Thiophene-based poly(arylene ether)s: 5. Imide–arylene ether statistical copolymers

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Imide–aryl ether thiophene copolymers were prepared and their thermal and mechanical properties were investigated. A key feature of these copolymers is the incorporation of the 2,5-thiophene moiety using 5,5′-bis[(3-aminophenoxy)thienyl-2] ketone or 5,5′-bis[(4-aminophenoxy)thienyl-2] ketone as diamines in polyimide syntheses. The preparation of these thiophene diamines involved the nucleophilic aromatic substitution of bis(5-chlorothienyl-2) ketone with either 3- or 4-aminophenol in *N*-methyl-2-pyrrolidinone using potassium carbonate. These diamines were reacted with various compositions of pyromellitic dianhydride and 4,4′-oxydianiline to synthesize the desired poly(amic acid)s. Films were cast and cured (300°C) to effect the imide formation, and the resulting films showed tough ductile mechanical properties with high glass transition temperatures that decreased with increasing thiophene diamine content.

(Keywords: thiophene-based polymers; imide–arylene ether copolymers; synthesis)

INTRODUCTION

High-temperature polymers are important materials for the microelectronics industry for applications such as interlayer dielectrics, passivation layers and structural resins. Aromatic polyimides derived from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) are the most widely used owing to their availability, ease of processing, excellent thermal stability and favourable mechanical properties. Although the semi-rigid polyimide fulfils many of the material requirements for microelectronic packaging, the retention of ordered structure at high temperatures prevents sufficient mobility to achieve properties such as auto-adhesion (i.e. the adhesion of polyimide to itself). This often presents a problem in the fabrication of multilayer components derived from these structures.

One approach in modifying the characteristics of polyimides was demonstrated by Yoon *et al.*[1]. In this study, blending poly(amic acid)s and poly(amic ester)s was shown to be an effective way of introducing a flexible polyimide into a rigid material. Other examples of altering the characteristics of rigid and semi-rigid polyimides without compromising the mechanical properties include the incorporation of heterocyclic units such as imide–aryl ether phenylquinoxaline[2] and benzoxazole[3] into random or statistical copolymers. Herein, we examine the introduction of the thiophene heterocycle for these same purposes.

Our previous work with thiophene-based polymers has focused on its incorporation into several distinct classes of polymers. Well established synthetic methodologies, as well as a new synthetic route (direct nucleophilic displacement on thiophene), lends versatility to the new approach. Thiophene-containing polyesters[4], poly(aramid)s[5], poly(benzoxazole)s[6] and poly(arylene ether ketone)s[7] have previously been reported with systematic placement of the thiophene ring to tailor the physical and processing properties of these materials. Specifically, changes in polymer properties created by an explicit geometrical perturbation of the primary structure of the chain were observed. By focusing on the intermediate geometry of the thiophene moiety (148° exocyclic bond angle *versus* 180° for 1,4-phenylene and 120° for 1,3-phenylene), larger thermal processing windows were targeted without the loss of properties associated with the 1,4-phenylene-based materials. In addition, the bilateral asymmetry of the heterocycle influenced such properties as melting points, glass transition temperatures and miscibility. Herein, we will discuss the synthesis of copolymer systems derived from various amounts of ODA and thiophene-containing diamines with PMDA.

EXPERIMENTAL

Materials

N-Methyl-2-pyrrolidinone (NMP) (Aldrich) was vacuum distilled from calcium hydride. 4,4′-Oxydianiline (ODA) (Davos Chemical Co.), pyromellitic dianhydride (PMDA) (Chriskev Co.), 3-aminophenol and 4-aminophenol (Aldrich) were used without further purification. All other materials were commercially available and were used as received.

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Monomer synthesis

Bis-(5-chlorothienyl-2) ketone (**1**)[8]. Oxalyl chloride (10.75 g, 0.085 mol) was added over 5 min to a stirred suspension of anhydrous aluminium chloride (22.60 g, 0.17 mol) in 75 ml of dry dichloromethane. A solution of 2-chlorothiophene (30.15 g, 0.25 mol) in 75 ml of dichloromethane was added dropwise and allowed to stir for 24 h at room temperature. The solution was poured onto crushed ice, from which the organic layer was immediately removed. The solution was dried by filtering through anhydrous sodium sulfate. The solvent was evaporated, yielding a purple solid. This material was washed with 200 ml of 5% KOH (2 ×), 200 ml 5% HCl (2 ×) and 500 ml of water. The product was recrystallized from ethanol in 40% yield.

5,5′-Bis[(3-aminophenoxy)thienyl-2] ketone (**2**). A three-necked flask equipped with a nitrogen inlet, overhead stirrer and a Dean–Stark trap was charged with **1** (0.01238 mol) and 3-aminophenol (0.03096 mol). The reactants were carefully rinsed into the flask with 30 ml of NMP and 15 ml of toluene. Finally, K_2CO_3 (0.04644 mol) was added (50% excess) to the flask. The mixture was heated to reflux at 145°C. Water generated during the phenoxide formation was removed over a 6 h period. After dehydration, the reaction temperature was increased to 165°C. Progress of the reaction was monitored by thin-layer chromatography (t.l.c.) using hexanes/ethyl acetate (80/20) as the eluent. The reaction was complete after 12 h. The crude mixture was dissolved in CH_2Cl_2 and washed repeatedly with water, 3% KOH solution and finally a saturated NaOH solution. The isolated product was recrystallized from methanol/water yielding 2.8 g (80%) of a bright orange powder **2**; m.p. = 164–166°C. ^{1}H n.m.r. (d_6-acetone, 250 MHz, 25°C): δ 7.80–7.84 (d, 1, thiophene H, *ortho* to C═O); 7.09–7.16 (ArH, *meta* to oxygen); 6.56–6.59 (d, 1, thiophene H, *ortho* to oxygen); 6.54 (ArH, *ortho* to oxygen, *ortho* to nitrogen); 6.50–6.61 (ArH, *ortho* to oxygen); 6.41–6.45 (ArH, *ortho* to nitrogen); 4.99 (NH_2). M.s.: $M^+ = 408$ g mol^{-1}.

5,5′-Bis[(4-aminophenoxy)thienyl-2] ketone (**3**). A three-necked flask equipped with nitrogen inlet, overhead stirrer and Dean–Stark trap was charged with **1** (3.757 g, 15.2 mmol) and 4-aminophenol (2.488 g, 22.8 mmol) and K_2CO_3 (4.72 g, 34 mmol). The reactants were carefully rinsed into the flask with 40 ml of NMP and 15 ml of dry toluene. The mixture was heated to reflux at 130°C. Water generated during phenoxide formation was removed through the Dean–Stark trap over a 6 h period. After dehydration, the reaction temperature was increased to 165°C. Progress of the reaction was monitored by h.p.l.c. using acetone/water (1/4) as the eluent. The reaction was complete after 6 h. The crude mixture was dissolved in CH_2Cl_2 and washed repeatedly with water, 3% KOH solution and finally a saturated NaOH solution. The isolated product was purified by flash chromatography using hexanes/ethyl acetate (95/5) as the eluent, affording 3.74 g of **3** (87%), a bright gold powder; m.p. = 178–180°C. ^{1}H n.m.r. (d_6-acetone, 200 MHz, 25°C): δ 7.72–7.74 (1, thiophene H, *ortho* to oxygen); 6.98–7.02 (2, ArH, *ortho* to nitrogen); 6.73–6.76 (2, ArH, *ortho* to oxygen); 6.47–6.45 (1, thiophene H, *ortho* to oxygen); 4.8 (NH_2). M.s.: $M^+ = 408$ g mol^{-1}.

Polymer synthesis

The copolymers were prepared according to the literature procedure[9] in a three-necked flask equipped with an overhead stirrer and nitrogen inlet and exit. The diamines (ODA and **2** or **3**) were rinsed into the flask with NMP. The diamine mixture was in order to dissolve either **2** or **3**. Once the diamines were in solution, the solutions were cooled to 0°C. To this solution, solid PMDA was added with slow stirring. The reaction mixture was allowed to warm to room temperature, affording a viscous polymer solution (24 h). The solution was filtered (0.45 μm) and stored cold until used.

Characterization

N.m.r. spectra were recorded on a IBM WP 250 spectrometer operating at 250.1 MHz (^{1}H) with chemical shifts reported in ppm relative to tetramethylsilane. A Hewlett–Packard GC–Mass Spectrometer (5890A–5971A) was used for monomer identification.

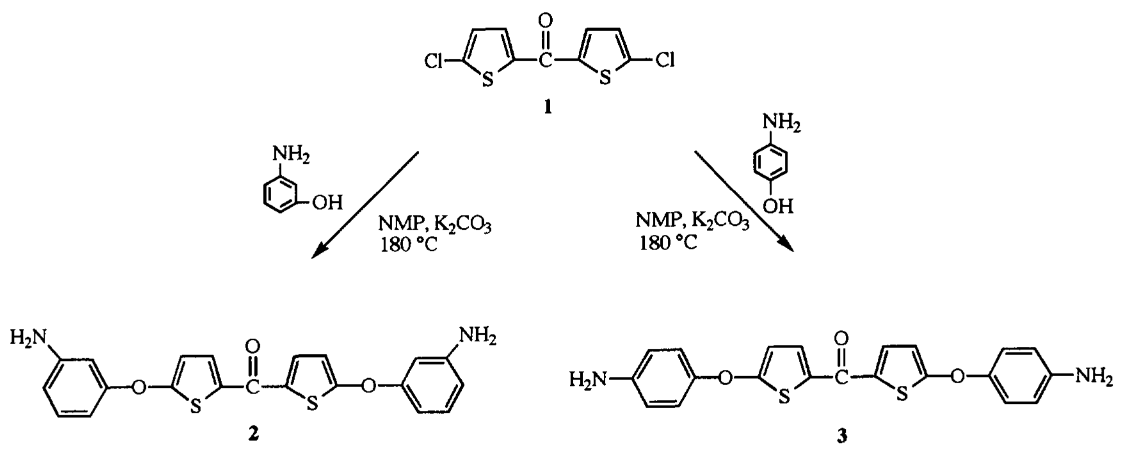
Films for mechanical and thermal analysis were cast from *N*-methyl-2-pyrrolidinone (NMP) and heated (5°C min^{-1}) to 300°C and held for 15 min. Glass transition temperatures, taken as the midpoint of the change in slope of the baseline, were measured on a DuPont DSC 2100 instrument with a heating rate of 10°C min^{-1}. Thermal gravimetric analyses (t.g.a.) of the polymer films were conducted on a Perkin–Elmer model TGA-7 in both isothermal and variable-temperature (5°C min^{-1} heating rate) modes. Dynamic mechanical measurements were made on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer in the tension mode with a heating rate of 10°C min^{-1} (10 MHz).

RESULTS AND DISCUSSION

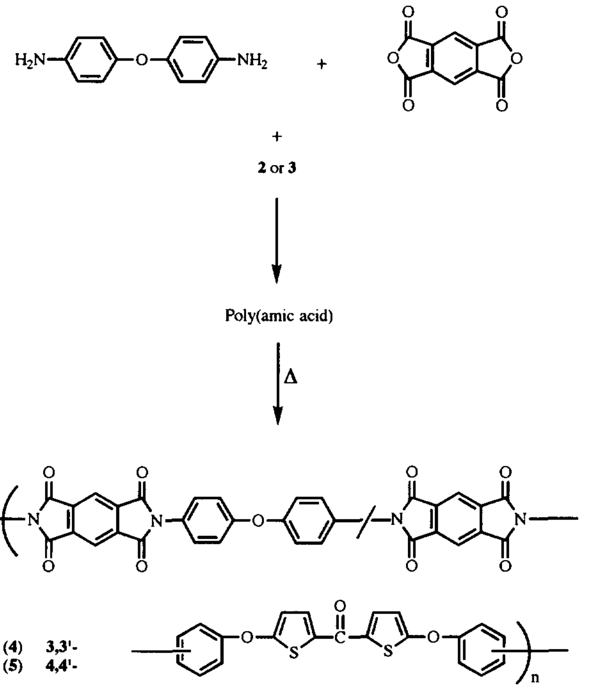
The synthetic approach used for the preparation of the bis(amino)thienyl ketones was based on a ketone-activated chloro-displacement by either 3- or 4-aminophenol. We have previously demonstrated the usefulness of nucleophilic displacement of keto-activated halothiophenes in the polymerization of the thiophene analogue of 4,4′-dichlorobenzophenone with several phenoxides. The high molar mass of the resulting poly(arylene ether ketone)s[8,10] is indicative of the quantitative nature of the substitution chemistry utilized in the formation of the thienyl–phenyl ether linkage. The success of these reactions opens the way to other polymer systems[11] in addition to monomers such as **2** and **3** via a simple, high-yield synthesis.

The details of the synthetic scheme are analogous to the phenyl sulfone- and ketone-based diamines previously reported by Kawakami *et al.*[12] and Hergenrother *et al.*[13], respectively. The diamines 5,5′-bis[(3-aminophenoxy)-thienyl-2] ketone **2** and 5,5′-bis[(4-aminophenoxy)-thienyl-2] ketone **3** were synthesized by the reaction of **1** with either 1,3- or 1,4-aminophenol, respectively, in NMP (165°C) in the presence of potassium carbonate (*Scheme 1*). Nearly quantitative conversion of **1** was observed as followed by t.l.c. and h.p.l.c. The resulting monomers, **2** or **3**, were isolated in approximately 85% yield and recrystallized or purified via flash chromatography to produce polymer-grade monomers.

The imide–aryl ether thiophene homopolymers and copolymers were prepared by a standard polyimide route via poly(amic acid) precursors in NMP. Monomers **2** or **3** were reacted with PMDA to give the resulting



Scheme 1



Scheme 2

Table 1 Thermal characteristics of imide–aryl ether copolymers

Sample no.	η (NMP)[a] at 25°C	TDA[b] (mol%)	T_g (°C)	*PDT* (°C)	I.t.g.a.[c] (%)	
					300°C	350°C
4a	0.32	100	230	430	0.10	0.31
4b	0.38	50	260	430	0.01	0.27
4c	0.42	10	[d]	455	0.03	0.05
5a	0.43	100	285	465	0.02	0.13
5b	0.69	50	304	470	0.03	0.10
5c	0.58	10	[d]	475	0.01	0.03
ODA/PMDA polyimide	–	0	[d]	480	–	0.04

[a] Inherent viscosities given for poly(amic acid)s (dl g^{-1})
[b] Thiophene diamine content
[c] Isothermal gravimetric analysis: weight loss (%)
[d] No observed glass transition temperature

homopolymers, **4a** and **5a**. In the cases of the random copolymers, **2** or **3** were reacted with specific compositions of ODA and PMDA to afford copolymers, **4b–c** and **5b–c**, respectively (*Scheme 2*). The polymer syntheses involved the incremental addition of PMDA to a solution of the desired diamine (0°C) in NMP to give a solids composition of approximately 20 wt%. Copolymer compositions were prepared with the addition of thiophene diamine (TDA) (**2** or **3**) varying from 10 to 50 mol%. PMDA is only marginally soluble in NMP at low temperatures, and the polymerization occurred at the solid/solution interface[9]. The polymerizations were allowed to return to room temperature and stirred for 24 h. The end of the reaction was evidenced by the increase in viscosity. (See *Table 1* for inherent viscosities of poly(amic acid)s.) The copolymer amic acid solutions were filtered and cured (300°C) to effect imide formation. A blocky chain microstructure is avoided in these copolymerizations since poly(amic acid) solutions are known to undergo transimidation, yielding random or statistical copolymers[9].

The thermal analysis for the copolymers (series **4** and **5**) and a PMDA/ODA homopolyimide are shown in *Table 1*. As with the polyimide homopolymer, no detectable T_g was observed for the polyimide copolymers containing high ODA compositions (**4c** and **5c**) by differential scanning calorimetry (d.s.c.) measurements. However, copolymers with the higher thiophene composition (**4a** and **b**) displayed T_g values in the 250°C range while **5b** and **c** showed T_g values of approximately 290°C. Presumably, the appearance of a T_g in both copolymers results from the presence of more ether linkages and increased chain mobility associated with the thiophene diamines.

Table 1 also contains the thermal gravimetric results of both copolymer series (**4** and **5**). The thermal stability was first assessed by the weight loss on isothermal ageing at 300 and 350°C (N_2 atmosphere). With the exception of **4a**, 0.01–0.03% weight loss was observed upon ageing at 300°C. At 350°C, the values increased significantly for the 1,3-phenylene copolymers with 10 and 50% thiophene diamine content. Series **5** at 350°C shows a slight increase in values again, with the highest TDA-containing copolymer (**5a**) having the highest value. The thermal stability was also judged by polymer decomposition temperature (*PDT*). The temperatures ranged from 430 to 455°C for series **4**. Series **5** values were approximately 480°C, which are comparable to the PMDA/ODA homopolymer.

Figures 1 and *2* contain examples of the dynamic mechanical results for the designated copolymers and are

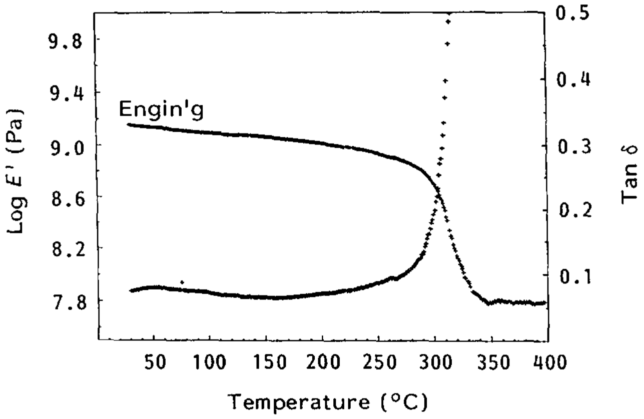


Figure 1 Dynamic mechanical thermal behaviour of copolymer **4a**

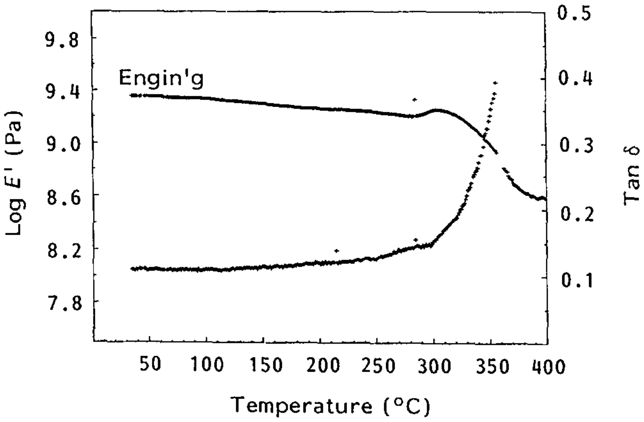


Figure 2 Dynamic mechanical thermal behaviour of copolymer **5b**

consistent with the calorimetry results. The effect of having the thiophene-containing comonomer with the high parent imide composition (**4c**) is clearly illustrated. The copolymer shows only a minimal drop in modulus at high temperatures, indicating both the absence of a T_g and the retention of the morphology characteristic of the parent polyimide. However, the copolymer **5b**, containing 50 mol% thiophene composition, shows significantly different behaviour. A larger decrease in modulus is observed at 300°C.

CONCLUSIONS

New thiophene-containing diamines were synthesized by the nucleophilic substitution of bis(5-chlorothienyl-2) ketone by both 3- and 4-aminophenol. These 5,5'-bis[(aminophenoxy)thienyl-2] ketone monomers were successfully reacted with PMDA and ODA to yield the corresponding poly(amic acid) solutions, which in turn were converted to give new imide–aryl ether thiophene copolymers. These copolymers displayed good film-forming properties consistent with other previously explored imide–aryl ether systems. The structural, mechanical and thermal properties of these copolymers were studied and compared to those of PMDA/ODA polyimide, with an observed lowering of the glass transition temperature and polymer decomposition temperature with the increased incorporation of the thiophene diamines.

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