New Polymerization Methodology: Synthesis of Thiophene-Based Heterocyclic Polyethers

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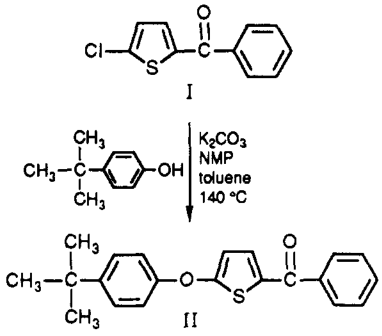
We describe a new polymerization methodology which employs thienyl–phenyl ether bond formation as the polymer-forming reaction in the step-growth polymerization of bis(5-chlorothienyl-2) ketone and 4,4′-isopropylidenediphenol which has general applicability to the synthesis of new aromatic heterocyclic polyethers. Our general synthetic approach[1,2] to tailor the performance and processability of polyethers and poly(arylene ether ketone)s—which are used extensively as matrix resins in structural composites—has focused on the development of new thiophene-based versions of these traditionally phenylene-based polymers; however, during our investigations we developed the new polymerization methodology allowing us to prepare a thiophene-based analogue of the commercially important high-performance resin poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK).

The property enhancements derived from incorporating the sulfur-containing heterocycle into aromatic polymers stem from the unique molecular geometry of the aromatic 2,5-thiophene moiety: its nonlinear geometry (a 148° exocyclic bond angle) is intermediate between that of *p*-phenylene and *m*-phenylene units. As shown by Samulski and co-workers[3,4] in low molar mass and polymeric liquid crystalline esters, the intermediate geometry of the 2,5-thiophene ring system yields a larger thermal processing window without deleteriously affecting desirable crystalline and liquid crystalline properties. Moreover, it is anticipated that the bilateral asymmetry of the heterocycle in the polymer backbone will become a new variable in macromolecular engineering strategies—backbone functionality—that can be advantageously exploited to manipulate the polymer melting point and its rate of crystallization, glass transition temperature (T_g) solubility, miscibility with other polymers, adhesion to metals, etc.

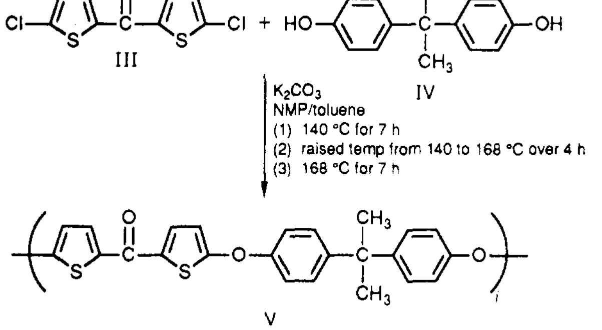
The synthesis of conventional, i.e., phenylene-based, poly(arylene ether ketone)s via the S_NAR nucleophilic substitution route generally requires a highly activated substrate in order to form high molar mass polymer avoiding the potentially deleterious $S_{RN}1$ mechanism which leads to side reactions resulting in low molar mass polymer.[5–7] PEEK is made commercially through the step-growth polymerization of an activated bisfluoride (4,4′-difluorobenzophenone) and a rigid bisphenol (hydroquinone). There is a significant element effect[8] that allows fluorine to be used with only a carbonyl electron-withdrawing group: chlorine does not make the ipso carbon electropositive enough for quantitative substitution using hydroquinone without side reactions, which is a necessary prerequisite for the synthesis of high molar mass polymers. High molar mass poly(arylene ether sulfone)s, however, can be synthesized via the quantitative displacement of chlorine from 4,4′-dichlorodiphenyl sulfone due to the greater electron-withdrawing character of the sulfone group relative to the carbonyl group.[9] Moreover, Hergenrother[10] reported that high molar mass poly(arylene ether ketone)s could only be obtained with activated dichloro monomers having a 1:1 ketone to halide ratio, such as with 1,4-bis(4-chlorobenzoyl)benzene; the monoketone bis(4-chlorophenyl) ketone having a 1:2 ketone to halide ratio could not be polymerized to high molar mass even with very reactive nucleophiles such as 4,4′-isopropylidenediphenol.[11] In these systems, quantitative displacement of the chloride (as evidenced by high molar masses) was enhanced by the introduction of two carbonyls in the monomer structure and condensation with the more reactive 4,4′-isopropylidenediphenol. Therefore, the utilization of bis(5-chlorothienyl-2) ketone as the activated bishalide monomer should *facilitate* quantitative nucleophilic displacement versus 4,4′-dichlorobenzophenone due to the increased reactivity of the aromatic heterocycle toward nucleophilic substitution[12,13] relative to the phenyl-based monomer.

To investigate whether nucleophilic aromatic substitution of activated halothiophenes proceeds with sufficient conversion to allow for the synthesis of high polymer, the following model reaction was first investigated.



The starting material, 2-benzoyl-5-chlorothiophene (I), was synthesized via Friedel–Crafts acylation of benzoyl chloride with 2-chlorothiophene.[14] The standard[15] conditions were employed for the subsequent nucleophilic substitution to produce 2-benzoyl-5-(4-*tert*-butylphenoxy)thiophene (II).[16] We found by thin-layer chromatography that the displacement of chlorine proceeds completely with no side reactions. Complete nucleophilic displacement demonstrates that this reaction meets the requirements necessary for high polymer formation via a step-growth reaction.

The model compound investigations were then extended to the synthesis of high polymer using bis(5-chlorothienyl-2) ketone (III) and 4,4′-isopropylidenediphenol (IV).



Synthesis of III was accomplished by a 2:1:1 ratio of 2-chlorothiophene/oxalyl chloride/aluminum chloride to give the ketone.[17] After two recrystallizations the purity of III was >99.9% by gas chromatography. The polymerizations were then performed using a stoichiometric ratio of III (0.035 54 M) and IV (0.035 54 M), with a 50% excess of potassium carbonate, in an 80:20 mixture of *N*-methylpyrrolidinone/toluene for 18 h as shown.

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The resulting thiophene-based poly(arylene ether ketone) (V)[18] was characterized by a number of techniques in order to confirm its composition, structure, and molar mass. Proton NMR analysis[19] showed easily distinguishable thiophene, phenyl, and methyl protons when compared with the starting materials. The key in the spectrum was the upfield shift of the thiophene proton next to the oxygen from 6.98 to 6.42 ppm, indicating formation of the thienyl ether linkage. A high molar mass was achieved as indicated by an intrinsic viscosity of 0.66 dL/g (NMP, 25 °C) and $\langle M_n \rangle = 3.9 \times 10^4$ with $\langle M_w \rangle / \langle M_n \rangle = 2.2$.[20] A solvent-cast, vacuum-dried film of the polymer was transparent, tough, flexible, and amber in color. The new polymer has a $T_g = 123$ °C (approximately 30 °C lower than 1,4-phenylene-based system).

In conclusion, it is apparent that nucleophilic displacement of activated bishalothiophenes with bisphenates leads to high molar mass polymers which is indicative of the quantitative nature of the substitution chemistry utilized in the formation of the thienyl–phenyl ether linkages. As a result of this new step-growth polymerization methodology, a large variety of heterocyclic polyethers containing aromatic units with built-in bilateral asymmetry are now possible.[21] This new methodology uses facile synthetic routes and economically feasible starting materials and opens the way to a large variety of heterocyclic, aromatic polyethers which are generally applicable for utilization as advanced materials for structural composites and microelectronics. Moreover, this chemistry should prove important for the synthesis of polymeric materials for the modification of electrodes,[22] in chelation chemistry,[23] in adhesion investigations,[24] and in design strategies for controlled structures such as in dendrimers[25] and nanoarchitectures.[26]

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Supplementary Material Available: ^1H NMR spectral data of III and V and a size-exclusion chromatogram, dilute-solution viscometric data, and a differential scanning calorimetry thermogram for V (5 pages). Ordering information is given on any current masthead page.

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(16) ^1H NMR ($CDCl_3$, 200 MHz, 23 °C): δ 7.81 (d, ortho to carbonyl), 7.30–7.55 (2, ArH ortho to isopropylidene linkage; 1, thiophene H ortho to carbonyl; 3, ArH meta and para to carbonyl), 7.18 (d, 2 ortho to oxygen), 6.42 (d, 1, thiophene H ortho to oxygen). MS: 336 (M^+).

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(18) The polymer was isolated by precipitation in methanol, extracted extensively with water to remove residual salts.

(19) ^1H NMR ($CDCl_3$, 200 MHz, 23 °C): δ 7.62 (d, 2, thiophene H ortho to C=O), 6.98–7.24 (dd, 8, ArH), 6.42 (d, 2, thiophene H ortho to O), 1.63 (s, 6, CH_3).

(20) Determined by GPC in THF using polystyrene standards.

(21) The generality of methodology has been successfully extended to other thiophene-based activated bischloride monomers such as 1,4- and 1,3-bis(2-chloro-5-thienyloyl)benzene to yield high molar mass poly(ether ketone)s: Berndt, S.; Sheares, V.; DeSimone, J. M. To be published elsewhere.

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