Imide-aryl ether benzothiazoles

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

(Received 31 January 1991; revised 3 May 1991; accepted 21 May 1991)

Novel imide-aryl ether benzothiazole copolymers were prepared and their morphology and mechanical properties investigated. Diamines containing preformed benzothiazole rings were prepared and used in conventional polyimide syntheses. The preparation of these diamines involved the nucleophilic aromatic substitution reaction of 2,6-bis(4-fluorophenyl)benzo[1,2,4,5]bisthiazole with either 3- or 4-aminophenol in the presence of K_2CO_3 in *N*-methyl-2-pyrrolidone to afford 2,6-bis(4-aminophenoxy-4-phenyl)benzo-[1,2,4,5]dithiazole and 2,6-bis(3-aminophenoxy-4-phenyl)benzo[1,2,4,5]dithiazole, respectively. The monomers were each reacted with pyromellitic dianhydride to synthesize the desired poly(amic acids). Films were cast and cured to 350°C to effect imidization, producing films with good mechanical properties. The copolymers exhibited good dimensional ($T_g > 400°C$) and thermal stability. Wide angle X-ray diffraction measurements showed that in one case a semicrystalline morphology was obtained producing a film with both a high modulus and low thermal expansion coefficient.

(Keywords: imide-aryl ether benzothiazoles; morphology; mechanical properties)

INTRODUCTION

Rigid-rod and extended chain high temperature polymers, including poly(benzothiazoles), poly(benzoxazoles) and selected polyimides, have very high moduli, low thermal expansion coefficients (TEC), exceptional thermal stability as well as many other desirable properties. The high degree of molecular rigidity in these systems dominates the morphology and subsequent mechanical properties. The poly(benzothiazoles) and poly(benzoxazoles) are generally processed from nematic liquid crystalline solutions in polyphosphoric acid into highly ordered or semicrystalline fibres[1,2]. Likewise, the extended chain polyimides are typically processed from *m*-cresol in the fully cyclized form into highly ordered fibres[3]. Drawbacks to these rigid-rod polymers is their limited solubility and intractability, precluding their uses in many applications. Conversely, the semi-rigid polyimides, such as those derived from biphenyl dianhydride (BPDA), with 1,4-phenylendiamine (PDA) and pyromellitic dianhydride (PMDA) with PDA, may be processed from the poly(amic acid) or poly(amic ester) soluble precursors in *N*-methyl-2-pyrrolidone (NMP) and thermally or chemically cured to effect imidization. These structures show TECs <5 ppm, high moduli and low stress upon thermal cycling making them viable candidates for the fabrication of multilayer microelectronic components. These desirable properties are reflective of the high degree of liquid crystalline or crystalline ordering manifested by these materials[4,5]. We felt it would be of interest to combine the characteristics of both the rigid and semi-rigid structures to obtain a highly ordered material yet processable from a soluble precursor. The synthetic approach involved the preparation of new diamines containing rigid benzothiazole moieties. Each of the diamines were reacted with PMDA to afford novel poly(amic acid) solutions which were thermally cured to the imide form.

A number of reports have appeared in the literature on the preparation of imide copolymers with various heterocyclic systems. Preston and co-workers[6–8] have prepared diamines containing preformed benzothiazole and benzoxazole rings which were reacted with dianhydrides to form imide-benzothiazole and imide-benzoxazole random copolymers, respectively. These copolymers were prepared in the form of their soluble poly(amic acid) precursor, 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 semicrystalline morphologies were observed.

A similar synthetic approach has been used in the preparation of new diamines used to synthesize imide-aryl ether benzothiazole statistical or random copolymers. It has been demonstrated that heterocycles such as benzoxazoles and phenylquinoxalines can activate halides towards nucleophilic aromatic substitution, and this reaction was used to prepare heterocyclic containing poly(aryl ethers)[9,10] and diamines[11,12]. In this paper the heterocycle activated halo displacement has been extended to a benzothiazole ring to prepare new diamines amenable to polyimide syntheses. Preliminary investigations of these copolymers have been published elsewhere[13]. The incorporation of the rigid aryl ether benzothiazole moiety into polyimide should enhance the ordering to produce a low TEC material. Further, these properties should be improved without sacrificing the thermal stability.

EXPERIMENTAL

Materials

4,4′-Oxydianaline (ODA, Davos Chemical Corporation) and PMDA (Chriskev Company) were used without further purification. *N*-cyclohexyl-2-pyrrolidone

0032-3861/92/071399-07
© 1992 Butterworth-Heinemann Ltd.

and NMP were vacuum distilled from P_2O_5 prior to use. 1,4-Dimercapto-1,5-diaminobenzene dihydrochloride (Day Chem) and 4-fluorobenzoic acid (Aldrich) were used without further purification. 4-Fluorobenzoyl acid chloride was prepared by the reaction of 4-fluorobenzoic acid (32.6 g, 232.7 mmol) with oxalyl chloride (44 g, 349.0 mmol) in ethyl acetate under N_2 for 24 h (room temperature). The reaction was concentrated and the product was distilled at 173°C (N_2 atmosphere) to give 32.3 g (88% yield) of 4-fluorobenzoyl chloride as a colourless liquid.

2-(4-Fluorophenyl)benzothiazole, 1. A three-necked 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 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 twice with water, dried ($MgSO_4$) and concentrated under reduced pressure. The light yellow powder was then transferred to a round-bottomed 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 sublimation: m.p. = 96–98°C; i.r. (KBr) cm^{-1} 1604, 1502, 1455, 1436, 1296, 1252. Analysis: calculated 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.

2-(3-Aminophenoxy-4-phenyl)benzothiazole, 2. A three-necked 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 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 affording a light yellow powder: m.p. = 94–96°C; i.r. (KBr) cm^{-1} 3381, 1602, 1481, 1313, 1238, 1170. Analysis: calculated 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]dithiazole, 3. A 500 ml round-bottomed flask equipped with a condenser was charged with 1,4-dimercapto-2,5-diaminobenzene dihydrochloride (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 in increments (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 twice with water, dried ($MgSO_4$) and concentrated under reduced pressure. The resulting yellow powder was placed in a sublimater 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 light yellow powder: m.p. = 314–317°C; i.r. (KBr) cm^{-1} 1526, 1426, 1411, 1311, 1209. Analysis: calculated 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.

2, 6-Bis(3-aminophenoxy-4-phenyl)benzo[1, 2, 4, 5]-dithiazole, 4. A three-necked flask with a N_2 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 with 14 ml of NMP and 20 ml of toluene and heated to reflux (~140–155°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: m.p. = 284–287°C; i.r. (KBr) cm^{-1} 1653, 1559, 1539, 1522, 1404, 1283. Analysis: calculated for $C_{32}H_{22}N_4S_2O_2$, C 68.79, H 3.97, N 10.03; found, C 67.91, H 3.96, N 9.50.

2, 6-Bis(4-aminophenoxy-4-phenyl)benzo[1, 2, 4, 5]-dithiazole, 5. A three-necked flask equipped with a N_2 inlet, overhead stirrer and Dean-Stark trap with a condenser was charged with **3** (2.2309 g, 0.0059 mol), 3-aminophenol (1.4500 g, 0.0732 mol) and K_2CO_3 (2.5000 g, 0.01811 mol). The contents were rinsed with 16 ml of NMP and 25 ml of toluene and heated to reflux temperature (~140–155°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 **5** crystallized from the NMP and was then isolated by filtration, washed with water (to remove salts) and then methanol (to remove excess aminophenol). The monomer was then recrystallized twice from NMP to afford **5** as a light brown powder: m.p. = 300–304°C; i.r. (KBr) cm^{-1} 1635, 1540, 1465, 1280. Analysis: calculated for $C_{32}H_{22}N_4S_2O_2$, C 68.79, H 3.97, N 10.03; found, C 67.90, H 4.17, N 9.97.

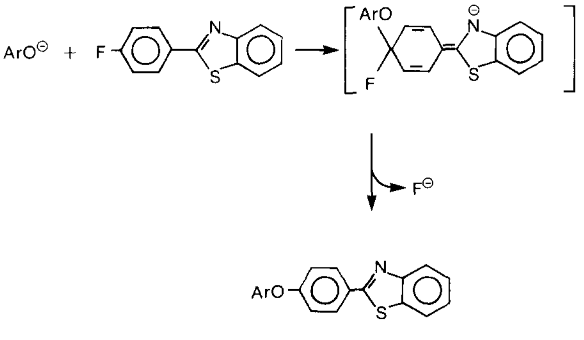
The copolymers were prepared according to the literature procedure[14] in a three-necked flask equipped with an overhead stirrer and N_2 inlet and exit. The diamines (ODA and **4** or **5**) were charged and washed with NMP and cooled to −10°C under a strong N_2 flow. To this solution, PMDA was added with slow stirring, and the reaction mixture was allowed to return to room temperature affording viscous polymer solutions (24 h) which were filtered (0.5 μm).

Films for thermal and mechanical analysis were cast from NMP solution of poly(amic acids) and heated to 350°C (5°C min^{-1} 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^{-1} (10 Hz) in the tension mode. Isothermal and variable temperature (5°C min^{-1} heating rate) thermal gravimetric analysis (t.g.a.) 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^{-1}. Stress measurements were made on a Flexus (F2300) at a heating rate of 5°C min^{-1}. Wide angle diffraction measurements were performed in both reflection and transmission geometrics using a sealed tube X-ray source where the incident radiation was monochromated using pyrolytic graphite. The wavelength of the incident radiation was 1.542 Å. The diffracted X-rays were detected with a scintillation counter mounted behind an analyser crystal that was step scanned over the angular range of interest.

RESULTS AND DISCUSSION

The synthetic approach used for the preparation of the diamine benzodithiazole was based on a thiazole activated fluoro displacement by amino-substituted phenoxides. It has been demonstrated that bis(4-fluorophenyl)bibenzoxazoles undergo facile fluoro displacement with phenoxides, and both high molecular weight poly(aryl ether benzothiazoles) and new diamines containing preformed benzoxazole moieties were prepared[10,12]. We felt that this heterocyclic activated nucleophilic displacement chemistry should be effective for systems derived from other heterocyclic systems such as a benzothiazole. The rationale for nucleophilic aromatic substitution from a benzothiazole ring is analogous to the benzoxazole ring system and is two-fold: the electron-poor thiazole ring would have the effect of an electron-withdrawing group; and a Meisenheimer complex would form as a stabilized intermediate during the transformation due to resonance of the negative charge into the thiazole ring (*Scheme 1*). This synthetic approach is analogous to the preparation of poly(aryl ether sulphone) where the electron-withdrawing sulphone group activates halides towards nucleophilic substitution as well as accepts a negative charge (Meisenheimer complex) during the transformation[15].

The electronic effect of the thiazole ring on both the benzo aromatic ring and the 2-phenyl group was evaluated by ^{1}H n.m.r. (*Figure 1*), since the deshielding of the protons *ortho* to a substituent is indicative of an electron-withdrawing group. ^{1}H n.m.r. spectral assignments for **1** show the *ortho* protons of the 2-phenyl ring (H_a) are at δ 8.2, further downfield than the *ortho* protons of benzo ring H_b and H_c, at δ 7.9 and 7.5, respectively. This indicates the thiazole has a greater electron-withdrawing effect on the 2-phenyl group than the benzo ring of the benzothiazole, analogous to the benzoxazole activated displacement. Comparison of the assignments of **1** with 4,4′-difluorobenzophenone, a conventional activated dihalide, previously published[10,12] shows the protons *ortho* to the benzothiazole (H_a) gave a chemical shift of δ 8.2, as compared to δ 7.9 for the protons *ortho* to the ketone in 4,4′-difluorobenzophenone. This demonstrates the electron-withdrawing effect of the 2-benzothiazolyl group on a benzene ring in the ground state is comparable to that of a ketone, and indicates the possibility of facile nucleophilic aromatic substitution at the *para* position of the 2-phenyl ring.



Scheme 1

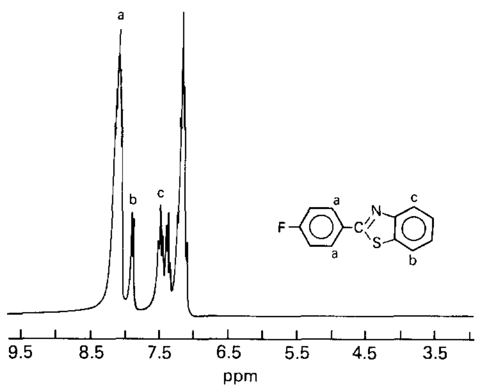
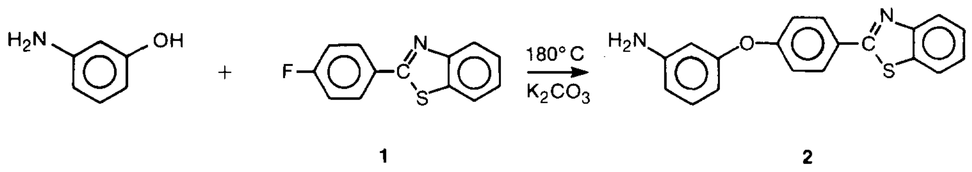


Figure 1 N.m.r. spectrum of **1**

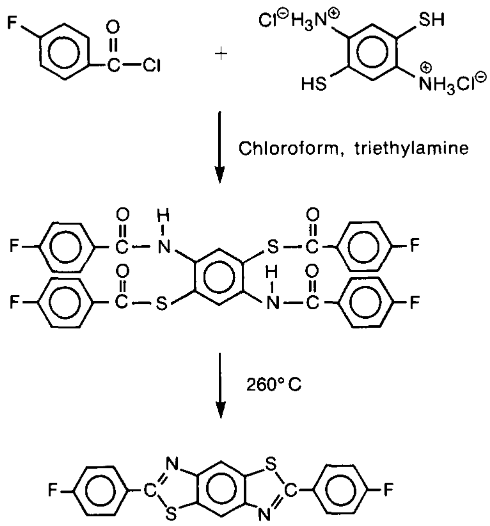
To demonstrate the feasibility of the benzothiazole activated aryl ether synthetic approach for the preparation of bis(amino)benzothiazole based monomers, a model reaction between **1** and 3-aminophenol in the presence of K_2CO_3 was investigated (*Scheme 2*). Quantitative conversion of **1** was observed by thin layer chromatography (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.

The preparation of the diamines containing the preformed benzothiazole rings required the synthesis of a bis(fluorophenyl)bisbenzothiazole to react with either 3- or 4-aminophenol. For our experiments we prepared **3** by the reaction of 1,4-dimercapto-2,5-diaminobenzene dihydrochloride with an excess of 4-fluorobenzoyl chloride in the presence of excess triethylamine (used as an acid acceptor as well as to deprotect the amino groups) in chloroform (−5°C) (*Scheme 3*). The reaction was then slowly heated to reflux temperatures for 3 h where the solution became clear. The chloroform solution was cooled, partitioned with water, washed and isolated. Quantitative conversion of 1,4-dimercapto-2,5-diaminobenzene was observed (high performance liquid chromatography) with the formation of a single product peak. The resulting yellow powder was placed in a sublimater and slowly heated to 260°C to effect ring closure. The powder was observed to melt at ~200–225°C and upon ring closure 4-fluorobenzoic acid was evolved, and the product, **3**, solidified into a dark crystalline powder (*Scheme 3*). Recrystallization from NMP afforded **3** as a polymer grade monomer.

The use of 1,4-dimercapto-2,5-diaminobenzene dihydrochloride affords a bis(fluorophenyl)benzodithiazole with the *trans* conformation. It has been shown that poly(benzothiazole) homopolymers prepared with the *trans* conformation are composed of rigid segments with catenation angles of nearly 180° resulting in a low solution solids concentration for the formation of the liquid crystalline phase[1]. Likewise, we surmise that diamines prepared from this conformation would result in polyimides with a high degree of crystalline or liquid crystalline ordering.



Scheme 2



Scheme 3

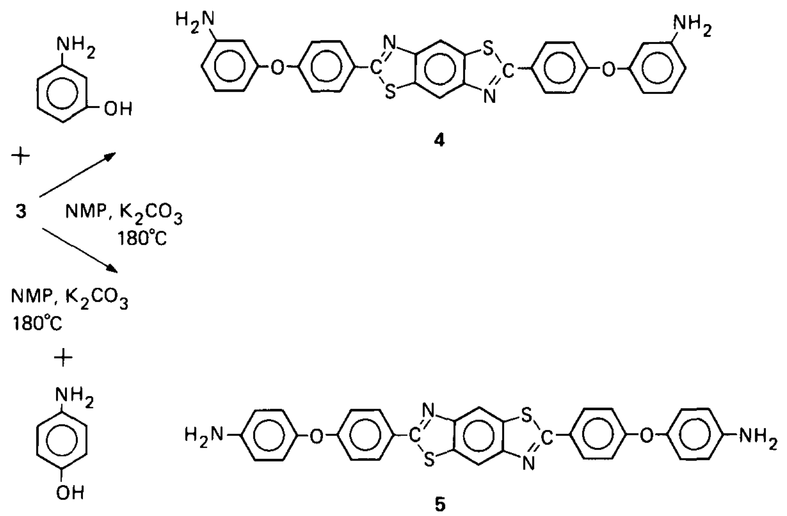
The synthesis of a number of thiazole-based diamines should be possible by the reacton of various bis(fluorophenyl)benzodithiazoles with two equivalents of either 3- or 4-aminophenol. Our first examples involved the preparation of **4** and **5** by the reaction of **3** with either 3- or 4-aminophenol, respectively, in a NMP/toluene solvent mixture in the presence of K_2CO_3 (*Scheme 4*)[11,13]. NMP is an aprotic dipolar solvent known to assist and/or stabilize the Meisenheimer complex as well as solvate the polar intermediates[14]. The toluene was used to azeotrope the water generated upon phenoxide formation ($\sim$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 in each case with the formation of a single product peak. Upon cooling, both **4** and **5** crystallized from the respective NMP solutions. The products were isolated by filtration in near quantitative yields (90%), 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 resulting diamines were then purified by recrystallization (twice) from NMP. It is important to note that this synthetic approach is analogous to the preparation of sulphone[16], ketone[17], phenylquinoxaline[11] and benzoxazole[12] based diamines.

The imide-aryl ether benzothiazole copolymers were prepared via the standard polyimide synthesis [i.e. poly(amic acid) intermediate] in NMP (*Scheme 5*)[14]. For our experiments we used PMDA as the dianhydride due to its availability and since polyimides derived from PMDA/ODA have been widely studied and will be used to facilitate comparison with the imide-aryl ether benzothiazole copolymers. The benzothiazole-containing diamines, either **4** or **5**, were charged into the flask and carefully rinsed with NMP (10% solids concentration). However, at this concentration and temperature the diamines were only marginally soluble. Prior to the addition of PMDA, the mixture was heated to 120°C to aid, at least partially, in dissolving either **4** or **5**. The flask was then cooled and PMDA was added in increments as solid to the slurry/solution of the respective diamines. Initially, PMDA was only marginally soluble in the NMP solution. Upon dissolution and polymerization, the respective diamines, **4** or **5**, reacted with PMDA at the solid–solution interface, analogous to an interfacial polymerization. This effect generated very high molecular weight early in the polymerization. The polymerizations were allowed to return to room temperature and stirred for 48 h to ensure complete molecular weight equilibration. High molecular weight poly(amic acid) solutions were obtained as judged by the high viscosities. Two new copolymers were prepared where either **4** or **5** were reacted with PMDA affording copolymers **6** and **7**, respectively (*Scheme 5*). The poly(amic acid) solutions were cast into films and cured to 350°C to effect imidization affording clear tough films.

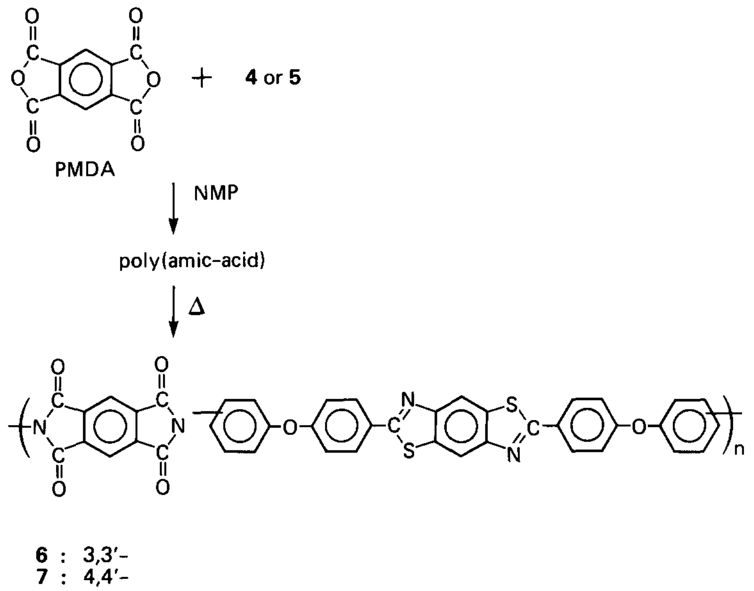
The thermal analysis for the copolymers prepared and a PMDA/ODA polyimide to facilitate comparison are shown in *Table 1*. As in the case for the polyimide homopolymer, no detectable glass transition temperature (T_g) was observed for the copolymers by differential scanning calorimetry (d.s.c.) measurements. The thermal stability, as judged by polymer decomposition temperature and isothermal weight loss upon ageing at 400°C for 8 h, for the copolymers was good and comparable to PMDA/ODA polyimide (*Table 1*). The decomposition temperatures were in the 480°C range and only $\sim$0.06 wt% h^{-1} weight loss was observed upon ageing at 400°C. Most notably, the TECs of the copolymers were substantially lower than that of PMDA/ODA polyimide and in the 25 ppm range (*Table 1*).

The dynamic mechanical behaviour for copolymers **6**, **7** and PMDA/ODA polyimide are shown in *Figure 2*. The 'liquid crystalline' or 'crystalline' ordering manifested by the polyimide homopolymer significantly influences the modulus–temperature profile[11,12]. The modulus is essentially invariant up to 400°C, except for a small drop at $\sim$370°C. At this transition, it has been reported that the specimen contracts, and upon repetitive scans, the transition shifts to higher temperatures and is significantly smaller in magnitude. This is reflective of an enhancement in ordering in the PMDA/ODA segments with thermal cycling[4,5,18].

The modulus–temperature profiles of the copolymers are somewhat similar to that of PMDA/ODA polyimide. Glass transition temperatures, as characterized by a large sharp modulus drop, were not observed for either of the copolymers. Instead, copolymer **6** shows a large, but broad transition at $\sim$320°C. This spectrum is somewhat similar to those observed for imide-aryl ether benz-



Scheme 4



Scheme 5

Table 1 Thermal characteristics of imide-aryl benzothiazole copolymers

Sample	Polymer decomposition temperature (°C)	Isothermal weight loss at 400°C (wt%)	TEC (ppm)
6	480	0.05	24
7	480	0.06	25
PMDA/ODA polyimide	480	0.04	40

oxazole copolymers derived from bis(aminophenoxy)-bibenzoxazoles containing both aryl ether and *meta* linkages. In many of the imide-aryl ether benzoxazole copolymers T_gs were observed in the 300–340°C range as the liquid crystalline PMDA/ODA segments diminished with increasing benzoxazole composition[12]. However, a T_g was not observed for copolymer **6**, and the broad modulus drop suggests that a liquid crystalline or even crystalline type ordering must exist.

Copolymer **7** shows markedly different modulus–temperature behaviour. In this copolymer, the modulus is invariant except for a very small drop at ~380°C, ~10°C higher than PMDA/ODA polyimide. This spectrum is very similar to the imide-aryl ether benzoxazole copolymers derived from the benzoxazole-containing diamines with *para* catenation, and the absence of a T_g was believed to result from the high chain rigidity[12]. It is also important to note that both copolymers **6** and **7** showed substantially higher moduli than PMDA/ODA polyimide consistent with the lower TEC values.

Wide angle X-ray diffraction studies were performed on copolymers **6** and **7** and compared to PMDA/ODA polyimide. PMDA/ODA polyimide shows reflections at $2\theta = \sim 5.5$–$6°$ and a broad halo centred at $2\theta = \sim 17.5°$[4]. The first reflection, corresponding to a Bragg spacing of ~15.5 Å, characterizes the intramolecular repeat of the PMDA/ODA molecule projected onto the chain axis. The second reflection with a Bragg distance of ~5 Å characterizes the separation distance of the adjacent

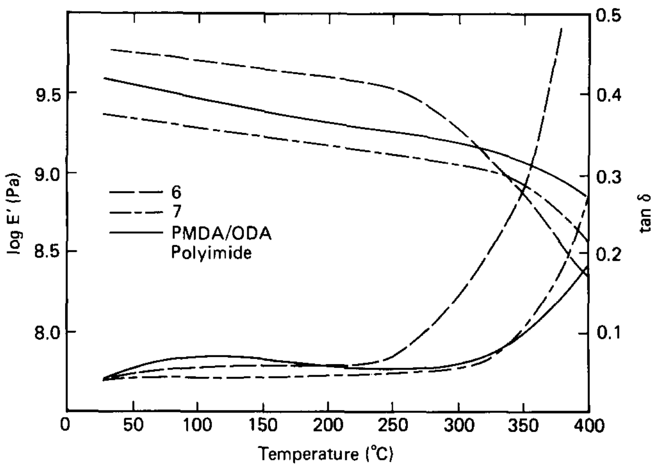


Figure 2 Dynamic mechanical spectra of copolymers and PMDA/ODA polyimide

Table 2 Mechanical properties of imide-aryl ether benzothiazoles

Sample	Modulus (MPa)	Yield stress (MPa)	Tensile stress (MPa)	Elongation (%)
6	3750	113	110	15
7	2660	–	96	7
PMDA/ODA polyimide	2000	–	120	40

chains. Copolymer 7 shows only a broad halo centred at $2\theta = \sim 20°$, corresponding to a Bragg spacing of ~4.5 Å, which characterizes the separation distance of the adjacent chains, typical of an amorphous polyimide. Furthermore, it has been demonstrated that the ordering and molecular orientation of PMDA/ODA polyimide results in anisotropic swelling behaviour in NMP, a non-solvent for polyimide, and ~30% solvent uptake is observed in the direction normal to the surface[18]. Conversely, copolymer 7 shows no swelling in NMP, consistent with an amorphous structure.

Copolymer 6 shows markedly different behaviour than the parent polyimide. As expected the reflection at ~15.5 Å was not observed, however, the broad amorphous reflection with a Bragg spacing of ~5 Å was also not observed. Instead six sharp reflections at $2\theta = \sim 14$, 18, 22, 24, 26 and 28° were observed, corresponding to Bragg spacings of ~6.3, 5.0, 4.1, 3.7, 3.4 and 3.2 Å, respectively. This is indicative of a highly crystalline morphology. Interestingly, the diffraction profile was independent of both the cure time and temperature, which is not entirely unexpected since no T_g or T_m were observed by d.s.c measurements. Copolymer 6 shows only a broad transition in the modulus–temperature profile at ~320°C analogous to other rigid-rod polyimides. Furthermore, since a three-dimensional structure was obtained in copolymer 6, no solvent uptake was observed after NMP swelling, providing no insight as to the molecular orientation.

Table 2 contains the mechanical properties of the imide-aryl ether benzothiazoles together with PMDA/ODA polyimide as a control. The moduli of 6 and 7 are substantially higher than PMDA/ODA polyimide, consistent with the dynamic mechanical behaviour. This is particularly the case for polymer 6 which shows semicrystalline morphology. Furthermore, the improved moduli are consistent with the reduction of the TEC values for both 6 and 7. The elongations and tensile strengths were low in comparison to PMDA/ODA polyimide. The mechanical behaviour of polymer 7 was similar to that of an ordered or rigid polyimide with a stress–strain curve similar to a work hardened metal with no distinguishable yield point, characteristic of small scale or local plastic deformation. As is the case for many extended chain polyimides, the elongation to break for 7 was low. Conversely, polymer 6 showed a distinguishable yield point with necking and drawing, typical of semicrystalline polymers.

An important criterion in the fabrication of multilayer microelectronic components derived from polyimide is low residual stress upon thermal cycling. The residual stress results, primarily, from the TEC mismatch of the polyimide with the rigid substrate. The objective of designing polyimides with a high degree of order is to produce materials to minimize this mismatch. PMDA/ODA polyimide has a residual stress of 28 MPa upon thermal cycling to 350°C when adhered to a silicon wafer. The semicrystalline imide-aryl ether benzothiazole copolymers, 7, shows a residual stress of 38 MPa when prepared in an analogous fashion.

Considering the high degree of crystallinity associated with copolymer 6, the increase in stress was not expected. However, since the stress is directly proportional to the modulus and TEC of the polymer among other things, the TEC drop was not sufficient to offset the substantial increase in modulus. This may, at least partially, explain the increase in residual stress upon thermal cycling.

CONCLUSIONS

Imide-aryl ether benzothiazole copolymers were prepared and their morphology and mechanical properties investigated. Benzothiazole-containing diamines were prepared via a novel thiazole activated halo displacement and then reacted with PMDA. The resulting poly(amic acids) were cast and cured (350°C) to effect imidization, affording films with moduli substantially higher than PMDA/ODA polyimide. The copolymers showed both good thermal and dimensional stability to high temperatures and no T_g was observed in either case. In one copolymer a semicrystalline morphology was observed by wide angle X-ray scattering. In both copolymers a low TEC and good mechanical properties were observed.

REFERENCES

1 Wolfe, J. F. *Encycl. Polym. Sci. Technol.* 1989, **11**, 601
2 Helminiak, T. E., Arnold, F. E. and Benner, C. L. *Polym. Prepr.* 1975, **16**, 659
3 Harris, F. W., Hsu, S. L. and Tso, C. C. *Polym. Prepr.* 1990, **31**, 342
4 Russell, T. P. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **22**, 1105
5 Takahashi, N., Yoon, D. Y. and Parrish, W. *Macromolecules* 1984, **17**, 2583
6 Preston, J., Dewinter, W. F. and Black, W. B. *J. Polym. Sci. A1* 1969, **7**, 283
7 Preston, J., Dewinter, W. F., Black, W. B. and Hofferbert Jr, W. L. *J. Polym. Sci. A1* 1969, **7**, 3027
8 Preston, J. *Heterocyclic Chem.* 1965, **2**, 441

9 Hedrick, J. L. and Labadie, J. W. *Macromolecules* 1990, **23**, 1561

10 Hilborn, J., Labadie, J. W. and Hedrick, J. L. *Macromolecules* 1990, **23**, 2854

11 Hedrick, J. L., Labadie, J. W. and Russell, T. P. in 'Polyimides: Materials, Chemistry and Characterization' (Eds. C. Feger, M. M. Khojasteh and J. E. McGrath), Elsevier, Amsterdam, 1989, p. 61

12 Hedrick, J. L., Hilborn, J., Labadie, J. W. and Russell, T. P. *Polymer* 1990, **31**, 2384

13 Hedrick, J. L. *Polym. Bull.* 1990, **24**, 371

14 Volksen, W. and Cotts, P. M. in 'Polyimides: Synthesis, Characterization and Applications' (Ed. K. L. Mittal), Plenum Press, New York, 1982, p. 163

15 Johnson, R. N. and Farnham, A. G. *J. Polym. Sci. A1* 1967, **5**, 2415

16 Kawakami, J. H., Kwiatkowski, G. T., Brode, G. L. and Bedwin, A. W. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 565

17 Hergenrother, P. M., Wakelyn, N. T. and Havens, S. J. *Polym. Prepr.* 1987, **28**, 92

18 Gattiglia, E. and Russell, T. P. *J. Polym. Sci., Polym. Phys. Edn.* 1989, **27**, 2131