Synthesis and properties of imide–aryl ether 1,2,4-triazole random copolymers*

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New imide–aryl ether copolymers containing a 1,2,4-triazole heterocyclic unit were prepared, and their structural, mechanical and thermal properties were studied. These copolymers contain an aryl ether 1,2,4-triazole linkage, which was incorporated into a semi-rigid backbone by the reaction of new 1,2,4-triazole diamines with 4,4'-oxydianiline (ODA) and pyromellitic dianhydride (PMDA). The 1,2,4-triazole diamines were prepared through a nucleophilic aromatic substitution reaction of 3,5-bis(4'-fluorophenyl)-4-phenyl-1,2,4-triazole with either 3- or 4-aminophenol in the presence of K_2CO_3 in a polar aprotic solvent mixture to afford 3,5-bis(3'-aminophenoxyphenyl)-4-phenyl-1,2,4-triazole and 3,5-bis(4'-aminophenoxyphenyl)-4-phenyl-1,2,4-triazole, respectively. The monomers were reacted with PMDA or co-reacted with ODA and PMDA to synthesize the desired poly(amic acid)s. Films were cast and cured at 350°C to effect imidization, producing films with good mechanical properties.

(Keywords: imide; aryl ether; random copolymer; 1,2,4-triazole; synthesis; properties)

INTRODUCTION

Polymers have become increasingly important in the microelectronics industry[1]. The use of polymers as dielectric materials, passivation layers and structural resins has stimulated much research on new stable systems, most notably polyimides. Their high resistivity and high dielectric breakdown voltages coupled with processability make these materials very attractive in industrial applications[2]. The aromatic polyimides are the most widely used and, in addition to the properties mentioned above, they also have excellent thermal and dimensional stability ($T_g > 400°C$) and good mechanical properties[3]. These properties are in part due to molecular packing (i.e. crystalline or liquid-crystalline morphologies) manifested by these materials[4,5]. There are, however, certain drawbacks associated with the formation of an ordered morphology coupled with the absence of a defined T_g; e.g. poor melt processability and limited self- or auto-adhesion. The adhesion problem arises from insufficient polymer mobility, such that interdiffusion is hindered. Consequently, it is of interest to investigate alternative polymer structures to conventional polyimides, without sacrificing the desired thermal stability and solution processability. One approach is to design polyimide copolymers containing rigid or semi-rigid heterocyclic units. There have been several examples of preformed heterocycles including oxadiazoles, triazoles, thiazoles, phenylquinoxalines and others[6–9] that have been incorporated into polyimides. These polymers were prepared by reacting the appropriate heterocyclic diamines with various dianhydrides to give the corresponding soluble poly(amic acid)s, which were subsequently thermally cured to yield polyimides. The resulting polymers showed good thermal stability; however, the crystalline or semicrystalline morphologies often observed made them difficult to process.

The incorporation of aryl ether linkages into the polymer backbone often enhances both the melt and solution processability. One of the most efficient means of introducing an aryl ether linkage is through nucleophilic aromatic substitution in which an activated aryl halide reacts with a phenoxide, generating an aryl ether linkage. It has been demonstrated that many heterocycles are sufficiently electron-withdrawing to activate aryl fluorides towards substitution, allowing for the preparation of diamines and polyimides containing preformed oxadiazoles[10], phenylquinoxalines[11], benzoxazoles[12] and benzothiazoles[13].

We have recently extended the heterocycle-activated displacement to the 1,2,4-triazole ring, leading to the preparation of new high-temperature poly(aryl ether)s[14]. Furthermore, it seemed plausible to use the triazole-activated displacement to prepare new diamines and polyimides. This paper will discuss the synthesis of imide–aryl ether 1,2,4-triazole copolymers as well as the results of the thermal and mechanical analyses.

EXPERIMENTAL

Materials

1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (*N*,*N*'-dimethylpropyleneurea, DMPU) (Aldrich) was vacuum distilled from calcium hydride. 3-Aminophenol (Aldrich) was purified by sublimation. 4,4'-Oxydianiline (ODA) (Davos Chemical Co.) and pyromellitic dianhydride (PMDA) (Chriskev Co.) were used without further purification. All other materials were commercially

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available and were used as received unless otherwise noted.

Characterization

N.m.r. spectra (in deuterated dimethylsulphoxide (DMSO-d_6) or $CDCl_3$) were recorded on an IBM WP 250 spectrometer operating at 250.1 MHz (^1H) and 62.9 MHz (^{13}C) with chemical shifts reported in ppm relative to tetramethylsilane. Elemental analyses and mass spectra were performed by Oneida Research Services.

Films for mechanical and thermal analyses were cast from *N*-methyl-2-pyrrolidone (NMP) and heated (5°C min^{-1}) to 350°C and held for 30 min. Glass transition temperatures, taken as the midpoint of the change in slope of the baseline, were measured on a DuPont DSC 1090 instrument at 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 with a heating rate of 5°C min^{-1} for the variable scans, and the isothermal scans were performed at both 350 and 400°C over an 8 h period. Dynamic mechanical measurements were made on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (d.m.t.a.) in the tension mode with a heating rate of 10°C min^{-1} (10 Hz). Wide-angle diffraction measurements were performed in both reflection and transmission geometries using a sealed tube X-ray source with 1.542 Å incident radiation. 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.

*1,4-Bis(4′-fluorophenyl)-2,3-diaza-1,3-butadiene (**A**)*

A 250 ml round-bottomed flask fitted with a magnetic stirring bar and reflux condenser was charged with 20.40 g (0.158 mol) of *p*-fluorobenzaldehyde and 175 ml of absolute ethanol. To this slurry 4.0 g (0.099 mol) $H_2NNH_2 \cdot H_2O$ was added while the reaction mixture was rapidly stirred. The mixture became warm and yellow crystals formed. The reaction was heated to 60°C for 12 h, after which the mixture was cooled and filtered. The yellow crystals were washed (three times) with ethanol and dried under vacuum to give 17.58 g (91% yield) of **A**: m.p. 180–182°C. ^1H n.m.r. (DMSO-d_6) δ (ppm): 8.72 (s, 2H), 7.97–7.91 (m, 4H), 7.39–7.32 (m, 4H).

*1,4-Dichloro-1,4-bis(4′-fluorophenyl)-2,3-diaza-1,3-butadiene (**B**)*

A 250 ml three-necked flask fitted with a magnetic stirrer, reflux condenser, thermometer and glass bubbler tube was charged with 17.7 g (0.073 mol) of **A** and 200 ml of glacial acetic acid. This slurry was stirred and Cl_2 was slowly bubbled into the reaction mixture, which warmed and became homogeneous. The flask was heated to maintain an internal temperature of 50°C, and the addition of Cl_2 was continued for 5 h. After the addition, the mixture was cooled to room temperature while being purged with N_2. The resulting yellow crystals were filtered, rinsed repeatedly with water and vacuum dried overnight. The filtrate was diluted with 200 ml of CH_2Cl_2, transferred to a separatory funnel and washed successively with aqueous sodium bicarbonate solution and water. The organic layer was dried over magnesium sulphate and filtered. The CH_2Cl_2 was allowed to evaporate to give yellow crystals, which were added to the filtered precipitate for a total yield of 17.5 g (77%) of **B**. ^1H n.m.r. ($CDCl_3$) δ (ppm): 8.19–8.10 (m, 4H), 7.21–7.12 (m, 4H).

*3,5-Bis(4′-fluorophenyl)-4-phenyl-1,2,4-triazole (**1**)*

A 50 ml three-necked round-bottomed flask fitted with an overhead stirrer was charged with 5.10 g (0.016 mol) of **B**, 4.55 g (0.049 mol) of freshly distilled aniline and 10 ml of xylene. The flask was fitted with a reflux condenser and heated with stirring to 140°C. The mixture started to solidify after 3 h and was allowed to react for a total of 5 h. After cooling and dilution with 50 ml of $CHCl_3$ the solution was washed successively with dilute HCl, aqueous sodium bicarbonate and water. The organic layer was dried over magnesium sulphate with activated charcoal, and filtered. The crude product was purified by repeated recrystallization from 4:1 MeOH/acetone to give 4.27 g (78% yield) of **1**: m.p. 246–247°C. ^1H n.m.r. ($CDCl_3$) δ (ppm): 7.51–7.45 (m, 3H), 7.40–7.37 (m, 4H), 7.14 (d, 2H), 7.0 (t, 4H). Analysis calculated for $C_{20}H_{13}N_3F_2$: C, 72.06; H, 3.94; N, 12.60; mol. wt 334. Found: C, 71.70; H, 3.96; N, 12.49; mol. wt 334 (mass spectroscopy).

*3,5-Bis[4′-(3-aminophenoxy)phenyl]-4-phenyl-1,2,4-triazole (**2**)*

A 25 ml three-necked flask fitted with an overhead stirrer and Dean–Stark trap was charged with 3.54 g (10.6 mmol) of **1**, 2.32 g (21.2 mmol) of 3-aminophenol, 5.9 g of K_2CO_3 and 17 ml of NMP. A small amount of toluene was added to effect the azeotropic removal of water. This mixture was stirred and heated to 140°C, at which point the toluene was collected and removed from the system. The temperature was maintained for 5 h while more toluene was added periodically and subsequently collected and drained from the trap. The mixture was then heated to 175°C for 5 days. The mixture, which contained a single product by t.l.c., was cooled and upon addition of 100 ml of CH_2Cl_2 a precipitate formed. The solid was extracted repeatedly with water and CH_2Cl_2 and subsequently filtered. The product **2** was recrystallized from boiling methanol and dried *in vacuo* to give 3.97 g (73.2%) of a tan powder: m.p. 265–275°C. ^1H n.m.r. (DMSO-d_6) δ (ppm): 7.50 (m, 3H), 7.43 t, 2H), 7.23 (d, 4H), 7.01 (t, 2H), 6.90 (d, 4H), 6.36 (d, 2H), 6.20 (s, 2H), 6.13 (d, 2H), 5.27 (s, 4H). ^{13}C n.m.r. (DMSO-d_6) δ (ppm): 178.1, 158.7, 156.5, 154.0, 153.8, 150.7, 130.4, 130.2, 129.9, 128.4, 120.7, 117.5, 110.1, 106.5, 104.6. Analysis calculated for $C_{32}H_{25}N_5O_2$: C, 75.13; H, 4.87; N, 13.69. Found: C, 73.76; H, 4.87; N, 13.35.

*3,5-Bis[4′-(4-aminophenoxy)phenyl]-4-phenyl-1,2,4-triazole (**3**)*

A 25 ml three-necked flask fitted with an overhead stirrer and Dean–Stark trap was charged with 3.56 g (10.7 mmol) of **1**, 2.38 g (21.7 mmol) of 4-aminophenol, 5.9 g of K_2CO_3 and 18 ml of DMPU. A small amount of toluene was added to effect the azeotropic removal of water. This mixture was stirred and heated to 140°C, at which point toluene was collected and removed from the system. The temperature was maintained for 5 h and more toluene was added periodically and subsequently collected and drained from the trap. The mixture was then heated to 165°C for 48 h. The mixture, which contained a single product by t.l.c., was cooled and transferred to a separatory funnel. Attempts to extract with CH_2Cl_2 and water resulted in the formation of an emulsion. Solvent was removed *in vacuo* and the semi-solid product was recrystallized three times from methanol/water to give 4.35 g (79.6%) of an off-white powder: m.p. 235–245°C. ^{1}H n.m.r. (DMSO-d_6) δ (ppm): 7.48 (m, 3H), 7.40 (t, 2H), 7.29 (d, 4H), 6.76 (d, 8H), 6.58 (d, 4H), 5.05 (s,4H).^{13}C n.m.r. (DMSO-d_6) δ (ppm): 178.2, 160.2, 153.8, 146.1, 144.4, 135.2, 130.1, 129.9, 128.4, 121.4, 120.3, 115.8, 114.9. Analysis calculated for $C_{32}H_{25}N_5O_2$: C, 75.13; H, 4.87; N, 13.69. Found: C, 73.83; H, 4.99; N, 13.48.

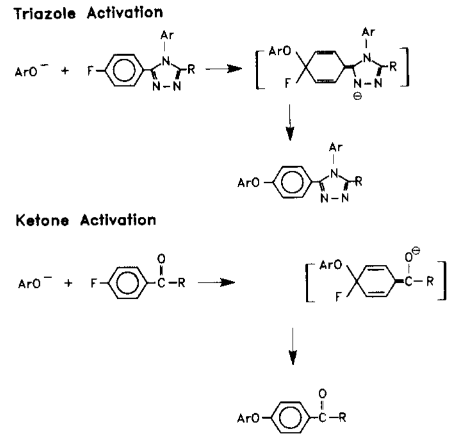
Polymer synthesis

The polyimide copolymers were prepared according to a literature procedure[15]. In a typical synthesis, a three-necked flask was equipped with an overhead stirrer and nitrogen purge. The diamines (**2**, **3** or ODA) were added, and the residues transferred by an NMP wash. The mixture was 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 viscous polymer solutions, which, after 24 h, were filtered through a 0.5 μm filter (measured intrinsic viscosities ranged between 0.4 and 1.0 dl g^{-1}).

RESULTS AND DISCUSSION

It is known that certain heterocycles can activate aryl fluorides towards nucleophilic displacement, leading to new high-temperature heterocycle-containing polymers[16,17]. New diamines containing the 1,2,4-triazole heterocyclic unit should be preparable as a route to new monomers for polyimide synthesis. It was anticipated that the triazole substituent would activate the aromatic ring towards substitution by functioning both as an electron-withdrawing substituent and as a stabilizing substituent for the anionic intermediate (*Scheme 1*). Previously, we have used ^{1}H n.m.r. analysis as a probe of the strength of an electron-withdrawing group[18,19]. The degree of deshielding of the protons *ortho* to a particular substituent is indicative of that substituent's electron deficiency (*Figure 1*). The ^{1}H n.m.r. spectral assignment of **1** shows that the protons *ortho* to the triazole unit are shifted downfield, but only slightly. Comparison of the spectra of **1** with that of a conventional activated dihalide, 4,4′-difluorobenzophenone, shows that while the protons *ortho* to the ketone group are observed at $\delta = 7.9$ ppm, those *ortho* to the triazole ring appear upfield at $\delta = 7.4$ ppm. In all previous examples where heterocyclic substituents were used in nucleophilic aromatic substitution, the protons *ortho* to the heterocycle were observed in the range of $\delta = 7.8$ to 8.2 ppm. By this criterion, the 1,2,4-triazole unit represents a weak electron-withdrawing heterocyclic substituent. For this reason, we anticipated that the reaction conditions for this system might be dramatically different from those previously employed.

A synthesis of the appropriately substituted bisfluoride was required to prepare the desired diamines. In a previous study[20], 3,5-bis(4′-hydroxyphenyl)-4-phenyl-1,2,4-triazole was synthesized by the reaction of 1,4-bis(4′-hydroxyphenyl)hydrazide with aniline hydrochloride at 250°C. Similarly, we tried the reaction of 1,4-bis(4′-fluorophenyl)hydrazide with aniline hydrochloride as a



Scheme 1

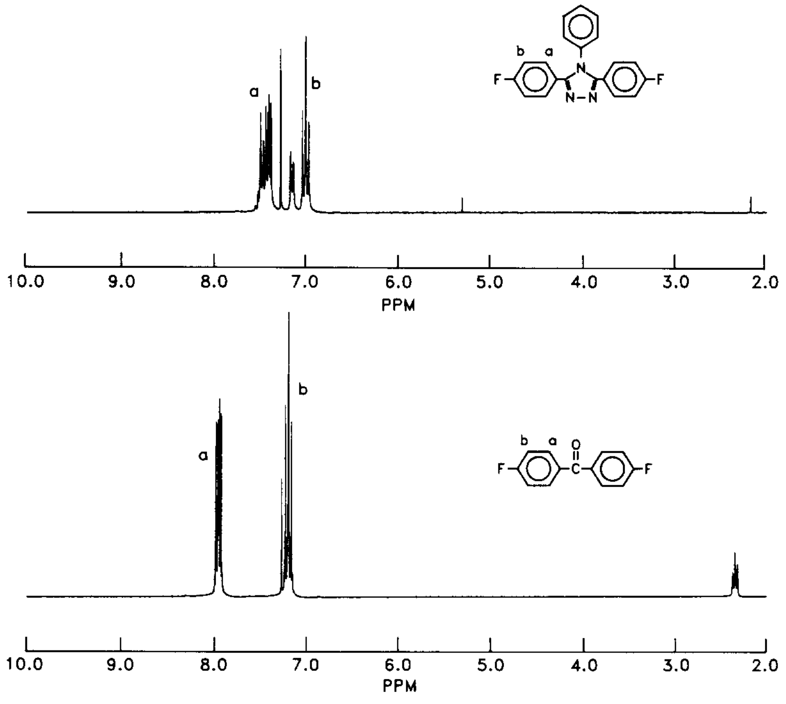


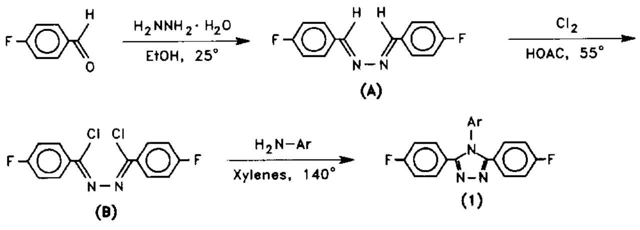
Figure 1 ^{1}H n.m.r. spectra of **1** (top) and 4,4′-difluorobenzophenone (bottom)

route to **1**, but this led instead to the formation of 2,5-bis(4′-fluorophenyl)-1,3,4-oxadiazole. The preparation of **1** was accomplished in a three-step synthesis similar to that described for 3,4,5-triphenyl-1,2,4-triazole[21] (*Scheme 2*). In the first step, 4-fluorobenzaldehyde was reacted with hydrazine hydrate to give **A** in ~90% yield, which could subsequently be chlorinated in glacial acetic acid, leading to the formation of **B**. When **B** was heated with aniline, a facile cyclocondensation reaction occurred, yielding the desired product **1** in 77% yield.

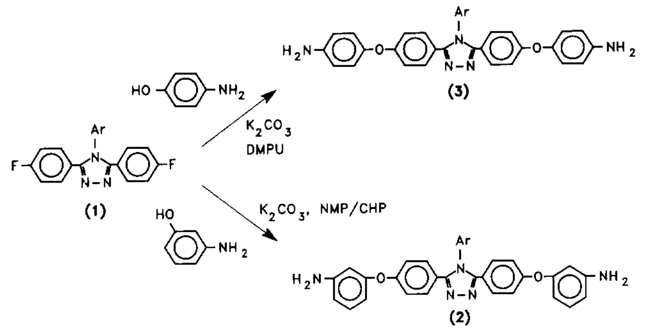
To demonstrate the utility of **1** in a nucleophilic aromatic substitution reaction, model reactions with *m*-cresol were performed. These were carried out under the same conditions employed in the synthesis of other aryl ether diamines. Initially, **1** and *m*-cresol were added in equimolar portions and heated in the presence of 100% molar excess of anhydrous K_2CO_3 in a 1:1 NMP/*N*-cyclohexyl-2-pyrrolidone (CHP) solvent mixture. NMP/CHP mixtures are very effective for dehydrating reaction mixtures at high temperatures since CHP is not miscible with water at temperatures above 100°C. A small amount of toluene was added and azeotropically distilled. The toluene reflux serves two purposes: (1) the toluene forms an azeotrope with water generated during the phenolate ion formation, thus helping to dehydrate the system, and (2) the refluxing solvent mixture maintains the internal reaction temperature below 160°C, so that phenolate ion formation occurs prior to nucleophilic substitution. As the toluene is removed, the internal reaction temperature rises and the nucleophilic aromatic substitution reaction proceeds.

Small aliquots were taken periodically from the reaction mixture and evaluated by t.l.c. (4:1 $CHCl_3$/acetone). The reactions were deemed completed when no starting material was detected and a single product was produced. In NMP/CHP at 185°C, the reaction rate of the bisfluorophenyl triazoles was much slower than observed previously for other heterocyclic fluorides[12–14]. After 16 h there are two spots upon t.l.c. analysis, presumably the mono- and bis-substituted products. This mixture was converted into a single product after approximately 5 days. The reaction flask was cooled and the product, 3,5-bis[4′-(3-methoxyphenoxy)phenyl]-4-phenyl-1,2,4-triazole, was washed with water to remove salts and then separated from the high-boiling solvents and residual *m*-cresol by flash column chromatography[22].

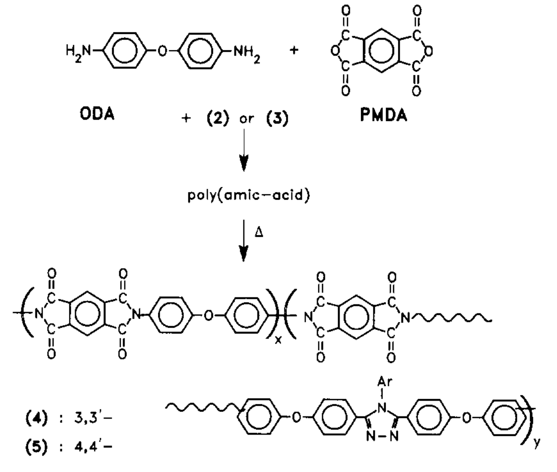
Alternatively the solvent *N,N*-dimethylpropyleneurea (DMPU) can be used since its use as a solvent in nucleophilic substitution reactions has been established[23]. We have observed that DMPU, when used with toluene as a dehydrating agent, accelerates many nucleophilic substitution reactions. The increased activity of DMPU is probably due to its effectiveness in solvating the polar intermediates and products formed. When the model reaction was studied in DMPU, it was complete in 24 h at a lower temperature (170°C) to give the methoxyphenyl product in essentially quantitative yield.



Scheme 2



Scheme 3



Scheme 4

The reaction of 3-aminophenol or 4-aminophenol with **1** yielded products **2** and **3** respectively in good yields (*Scheme 3*). For the synthesis of **2**, a NMP/CHP mixture was used as the reaction solvent, while DMPU was employed in the synthesis of **3**. Both diamines were recrystallized and analysed by n.m.r. prior to polymerization.

The diamine monomers were reacted with PMDA and/or ODA to give a new series of imide–aryl ether copolymers after curing. The copolymers were prepared by a standard polyimide route via the poly(amic acid) precursor (*Scheme 4*). Since polyimides derived from PMDA/ODA have been widely studied, PMDA/ODA polyimide was used for comparison with the imide–aryl ether triazole copolymers. A flask was charged with either **2** or **3**, and whenever appropriate ODA, and rinsed with NMP. Gentle heating was necessary to effect dissolution of the diamines. The flask was then cooled to 0°C and PMDA was added as a solid to the solution of the respective diamines. PMDA was only marginally soluble in NMP at this temperature and the polymerization occurred at the solid/solution interface. The relative amounts of monomers and NMP used was adjusted to maintain a solids content of 15%. The viscosity of the solution, which visibly increased during initial interfacial polymerization, dropped somewhat after stirring (24 h) due to molecular-weight equilibration. The high-molecular-weight poly(amic acid) solution was filtered, cast into a film then cured to 350°C to effect imidization.

Two series of copolymers were prepared using either **2** or **3** with PMDA and ODA in varying stoichiometric ratios to give polymers **4a–c** and **5a–c** respectively. Copolymer compositions were varied so as to alter the weight percentage of the triazole monomer, **2** or **3**, relative to that of PMDA and ODA. The triazole compositions ranged from 28 to 73 wt%, denoted as copolymers **4a–c** and **5a–c**, with the copolymers **4a** and **5a** being either **2** or **3** chain extended with PMDA respectively.

The thermal analyses of the copolymers are shown in *Table 1* along with PMDA/ODA for comparison. Thermal stability was assessed by the onset of thermal decomposition, denoted as the polymer decomposition temperature (*PDT*), and isothermal ageing at both 350 and 400°C. While all of the copolymers showed good stability to high temperatures, they were not as stable as PMDA/ODA polyimide. Copolymers **4a–c** had *PDT*s ranging from 425 to 490°C, compared with 480°C for PMDA/ODA. Copolymers **5a–c** had on average slightly higher *PDT*s, 465 to 480°C. Though both series of copolymers showed significant isothermal weight loss at 400°C, **5a–c** appeared more stable at 350°C than the others. As a consequence of the lower thermal stability at 400°C, the cure temperature for the copolymers was limited to 350°C.

Calorimetric measurements for **4a–c** and **5a–c** are shown in *Table 1* together with PMDA/ODA polyimide for comparison. As previously mentioned, no detectable T_g is observed for the PMDA/ODA polyimide homopolymer[24]. Likewise, the copolymers with high ODA compositions **4c** and **5c** showed no T_g up to 450°C, consistent with the retention of the rigid or semi-rigid structure. However, copolymers **4b**, **c** and **5b**, **c** showed T_g values ranging from 270 to ~345°C, consistent with increased flexibility caused by the decrease in the amount of rigid imide linkages. The T_g values of the copolymer series **4** were lower owing to the *meta*-catenation in the polymer backbone. The dynamic mechanical spectra for copolymers **4a–c** and **5a–c** are shown in *Figures 2* and *3*, respectively. The modulus–temperature profile for cured PMDA/ODA polyimide is essentially invariant except for a small decrease at ~365°C, which shifts to higher temperatures and diminishes with repetitive thermal cycling. Furthermore, the liquid-crystalline morphology of this material is enhanced with thermal cycling[4,5]. Copolymer **4c** showed a modulus–temperature profile similar to that of PMDA/ODA polyimide, i.e. an invariant modulus up to 340°C, at which point a small drop (~half a decade) was observed. This suggests that the ordered morphology characteristic of the parent polyimide was retained. At higher compositions of the triazole-containing diamine (**4a**, **b**), a large drop in modulus was observed, indicative of a T_g, which is also consistent with the calorimetry measurements. However, at temperatures above this transition, the samples did not flow as an amorphous melt, as evidenced by the plateau in the modulus extending to high temperatures. The modulus–temperature profiles of copolymers **5a–c** are nearly identical to those of **4a–c**, except that they are shifted to higher temperatures. Copolymer **5c** shows a small decrease in modulus at ~360°C and then a plateau to high temperatures, while copolymers **5a** and **5b** show a large modulus drop at ~340 and ~345°C, respectively, consistent with the T_g values observed by the calorimetry measurements.

The morphology of PMDA/ODA polyimide and related structures has been investigated by a number of techniques including swelling, WAXD and mechanical property measurements[4,5,25]. These studies show a local ordering of the molecules as well as an orientation of the

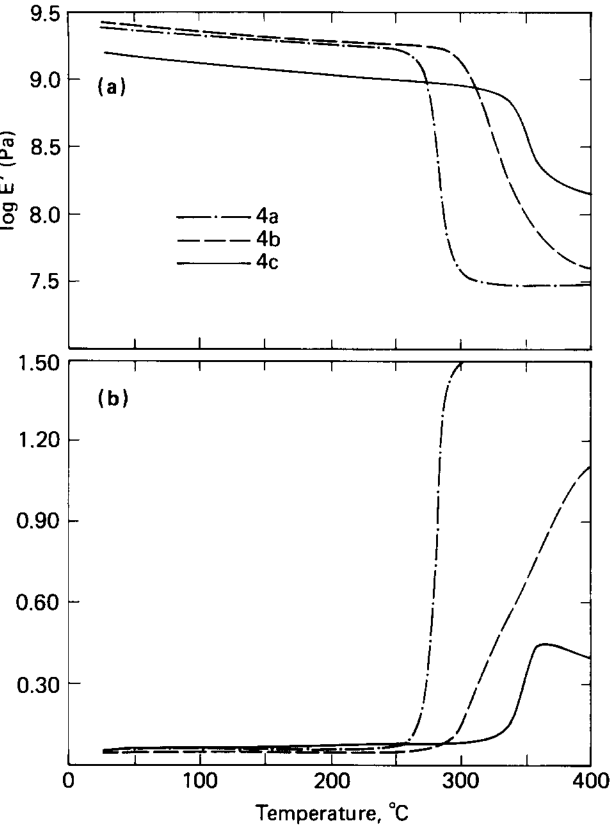


Figure 2 Dynamic mechanical behaviour for copolymers **4a–c**: (a) modulus *versus* temperature and (b) tan δ *versus* temperature

Table 1 Thermal properties of imide–aryl ether triazole copolymers

Sample no.	Triazole composition (wt%)	T_g (°C)	*PDT*[a] (°C)	Isothermal wt loss, 350°C (N_2) (wt% h^{-1})	Isothermal wt loss, 400°C (N_2) (wt% h^{-1})
4a	73	270	425	0.48	0.44
4b	57	314	470	0.57	0.56
4c	27	–[b]	490	0.28	0.37
5a	73	338	470	0.29	0.63
5b	57	345	465	0.23	0.45
5c	27	–[b]	480	0.14	0.30
PMDA/ODA polyimide	–	–[b]	480	–	0.04

[a] Polymer decomposition temperature
[b] T_g not detectable by d.s.c.

Table 2 Mechanical properties of imide–aryl ether triazole copolymers

Sample no.	Triazole composition (wt%)	Modulus (MPa)	Yield stress (MPa)	Tensile stress (MPa)	Elongation (%)
4a	73	2600	118	112	6
4b	57	1700	108	107	9
4c	27	1950	92	78	11
5a	73	2150	82	65	13
5b	57	2170	78	64	61
5c	27	1720	85	67	71
PMDA/ODA polyimide	–	2200	–	120	84

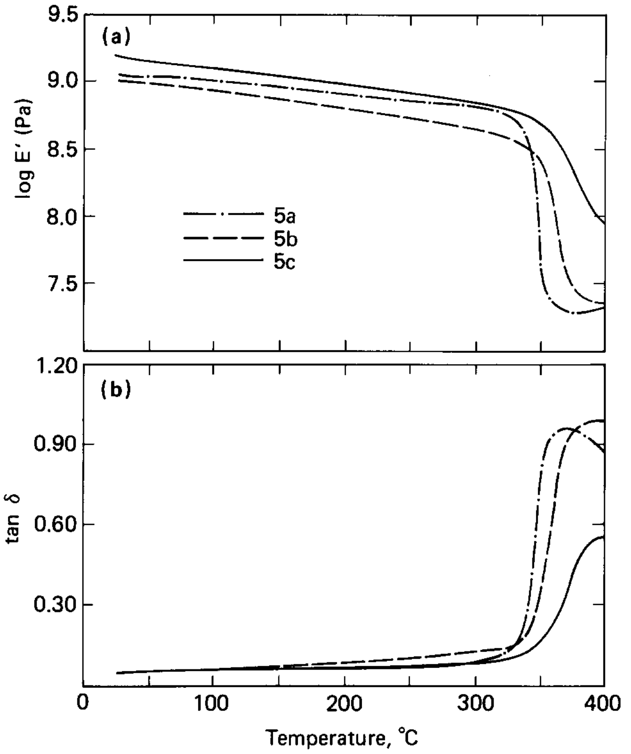


Figure 3 Dynamic mechanical behaviour for copolymers **5a–c**: (a) modulus *versus* temperature and (b) tan δ *versus* temperature

molecules with respect to the substrate. Both factors can markedly alter both the swelling characteristics and mechanical properties of the polymer. However, WAXD measurements on copolymers **5a–c** and **4a–c** showed no evidence of crystalline or liquid-crystalline type order. This was anticipated with the introduction of the bulky triazole heterocycle.

Table 2 shows the mechanical properties of the random imide–aryl ether triazoles together with those of PMDA/ODA polyimide. The moduli values of the triazole-containing polyimides were comparable to that of PMDA/ODA polyimide (~2000 MPa). The stress–strain curves for the copolymers were also similar to that of the PMDA/ODA polyimide, where the shape of the stress–strain curve is similar to that of a 'work-hardened' metal. This is characteristic of a material that undergoes a very localized or small-scale plastic deformation process. The elongations for copolymers **5a–c** were high and consistent with the values for tough, ductile polyimides. Conversely, the elongation values for copolymers **4a–c** were only approximately 10%, a feature presumably resulting from the *meta*-linkages in the polymer backbone.

CONCLUSIONS

In this study a new series of imide–aryl ether 1,2,4-triazole random copolymers was prepared. The synthesis was made possible by the preparation of new diamines derived from 3,5-bis(4′-fluorophenyl)-4-phenyl-1,2,4-triazole with either 3- or 4-aminophenol. These aryl ether–diamines were used in a conventional poly(amic acid) synthesis with PMDA and ODA as comonomers to give the corresponding copolymers. These amic acid copolymers were solution cast and cured to give the desired poly(imide–aryl ether)s. The structural, mechanical and thermal properties of these copolymers were studied and compared with those of PMDA/ODA polyimide. The copolymer properties were slightly diminished from those of PMDA/ODA polyimide in terms of both thermal stability and mechanical properties.

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