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Imide-aryl ether benzothiazole copolymers

James L. Hedrick

IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099, USA

Summary

Imide-aryl ether benzothiazole random copolymers were investigated. A new diamine containing preformed benzothiazole rings was prepared by a thiazole activated nucleophilic aromatic substitution reaction. The synthesis involved the reaction of 2,6-(bis(4-fluorophenyl))benzo[1,2,4,5]bisthiazole with 3-aminophenol in the presence of K_2CO_3 in N-methylprrolidone (NMP) to afford bis(3-aminophenoxy)phenylbenzo [1,2,4,5]bisthiazole in high yield. This new diamine was readily purified and co-reacted with various compositions of 4,4′-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) producing a series of imide-ary ether benzothiazole random copolymers. Films were cast and cured (350 °C) to effect imidization, affording tough films with moduli significantly higher than PMDA/ODA polyimide. The thermal stability of the copolymers was good with thermal decomposition temperatures in the 480 to 510 °C range, and the thermal expansion coefficients were lower than PMDA/ODA polyimide and in the 25-30 ppm range.

Introduction

High temperature polymers are important in the microelectrics industry for such applications as interlayer dielectrics and passivation layers, and aromatic polyimides derived from pyromellitic anhydride (PMDA) and 4,4′-oxydianaline (ODA) are the most widely used due to their availability, excellent thermal and dimensional stability (Tg > 400 °C) and good mechanical properties. The good mechanical properties result, in part, from the liquid crystalline or crystalline morphology manifested by this material (1,2). However, there are many drawbacks to the use of PMDA/ODA polyimide in the fabrication of multilayer components which include auto-adhesion (the adhesion of polyimide to itself) and residual stress upon thermal cycling. Several schemes have been developed and published on the modification of the adhesion characteristics of PMDA/ODA polyimide which include the incorporation of diamines with preformed phenylquinoxaline and benzoxazole linkages (3,4). These copolymers manifested a T_g below 400 °C and adhesion was achieved once sequentially cast layers were cured to 400 °C. The residual stress developed in polyimides upon thermal cycling is lower for structures with high moduli and low thermal expansion coefficients (TEC). The semi-rigid PMDA/ODA polyimide has a relatively low modulus and a TEC of 35 to 40 ppm. Conversely, rigid-rod polyimides such as those derived from biphenyl dianhydride (BPDA) and p-phenylene diamine (PDA) as well as PMDA and PDA have high moduli and TEC's below 5 ppm resulting in a low stress material upon thermal cycling. These characteristics are reflective of the enhanced ordering manifested by these polyimides. Although these polyimides show low stress, drawbacks to their highly ordered morphology and the absence of a T_g is poor auto-adhesion. In this paper, the synthesis of a new rigid diamine which contains preformed benzothiazole and aryl ether linkages will be discussed. This diamine was co-reacted with various compositions of PMDA and ODA in an effort to enhance the ordering while lowering the T_g.

A number of reports have appeared in the literature on the preparation of imide copolymers with various heterocyclic systems. Preston and coworkers (5-7) have prepared diamines containing preformed benzothiazole and benzoxazole rings which were reacted with dianhydrides to form imide-benzothiazole and imide-benzoxazole random copolymers, respectfully. These copolymers were prepared in the form of their soluble poly(amic-acid) precurser, which could be fabricated and thermally cured to obtain the desired materials. Films of the copolymers demonstrated both good mechanical properties and thermal stability. Furthermore, in some cases semi-crystalline morphologies were observed.

A similar synthetic approach has been used in the preparation of a new diamine used to synthesize a series of imide-aryl ether benzothiazole statistical or random copolymers. It has been demonstrated that hetrocycles such as benzoxazoles and phenylquinoxalines can activate halides towards nucleophilic aromatic substitution, and this reaction was used to prepare heterocyclic containing poly(aryl ethers) (8,9) and diamines (3,4). In this paper the heterocyclic activated halo-displacement has been extended to a benzothiazole ring to prepare new diamines amenable towards polyimide syntheses. Since poly(benzothiazole) homopolymers are known to be highly ordered materials (10,11), the incorporation of the benzothiazole into polyimide should enhance the ordering to produce a low TEC polymer. Further, these properties should be improved without the sacrifice of the thermal stability.

Experimental

2-(4-Fluorophenyl)benzothiazole, **1**. A three neck flask equipped with a condenser was charged with 2-aminothiol (11.57 g, 0.0924 mol), and triethylamine (19.6 g, 0.1937 mol) which were carefully washed in with chloroform (250 mL). 4-Fluorobenzoyl chloride (29.2045 g, 0.1848 mol) was added dropwise through an addition funnel (−5 °C). The reaction was allowed to return to room temperature and stirred for 24 h. The reaction was partitioned between chloroform and water, washed 2x with water, dried ($MgSO_4$) and concentrated under reduced pressure. The light yellow powder was then transferred to a round bottom flask equipped with a condenser and slowly heated to 260 °C to effect cyclization (3 h). The disubstituted monomer melted at 125 °C and upon ring closure, the monomer solidified and 4-fluorobenzoic acid sublimed into the condenser. The resulting yellow solid, **1**, was purified by sublimination. The spectra properties were consistent with the assigned structure. Anal. Calcd. for $C_{13}H_8N_1S_1F_1$: C, 68.10; H, 3.52; N, 6.11. Found: C, 68.01; H, 3.53; N. 5.69.

3-Aminophenoxyphenyl-2-benzothiazole, **2**. A three neck 25 mL flask equipped with a Dean-Stark trap with condenser was charged with **1** (0.7532 g, 0.00328 mol), 3-aminophenol (0.3867 g, 0.003515 mol) and K_2CO_3 (0.4851 g, 0.003515 mol). The contents were carefully washed in with 5 mL of NMP and 10 mL of toluene. The reaction mixture was heated at the reflux temperature (140-150 °C) to azeotrope the water generated from phenoxide formation. Upon dehydration, the reaction temperature was raised to 180 °C to effect the displacement reaction (24 h). The product was isolated in water and purified by flash chromatography to yield **2** in quantitative yield. The spectral properties were consistent with the assigned structure. Anal. Calcd. for $C_{19}H_{14}N_2S_1O_1$: C, 71.67; H, 4.92; N, 9.78. Found: C, 72.26; H, 4.65; N, 8.67.

2,6-(Bis-4-fluorophenyl)benzo[1,2,4,5]bisthiazole, **3**. A 500 mL round bottom flask equipped with a condenser was charged with 2,5-diamino-1,4-benzenedithiol dihydrochloride (DayChem) (1.6500 g, 0.00673 mol), triethylamine (4.200 g, 0.04152 mol) and 400 mL of chloroform. The reaction was cooled to −5 °C and 4-fluorobenzoyl chloride (4.2533 g, 0.02692 mol) was added incrementally (1 h). At this time, excess 4-fluorobenzoyl chloride (2.000 g, 0.01265 mol) was added and slowly heated to reflux (3 h) where the solution became clear. The reaction mixture was cooled, partitioned between chloroform and water, washed with dilute base, washed with water (2X), dried ($MgSO_4$) and concentrated under reduced pressure. The resulting yellow powder was placed in a sublimator and slowly heated to 260 °C to effect ring closure which evolved fluorobenzoic acid. The remaining dark powder was recrystallized twice from NMP to afford **3** as a polymer grade monomer, with the expected spectral properties. Anal. Calcd. for $C_{20}H_{10}N_2S_2F_2$: C, 63.14; N, 7.36; H, 2.65: Found: C, 63.01; N, 7.36; H, 2.73.

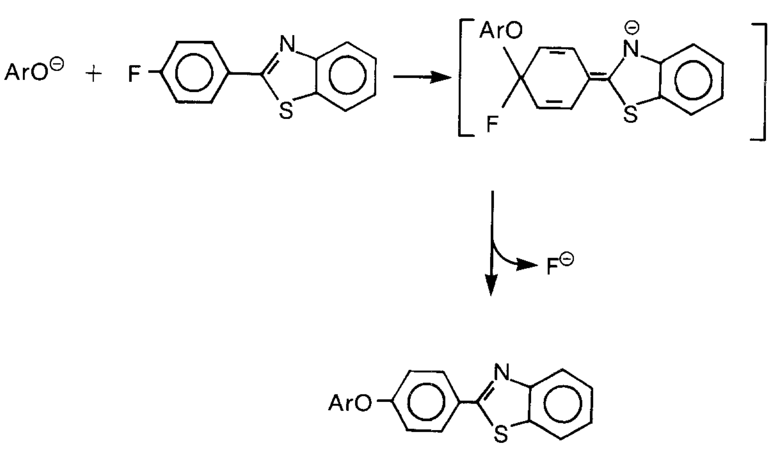
Bis(3-aminophenoxyl)phenylbenzo[1,2,4,5]thiazole, **4**. A three neck flask with a nitrogen inlet, overhead stirrer and Dean-Stark trap with condenser was charged with **3** (1.7638 g, 0.0046 mol), 3-aminophenol (1.1200 g, 0.0102 mol) and K_2CO_3 (2.5000 g, 0.01811 mol). The contents were carefully washed in with 14 mL of NMP and 20 mL of toluene and heated to reflux (~140 to 155 °C). The water generated upon phenoxide formation was removed as the toluene azeotrope, and upon dehydration the reaction was heated to 180 °C to effect the displacement reaction (24 h). Upon cooling, **4** crystallized from the NMP and was then isolated by filtration, washed with water (to remove salts) and methanol to remove excess aminophenol. The monomer was then recrystallized twice from NMP to afford **4** as a light brown powder. Anal. Calcd. for $C_{32}H_{22}N_4S_2O_2$: C, 68.79; H, 3.97; N, 10.03. Found: C, 68.61; H, 3.95; N, 10.19.

The copolymers were prepared according to the literature procedure (12). In a three neck flask equipped with an overhead stirrer and nitrogen inlet and exit. The diamines (ODA and **4**) were charged and washed in with NMP and cooled to −10 °C under a strong nitrogen flow. To this solution, PMDA was added with slow stirring, and the reaction mixture was allowed to return to room temperature affording a viscous polymer solution (48 h). The solution was filtered (0.5μm) and stored cold until used.

Films for thermal and mechanical analysis were cast from NMP and heated to 350 °C (5 °C/min. heating rate) and held for 30 min. Glass transition temperatures, taken as the mid point of the change in slope of the baseline, were measured on a DuPont DSC 1090 instrument with a heating rate of 10 °C/min. (10 Hz) in the tension mode. Isothermal and variable temperature (5 °C heating rate) thermal Gravimetric Analysis (TGA) were performed on a Perkin-Elmer model TGA-7. Mechanical property measurements were performed on an Instron tensile tester at a strain rate of 10 mm/min.

Results and Discussion

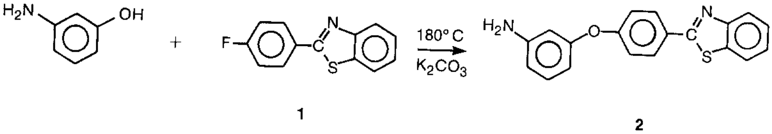
The synthetic approach used for the preparation of the bisbenzothiazole containing diamine was based on a thiazole activated fluoro-displacement by an amino-substituted phenoxide. The rationale for the facile nucleophilic aromatic substitution from a benzothiazole substituted ring was two fold (a) The electron poor thiazole ring would have the effect of an electron withdrawing group, (b) A Meisenheimer complex would form as a stabilized intermediate during the transformation due to resonance of the negative charge into the



Scheme 1

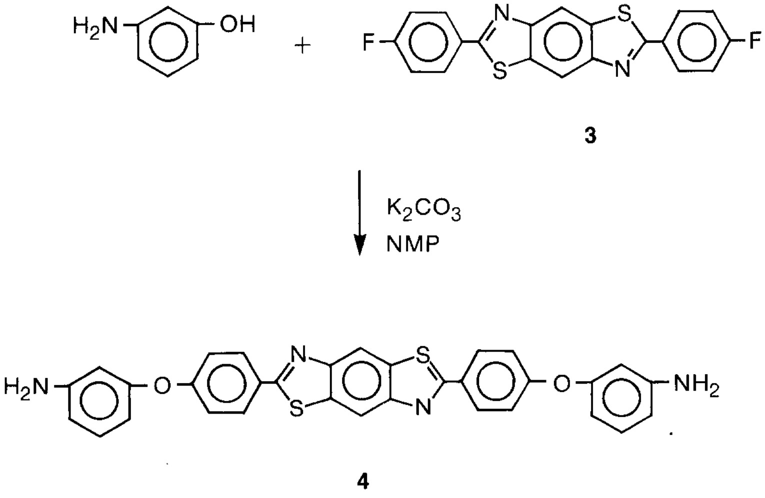
oxazole ring (Scheme 1). This synthetic approach is analogous to the preparation of sulfone (13), ketone (14), phenylquinoxaline (3) and benzoxazole (4)-based diamines.

To demonstrate the feasibility of the benzothiazole activated aryl ether synthetic approach for the preparation of bis(amino) benzathiazone based monomers, a model reaction between 1 and 3-aminophenol in the presence of K_2CO_3 was investigated (Scheme 2). Quantitative conversion 1 was observed by TLC (methylene chloride/methanol) with the formation of a single product peak. The desired product was isolated in near quantitative yield demonstrating that the thiazole activated fluoro-displacement is a suitable route for the preparation of diamines containing preformed benzothiazole rings.



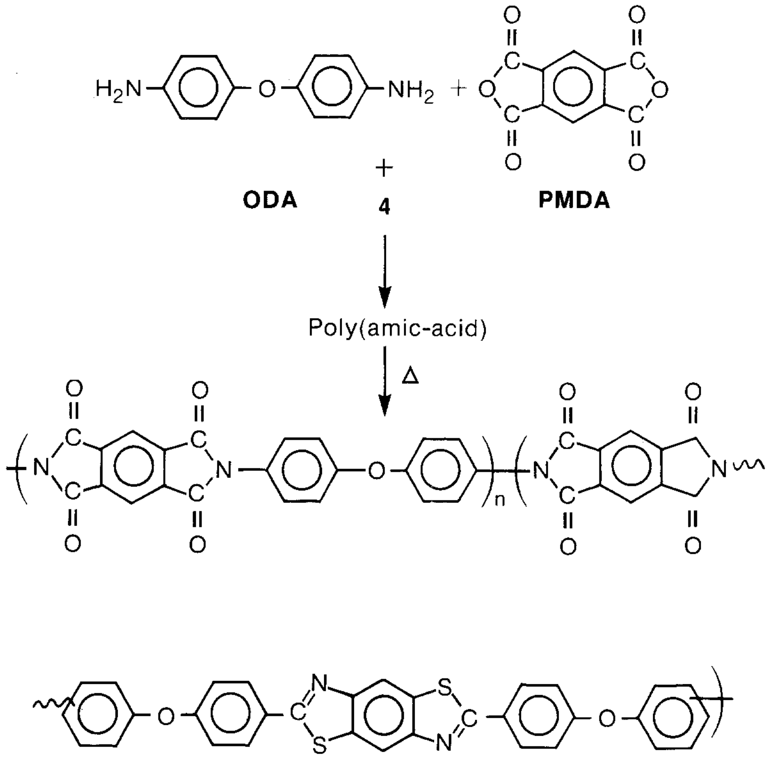
Scheme 2

The benzothiazole containing diamine, 4, was synthesized by the reaction of 3 with 3-aminophenol in NMP/toluene solvent mixture in the presence of K_2CO_3 (Scheme 3). The toulene was used to azeotope the water generated upon phenoxide formation (~150 °C), and upon dehydration (4-6 h) the reaction temperature was increased to 180-190 °C to effect the displacement reaction (24 h). As in the case of the model reaction, quantitative conversion of 3 was observed with the formation of a single product peak. Upon cooling, 4 crystallized from the NMP solution. The product was filtered, rinsed with deoxygenated methanol (to remove excess 3-aminophenol) and then with deoxygenated water to remove excess K_2CO_3 as well as salts formed during the reaction. The diamine was then purified by recrystallization (twice) from NMP.



Scheme 3

The imide-aryl ether benzothiazole copolymers were prepared via the standard polyimide synthetic route (i.e., poly(amic-acid) intermediate) in NMP (Scheme 4). The two diamines, 4 and ODA, were charged into the flask, carefully rinsed in with NMP and cooled to −5 °C. However, 4 was only marginally soluble in the NMP at this temperature and composition. The PMDA was added in increments as a solid to the slurry/solution of the



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Scheme 4

diamines. Initially, the PMDA was only marginally soluble in NMP. Upon dissolution and polymerization of PMDA, **4** reacts with PMDA at the solid/solution interface. The polymerization was then stirred for 48 h at room temperature to insure complete randomization (12). High molecular weight poly(amic-acid) solutions were obtained as judged by the high viscosities. Copolymer compositions were prepared so as to vary the weight percent of **4**, the benzothiazole component, relative to the total weight of PMDA and ODA, the polyimide component. The benzothiazole compositions ranged from 25 to 70 wt.% (copolymers **5a-c**) with the latter sample (**5c**) being **4** chain extended with PMDA (Table 1). The copolymer solutions were filtered and cured 350 °C (30 min) to effect imidization.

The thermal analysis for the copolymers prepared and a PMDA/ODA polyimide to facilitate comparison are shown in Table 1. As in the case for the polyimide homopolymer, no detectable T_g was observed for the polyimide copolymers by calorimetry measurements. The thermal stability, as judged by the polymer decomposition temperature (PDT) and isothermal weight loss at 400 °C, for the copolymers was good and comparable to the parent polyimide. Most noteably the thermal expansion coefficient (TEC) of **5c** was 25 ppm which is considerably lower than PMDA/ODA polyimide (40 ppm).

The dynamic mechanical behavior for copolymers **5a-c** are shown in Figure 1. The incorporation of the benzothiazole containing diamine into polyimide significantly enhanced the modulus, and the modulus increases with increasing benzothiazole composition. This is consistent with the low TEC. The ordering observed in PMDA/ODA polyimide significantly influences the modulus temperature profile. The modulus is

TABLE 1. Thermal analysis of imide-aryl ether benzothiazole copolymers

Sample No.	Benzothiazole Composition, wt.%	PDT, °C	Isothermal wt. loss, 400 °C	TEC, ppm
5a	25	517	0.02	--
5b	50	490	0.04	--
5c	70	480	0.05	25
PMDA/ODA Polyimide		480	0.04	40

essentially invariant up to 400 °C, except for a small drop ca. 350 °C (3). The imide-aryl ether benzothiazole copolymers show similar modulus-temperature behavior except the transition is shifted to lower temperatures, consistent with the incorporation of both meta- and ether-linkages. Preliminary, wide angle x-ray diffraction studies indicate that the liquid crystalline like ordering characteristic of PMDA/ODA is retained in copolymer **5a**, whereas copolymer **5c** appears to be semi-crystalline. This is consistent with the high modulus and low TEC and its anticipated that this material will have low residual stress upon thermal cycling.

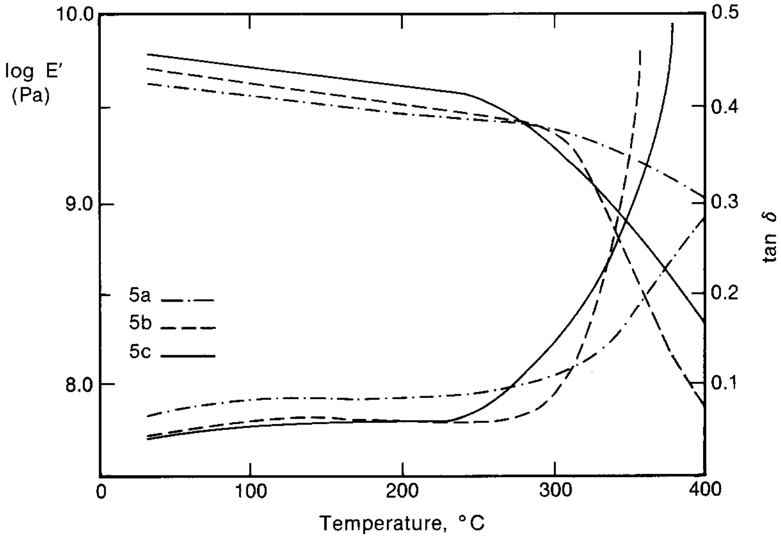

Figure 1. Dynamic mechanical behavior for copolymers **5a-c**.

Conclusions

Imide-aryl ether benzothiazole random copolymers were prepared and their thermal properties investigated. Benzothiazole containing diamines were prepared via a novel nucleophilic aromatic substitution reaction and co-reacted with various compositions of ODA and PMDA. The resulting poly(amic-acids) were cast and cured (350 °C) to effect imidization, affording tough films with high moduli and good thermal stability. Future publications will discuss the morphology and mechanical properties in more detail.

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