added  $\alpha,\alpha'$ -dibromo-m-xylene (0.3606 g, 1.366 mmole). The reaction was brought to 80 °C for another 24 hr. Upon cooling to room temperature, the reaction mixture was poured into 10% HCl (300 mL) giving a precipitation. The crude product was washed with distilled water (2 x 50 mL) to give 72c as a light yellow powder which was dried under vacuum at 50 °C: 0.319 g (49%); mp > 280 °C dec; IR (KBr) 2929, 2850, 1699, 1426, 1394, 1339, 1168, 776  $cm^{-1}$ ;  $^1H$  NMR (DMSO- $d_6$ )  $\delta$  7.3 (bs, 2H), 4.45 (s, 2H), 2.63 (s, 2H), 1.30 (bs, 6H);  $\eta_{inh}$  (DMSO; 30 °C) 0.051.

**Attempted polymerization of 3,3'-(1,8-dimercaptooctane)-bismaleimide with decafluorobiphenyl (65)**

The experimental procedure is essentially as described under attempted polymerization above. The stoichiometric ratio used was the same as employed above, except that decafluorobiphenyl (0.4564 g, 1.366 mmole) was used in

this reaction instead of  $\alpha,\alpha'$ -dibromo-m-xylene. The product isolated was 0.475 g (59 %) of light brown material which melted with decomposition at 260 °C. IR (KBr) 2929, 2850, 1727, 1466, 950, 712  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ) as well as  $^{19}\text{F}$ -NMR gave poor resolution. No further attempt was made in solving these spectral problems. The inherent viscosity in  $\text{CHCl}_3$  at 30 °C was 0.091.

**Polymerization of sodium 3,3'-(1,6-Dimercaptohexane)-bismaleimide with  $\alpha,\alpha'$ -dibromo-m-xylene (68b)**

To a solution of sodium 3,3'-(1,6-dimercaptohexane)-bismaleimide (0.5306 g, 1.366 mmole) and  $\alpha,\alpha'$ -dibromo-m-xylene (0.3606, 1.366 mmole) in acetone (20 mL) was added 18-crown-6 (0.1000 g, 0.3780 mmole). The magnetically stirred reaction mixture was heated under nitrogen at 80 °C for 24 hr. Upon cooling to room temperature, the reaction mixture was poured into 10% HCl (300 mL) giving a precipitation. The crude product was washed with distilled water (2 x 50 mL) to give 68b as a brown material which was dried under vacuum at 50 °C: 0.39 g (64%); mp 178-182 °C; IR (KBr) 2929, 2949, 1780, 1701, 1610, 1426, 1394, 1339, 1168, 1018, 720  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  7.60 (m, 2H), 4.75 (s, 2H), 4.03 (s, 1H), 3.81 (s, 1H), 2.90 (s, 2H), 2.78 (m, 1H), 1.56 (s, 4H);

$\eta_{inh}$  (CHCL<sub>3</sub>; 30 °C) 0.15 dL/g.

**Polymerization of sodium 3,3'-(1,8-dimercaptooctane)-bismaleimide with  $\alpha,\alpha'$ -dibromo-m-xylene (68c)**

The experimental procedure is essentially as described under general procedure for polymerization of sodium bisimides with  $\alpha,\alpha'$ -dibromo-m-xylene except that sodium 3,3'-(1,8-dimercaptooctane)bismaleimide (0.5690 g, 1.366 mmole) was used. The product (68c) isolated was a brown material: 0.382 g (59%); mp 163-172 °C; IR (KBr) 2929, 2854, 1778, 1710, 1610, 1398, 1280, 1174, 706 cm<sup>-1</sup>; <sup>1</sup>H NMR (acetone-d<sub>6</sub>)  $\delta$  7.56 (m, 2H), 4.83 (s, 2H), 4.10 (m, 1H), 3.80 (m, 1H), 3.15 (s, 2H), 2.70 (m, 1H), 1.62 (s, 6H);  $\eta_{inh}$  (CHCL<sub>3</sub>; 30 °C) 0.20 dL/g.

**Polymerization of sodium 3,3'-(1,10-dimercaptodecane)-bismaleimide with  $\alpha,\alpha'$ -dibromo-m-xylene (68d)**

The experimental procedure is essentially as described under general procedure for polymerization of sodium bisimides with  $\alpha,\alpha'$ -dibromo-m-xylene, except that sodium 3,3'-(1,10-dimercaptodecane)bismaleimide (0.6073 g, 1.366 mmole) was used. The product (68d) isolated was a light brown compound: 0.467 g (68%); mp 160-165 °C; IR (KBr) 2929, 2850, 1775, 1711, 1608, 1430, 1399, 1343, 1279, 1172, 701 cm<sup>-1</sup>; <sup>1</sup>H NMR (acetone-d<sub>6</sub>)  $\delta$  7.53 (m, 2H), 4.82

(s, 2H), 4.01 (bm, 2H), 3.78 (m, 1H), 3.01 (s, 2H), 2.81 (m, 1H), 1.56 (s, 8H);  $\eta_{inh}$  (CHCl<sub>3</sub>; 30 °C) 0.31 dL/g.  
Anal. Calcd for C<sub>26</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: C, 62.15; H, 6.77; N, 5.58; S, 12.76. Found: C, 62.32; H, 6.56; N, 5.70; S, 12.20.

**Attempted polymerization of sodium 3,3'-(1,8-dimercapto-octane) with decafluorobiphenyl (65)**

To a solution of sodium 3,3'-(1,8-dimercaptooctane) bismaleimide (0.5690 g, 1.366 mmole) and decafluorobiphenyl (0.4564 g, 1.366 mmole) in acetone (20 mL) was added 18-crown-6 (0.1000 g, 0.3780 mmole). Following the same method described under general procedure for polymerization of sodium bisimides above, the product (66c) was isolated as a light yellow powder: 0.561 g (69%); mp 180-185 °C; IR (KBr) 2921, 2858, 1779, 1723, 1481, 1068, 990, 722 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) 3.01 (m, 2H), 1.50 (bs, 6H); <sup>19</sup>F NMR  $\delta$  187 (s, 2F), 192 (s, 2F);  $\eta_{inh}$  (CHCl<sub>3</sub>, 30 °C) 0.019 dL/g.

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