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New Thiophene-based Materials

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13. ABSTRACT (Maximum 200 words)

**ABSTRACT:** Our research is focused on the general synthesis of a new class of high performance aromatic thermoplastic and thermosetting engineering polymers from thiophene-based monomers. We are interested in the introduction of changes in polymers by an explicit geometric perturbation of the primary structure of the polymer chain—substituting various amounts of thiophene into several classes of phenylene-based polymers. The anticipated property enhancements stem from unique molecular geometry of the aromatic 2,5-thiophene moiety; its nonlinear structure with an exocyclic bond angle of 148° is intermediate between that of 1,4-phenylene (180°) and 1,3-phenylene (120°) commonly used to prepare high performance materials. Often, the former are difficult to process and the latter exhibit poor mechanical properties. By focusing on the intermediate geometry of the thiophene moiety, we anticipate larger thermal processing windows without losing the desirable crystalline (and liquid crystalline) properties associated with the 1,4-phenylene-based materials. In addition, the bilateral asymmetry of the heterocycle will certainly influence the melting points, rates of crystallization, glass transition temperatures, solubility, miscibility with other polymers, adhesion, etc. relative to conventional phenylene-based materials. Our investigations of several distinct classes of polymers: thiophene-based poly(ester)s, poly(aramid)s, poly(benzoxazole)s, poly(arylene ether ketone)s, and poly(imide)s via the combination of a new route along with established methodologies will be presented.

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## New Thiophene-based Materials

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### Introduction.

The synthesis of new processible thermoplastics and fibers that possess enhanced elevated-temperature performance is a major priority in the field of high performance composites. One of the most recent approaches to modifying such materials is the incorporation of heterocyclic units into the polymer backbone. Our efforts in this area are focused on thiophene-based engineering polymers.

Specifically, we are interested in the induction of changes in polymers by an explicit geometric perturbation of the primary structure of the polymer chain—substituting various amounts of thiophene into several classes of phenylene-based polymers. The anticipated property enhancements stem from the unique molecular geometry of the aromatic 2,5-thiophene moiety: its nonlinear structure with an exocyclic bond angle of  $148^\circ$  is intermediate between that of 1,4-phenylene ( $180^\circ$ ) and 1,3-phenylene ( $120^\circ$ ) commonly used to prepare high performance materials. The dramatic differences between the polymers based on 1,4-phenylene versus 1,3-phenylene, independent of polymer class are well-documented. Often, the former are difficult to process (thermal intractable and low solubility) and the latter exhibit poor mechanical properties. By focusing on the intermediate polymer geometries via the thiophene moiety, we anticipate larger thermal processing windows without losing the desirable crystalline (and liquid crystalline) properties associated with the 1,4-phenylene-based system polymer materials. In addition, the bilateral asymmetry of the heterocycle will certainly influence melting points, rates of crystallization, glass transition temperatures, solubility, miscibility with other polymers, adhesion, etc., relative to conventional phenylene-based materials. Herein, we report our investigations of several distinct classes of polymers: thiophene-based poly(ester)s, poly(aramid)s, poly(benzoxazole)s, poly(arylene ether ketone)s, and poly(imide)s.

### Results and Discussion.

The origin of thiophene as a viable structural unit in polymers began as an exercise in understanding the molecular attributes essential for liquid crystal (LC) formation (mesomorphism). In an effort to ascertain the limiting geometries that are compatible with liquid crystallinity, a homologous series of low molar mass compounds were synthesized having the structure (I). It was known that when  $X=1,4$ -phenylene, 4,4'-biphenyl, and 2,6-naphthalene, a classical LC was obtained; when  $X=1,3$ -phenylene, liquid crystallinity was not observed. We discovered that contrary to reports in the literature, when  $X=2,5$ -thiophene, a viable mesogenic core was

achieved having a nematic, smectic-A, and smectic-C textures. This demonstrated that the  $148^\circ$  core angle was indeed compatible with thermotropic mesomorphism.

We subsequently extended this finding to liquid crystalline polymers (LCPs) based on terephthalic acid, isophthalic acid, 2,5-thiophene carboxylic acid and (substituted) hydroquinones (II).<sup>1</sup> The linear poly(ester)s containing terephthalic acid decompose before melting, while the isophthalic acid based polymers melt into an isotropic phase. The 2,5-thiophene-based polymers (II) melt at lower temperatures than the 1,4 system and exhibit stable nematic liquid crystalline phases without loss of thermal stability—a potentially significant processing advantage.

Therefore, we sought to explore the consequences of substituting thiophene into other traditional liquid crystalline systems. We moved to the poly(aramid)s (III)<sup>2,3</sup> and poly(benzoxazole)s (IV)<sup>4</sup> using 2,5-thiophene diacid chloride monomer systems. The resulting polymers showed classical nematic texture under crossed polarizers. These results demonstrate that the placement of the  $148^\circ$  kink into the backbone of conventional LCPs does not reduce its persistence length below the critical value needed for lyotropic mesomorphism. In addition, evidence shows that the thiophene-based poly(aramid) may be processed at lower temperatures than the phenyl analogue (KEVLAR, DuPont). An enhancement of processibility could therefore be realized, again without loss of the desirable liquid crystalline behavior. TGA analysis performed in nitrogen for both the thiophene-based poly(aramid) and poly(benzoxazole) showed negligible weight loss at least up to  $500^\circ\text{C}$ . These materials had inherent viscosities on the order of 2.70 dL/g (0.5g/dL in concentrated sulfuric acid).

Having proven the viability of thiophene as a tool for manipulation of molecular structure and consequent polymer design in liquid crystalline systems, it became desirable to make the substitution in other classes of polymers. Because of the potential for low cost composite fabrication, we began with poly(arylene ether ketone)s, based on bis(*p*-fluorobenzoyl)arylene monomers, where we systematically varied the central aromatic moieties from the linear 1,4-phenylene unit to the 2,5-thiophene ( $148^\circ$ ) and the 1,3-phenylene ( $120^\circ$ ) structures (V).<sup>5</sup> We demonstrated that we could achieve high molecular weight polymers when these monomers were polymerized with 4,4'-isopropylidenediphenol as evidenced by intrinsic viscosities ranging from 0.8 to 1.2 dL/g (NMP,  $25^\circ\text{C}$ ). The glass transition temperatures of the amorphous materials showed a dependence on the core angle of the substituted aromatic unit ranging from  $166^\circ\text{C}$  for 1,4-phenylene,  $158^\circ\text{C}$  for 2,5-thiophene, and  $152^\circ\text{C}$  for the 1,3-phenylene based polymers. All of the materials had comparable thermal and thermooxidative stabilities. In addition, the thiophene containing polymers showed increased reactivity as evidenced by shorter reaction times and lower reaction temperatures.

We extended the synthesis of poly(arylene ether)s to include direct analogues of ICI's poly(ether ether ketone) (PEEK). PEEK is made commercially from 4,4'-difluorobenzophenone and hydroquinone. In order to directly substitute a thiophene unit in this polymer it was necessary to use a polymerization reaction that involved nucleophilic substitution of a halogen bonded directly to thiophene. To investigate such a mechanism,

we designed a model nucleophilic substitution reaction using a monofunctional activated halothiophene based on 2-benzoyl-5-chlorothiophene and *t*-butylphenol. The reaction was found to proceed quantitatively by TLC resulting in the formation of a phenyl thienyl ether linkage. Our observation that the reaction went quantitatively using only the chloro-derivative as opposed to the fluoro-derivative, which is necessary for high molecular weight PEEK, is not surprising since it is known that nucleophilic substitution reactions on halothiophenes proceed with greater efficiency than their halobenzene analogues. Indeed, our polymerization of the thiophene analogue of 4,4'-dichlorobenzophenone with 4,4'-isopropylidenediphenol resulted in a high molecular weight thiophene-containing poly(arylene ether ketone) as evidenced by an intrinsic viscosity of 0.66dL/g (NMP, 25 °C)(VI).<sup>6</sup> The number average molar mass was found to be approximately 39,000 g/mol by GPC(polystyrene standards). The glass transitions temperature was 124°C (approximately 30 °C less than the 1,4-based system). Thermogravimetric analysis indicates that the polymer has a 5% weight loss at 419 °C under nitrogen atmosphere and 5% weight loss in air at 430 °C. A solvent cast, vacuum dried film of the polymer was of very high quality is tough, creasable, transparent and has an amber color. Attempts have been made to improve the reactivity of the dihalide monomers, as well as enhance their thermal characteristics, by introducing two carbonyls into the polymer repeat unit. Capitalizing on this effect, we have extended our monomer system to include wholly aromatic diketone monomers. This modification will lead to a one to one ratio of ketone to chlorine from which we anticipate enhanced reactivity and thermal properties. The syntheses of the more reactive 1,3 and 1,4-bis(2-chlorothiophenyl)benzene with 4,4'-isopropylidenediphenol were carried out as previously described for the poly(arylene ether)s. As expected, the result was high molecular weight polymers with an increased glass transition temperatures. Further molecular weight and thermal stability testing is in progress.

Realizing that poly(imide)s currently share the spotlight of current research in high performance polymeric matrix resins, systematic investigation of thiophene-based poly(imide)s was pursued. The materials were synthesized from a series of novel monomers based on bis(*p*-amino benzoyl)arylene monomers and oxydiphthalic anhydride to give the resulting poly(amic) acids with inherent viscosities on the order of 0.4dL/g (NMP, 25°C) in all cases. The subsequent dehydrocyclization resulted in the poly(imide) (VII). Detailed thermal and dielectric characterization is underway.

#### Conclusions.

The widespread applicability of this concept is evidenced by the synthesis of several distinct classes of polymers. In all of these cases, synthetic routes are via inexpensive monomers synthesized from thiophene-2,5-diacid chloride or halothiophene derivatives. Furthermore, misconceptions about the perceived thermal instability of thiophene-based polymers have been reputed. Clearly, the reported cases were very low molecular weight species and findings were undoubtedly determined by the behavior of endgroups. Our studies prove that thiophene-based polymers have comparable thermal stability to phenyl-based systems. Moreover, the versatility of our approach has been extended through a new route to high molecular weight polymers—the direct nucleophilic

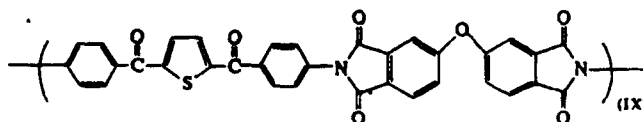
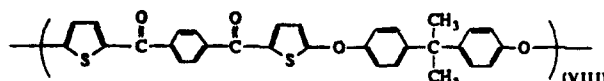
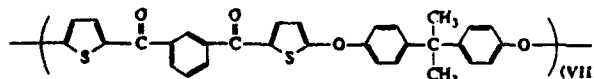
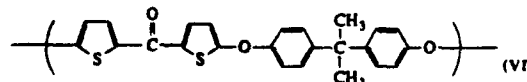
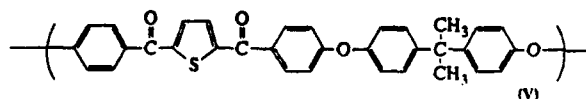
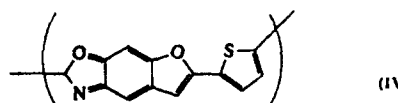
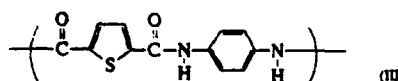
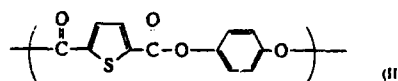
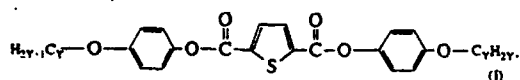
displacement with model compounds, was found to proceed quantitatively, a prerequisite for high molecular weight step growth polymers. Thus, the combination of this new route, along with well established synthetic methodologies using new thiophene monomers, has resulted in the synthesis of a variety of polymeric materials with thiophene systematically and judiciously placed into polymers with the very feasible goal of economically tailoring the physical and processing properties of high performance materials.

#### Acknowledgement.

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