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GRANT: N00014-92-J-1374

R&T Code: 413x00

Technical Report No. 3

Thiophene-based Poly(arylene ether ketone)s:
Polymerization of Bis(5-chlorothieryl-2)ketone with
4,4'-Isopropylidenediphenol

by

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Submitted for Publication

in

Polym.Prepr. (Am.Chem.Soc.Div.Polym.Chem.)

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JUN 05 1992

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May 20, 1992

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92-14771



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REPORT DOCUMENTATION PAGE

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE May 20, 1992	3. REPORT TYPE AND DATES COVERED Technical Report #3	
4. TITLE AND SUBTITLE Thiophene-Based Poly(arylene ether ketone)s: Polymerization of Bis(5-chlorothieryl-2)ketone with 4,4'-Isopropylidenediphenol		5. FUNDING NUMBERS N00014-92-J-1374	
6. AUTHOR(S) V.V. Sheares, S.C. Berndt and J.M. DeSimone			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry CB#3290 Venable & Kenan Labs. University of North Carolina Chapel Hill, NC 27599-3290		8. PERFORMING ORGANIZATION REPORT NUMBER N00014-92-J-1374	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000		10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Polym.Prepr. (Am.Chem.Soc.Div.Polym.Chem.), in press			
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13. ABSTRACT (Maximum 200 words) ABSTRACT: Our research is focused on the general synthesis of a new class of wholly aromatic thermoplastic engineering polymers based on novel thiophene monomers. Structural aerospace and automotive composites that utilize thermoplastic matrix resins have the potential to offer significant performance and processing advantages over thermosetting matrix resins; therefore, research is targeted for the development of such advanced thermoplastic resins using new chemistry methodologies. Introduction of 2,5-thiophene units would allow for the synthesis of novel thermoplastic poly(arylene ether ketone)s possessing a wider processing window related to the unique molecular geometry of the 2,5 thiophene moiety; its nonlinearity has a 148° angle which is between the 180° and 120° angles associated with the commercially utilized p- and m- phenylene units. Our primary focus was to synthesize direct analogues of ICI's Poly(ether ether ketone), PEEK, elucidating whether nucleophilic aromatic substitution reactions on activated halothiophenes proceed with sufficient conversions to allow for the synthesis of novel thermoplastic poly(arylene ether ketone)s. The short-term objective was to synthesize model compounds by direct nucleophilic substitution of chlorine on thiophene by addition of the activated 2-benzoyl-5-chlorothiophene to <i>t</i> -butylphenol treated with potassium carbonate. Apparently, nucleophilic displacement has been quantitatively achieved (by TLC) with only a keto-activating group which contrasts the phenyl derivative which requires stronger electron-withdrawing groups, such as a sulfone moiety. This model compound study and the extension to monomer and polymer syntheses will be discussed.			
14. SUBJECT TERMS Thiophene-based polymers; poly(arylene ether ketone)s; bis(5-chlorothieryl-2)ketone; bisphenol-A.		15. NUMBER OF PAGES 2	16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

Thiophene-based Poly(arylene ether ketone)s:
Polymerization of Bis(5-chlorothieryl-2)ketone with 4,4'-
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Introduction.

Research in the area of high performance polymeric matrix resins is a continuous challenge to synthesize materials that are cost effective, processible, and stable. During the past decade, the commercialization of ICI's poly(ether ether ketone) (PEEK) has contributed to the enhanced scientific interest in poly(arylene ether ketone)s as viable candidates for low cost composite fabrication. Current research seeks to design materials that add to the attractive chemical, physical, and mechanical properties inherent in this class of polymers, resulting in the extension of poly(arylene ether ketone)s into a wider variety of high performance applications.

One recent approach to modify these materials is the incorporation of heterocyclic units into the polymer backbone. The goal is to retain the characteristics of the heterocyclic system while improving processibility. Imidazoles,¹ benzoxazoles,² and pyrazoles³ have been previously utilized in poly(arylene ether)s for this purpose. Our efforts in this area are focused on preparation of thiophene-containing polymers. Our investigations are focused on the intermediate 2,5-thiophene geometry (148°) in comparison to the linear 1,4-phenylene (180°) and the kinked 1,3-phenylene (120°) structure. In addition, the sulfur atom may provide a way of introducing backbone functionality to the polymer main chain, impacting chelation, adhesion, and miscibility.

The feasibility of thiophene-containing poly(arylene ether ketone)s was realized in work previously described in our lab.^{4,5} The successful synthesis of high molecular weight polymer based on 2,5-bis(p-fluorobenzoyl)thiophene clearly demonstrates the stability of the thiophene containing monomer to usual polymerization reaction conditions. Moreover, the resulting polymer has intermediate thermal properties to the 1,4- and 1,3-phenylene analogues.

It became desirable to extend this concept to include the synthesis of thiophene analogues of ICI's PEEK. In conventional synthesis of poly(arylene ether ketone)s such as PEEK, fluorine displacement may be activated by a sulfone or ketone group. Chlorine generally requires the more electron withdrawing sulfone to avoid the S_N1 mechanism and subsequent premature termination of chain ends leading to oligomeric species.^{6,7,8} As such, 4,4'-dichlorobenzophenone has been found to generally not be reactive enough for high polymer formation with hydroquinone. Our use of the thiophene analogue of 4,4'-dichlorobenzophenone takes advantage of the fact that the S_NAr mechanism is known to be a more facile reaction in aromatic heterocycles than in the benzene-based analogues.^{9,10}

Another approach to improving the reactivity of the dihalide monomers, as well as enhancing their thermal characteristics has been by introducing two carbonyls into the polymer repeat unit.¹¹ Capitalizing on this effect, we have extended our monomer system into wholly aromatic diketone monomers, where the activated halides are found on thienyl ring systems. This modification will lead to a one to one ratio of ketone to chlorine from which we anticipate enhanced reactivity and thermal properties.

Previous work has been presented describing the successful synthesis of high molecular weight thiophene-based poly(arylene ether ketone)s from the monoketone.¹² Herein, we report a modification in reaction conditions, in addition to the most recent intrinsic viscosity, gel permeation chromatography, and thermogravimetric data. We also describe the synthesis and polymerization of diketone dichlorides. These polymer syntheses point to the potential of the new methodology proceeding via the formation of a phenyl-thienyl ether linkage as the polymer forming reaction.

Experimental

Bis(5-chlorothieryl-2)ketone Monomer

Oxalyl chloride (0.08475 mol) was added over five minutes to a stirred suspension of anhydrous aluminum chloride (0.1695 mol) in 75 mL of dry dichloroethane. A solution of 2-chlorothiophene (0.25425 mol) in 75 mL of dichloroethane was added dropwise and was allowed to stir for 24 h at room temperature and poured on to crushed ice. The organic layer was separated immediately, dried by filtering through anhydrous sodium sulfate, and stripped of solvent *in vacuo*. The dry solid was washed with 200 mL of 5% KOH solution twice, 200 mL of 5% HCl twice, and 500 mL of water. The product was recrystallized from ethanol in a 40% yield. The crystals were light yellow in color.

1,3-Bis(2-chlorothiophenoyl)Benzene Monomer

A solution of 2-chlorothiophene (0.128 mol) in 20 mL of carbon disulfide was added to a stirred suspension of isophthaloyl chloride (0.064 mol) and anhydrous aluminum chloride (0.1408 mol) in 100 mL of carbon disulfide. The reaction mixture was heated to reflux, stirred under nitrogen for 3 h, and poured into 300 mL of water. The organic layer was separated immediately, washed with 300 mL of 10% NaOH twice, 300 mL of 5% HCl twice, and 500 mL of water. The product was recrystallized twice from ethyl acetate in a 75% yield resulting in light yellow crystals.

Polymer Synthesis

A typical polymer synthesis was conducted in a three-necked, 100-mL, round-bottom flask equipped with a mechanical stirrer, gas inlet, thermometer, Dean Stark trap, and condenser. A detailed synthetic procedure for the preparation of the polymer from (IV) is provided. The flask was charged with bis(5-chlorothieryl-2)ketone (0.01140 mol), 4,4'-isopropylidenediphenol (0.01140 mol) in 25 mL of DMAc via syringe. To this solution was added potassium carbonate (0.0171 mol). Note that the potassium carbonate was used in 50% excess. The salt was washed into the flask using 5 mL of DMAc. To this solution, approximately 8 mL of toluene was added. This mixture was then heated to reflux at an optimum temperature of 150°C. Water generated during the phenoxide formation was removed over a 6 h period. The reaction temperature was then increased to 175°C for another 12 h. Completion of the polymerization was estimated by the increase in the viscosity. The polymer was coagulated in a ten-fold excess of methanol, dried and reprecipitated from chloroform into methanol.

Characterization

Proton NMR spectra were taken in CDCl₃ on a Bruker AC-200 at 200.113 MHz. A Hewlett-Packard GC-mass spectrometer (5890A-5971A) was used for product identification. Molecular weights were determined using the Waters 150-CV gel permeation chromatograph with polystyrene standards. Glass transition temperatures were obtained using a Perkin-Elmer DSC - 7. The values reported were obtained from the second heat at the midpoint using a 10 °C/min heating rate. Thermogravimetric analysis was obtained using the Perkin-Elmer TGS - 4.

Results and Discussion.

Monomer synthesis (I) was accomplished by a simple Friedel-Crafts acylation using a (2:1:1) ratio of (2-chlorothiophene: oxalyl chloride: aluminum chloride) to give the ketone. By GC the monomer purity was >99.9%. The polymerization was performed using a stoichiometric ratio of monomers, 50% excess of potassium carbonate, and a polar, aprotic solvent at 20% solids. The resulting thiophene-based poly(arylene ether) (IV) was of high molar mass as evidenced by an $[\eta] = 0.66$ dL/g (NMP, 25°C). The number average molecular weight was found to be approximately 39,000 g/mol by GPC (polystyrene standards). The glass transition 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 a bimodal 5% weight loss in air at 430°C.¹³ A solvent cast, vacuum dried film of the polymer was of very high quality. It has a transparent, amber color and is very creasable.

The syntheses of the more reactive 1,3 and 1,4-bis(2-chlorothiophenoyl)benzene monomers (II and III) were accomplished in a similar manner as the monoketone using a (2:1:2.1) ratio of (2-chlorothiophene: isophthaloyl or terephthaloyl chloride: aluminum chloride)

to give the diketone product. Purity was again determined by GC to be greater than 99.9%. Polymerizations were carried out as previously described to achieve high molecular weight polymers.(V and VI)

Conclusions.

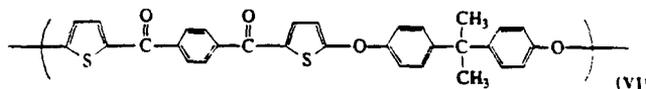
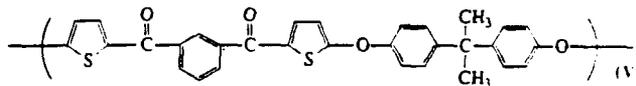
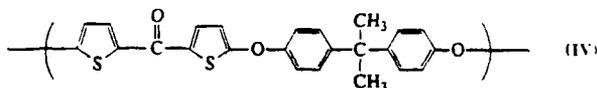
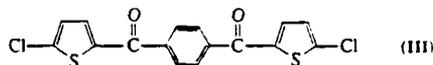
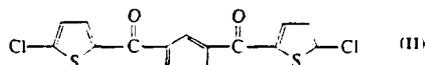
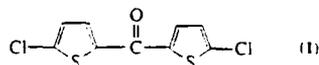
A new synthetic route was utilized to produce high molecular weight, thermally, and thermooxidatively stable thiophene containing polymer based on (IV). We anticipate that the difference in the glass transition temperature as compared with the phenyl analogue originates from the increased free volume inherent in the 148° kink in the polymer backbone. In addition, the origin of the bimodal TGA curve in air is currently under investigation. We successfully extended our monomers into wholly aromatic diketones. As expected, the resulting high molecular weight polymers showed increased glass transition temperatures. These successful syntheses based on the diketone monomers further validate the use of a new step-growth polymerization methodology via formation of a phenyl-thienyl ether linkage.

Acknowledgement.

We gratefully acknowledge financial support of this program through a Kodak Corporate Research Fellowship to VVS. In addition, we also thank the Office of Naval Research and the University of North Carolina at Chapel Hill for financial support.

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