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Imide–aryl ether phenylquinoxalines 2

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Novel imide–aryl ether phenylquinoxaline copolymers were prepared and their morphology and thermal properties investigated. A key feature of these copolymers is the incorporation of an aryl ether phenylquinoxaline linkage into a semi-rigid polyimide backbone based in pyromellitic dianhydride (PMDA) with 4,4'-oxydianiline (ODA) and either 2,3-bis-[(3-aminophenoxy)phenyl]quinoxaline or 2,3-bis-[(4-aminophenoxy)phenyl]quinoxaline as co-diamines. These monomers were prepared by a novel nucleophilic aromatic substitution reaction of 2,3-bis(4-fluorophenyl)quinoxaline with 4- or 3-aminophenol in the presence of K_2CO_3. These diamines were used as co-monomers with PMDA and ODA to synthesize poly(amic-acids) which were cast and cured (350°C) to effect imidization, affording tough films. The copolymers with high phenylquinoxaline compositions displayed glass transition temperature values in the 300°C range. The thermal stability of the copolymers was comparable to that of the parent polyimide, with decomposition temperatures between 455 and 480°C. The morphology of the copolymers was investigated by dynamic mechanical thermal analysis and wide angle X-ray diffraction. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: copolymers; synthesis; morphology)

Introduction

Due to the advantages in cost, availability, processing, thermal stability and their excellent mechanical properties, aromatic polyimides are the most commonly used materials in microelectronic fabrication, with applications as interlayer dielectrics, passivation layers and structural resins. The semi-rigid and rigid polyimides, including those derived from pyromellitic dianhydride (PMDA) with 4,4'-oxydianiline (ODA), PMDA with 1,4-phenylenediamine (PDA), and biphenyldianhydride (BPDA) with PDA, all possess low residual thermal stress due to their high modulus and low thermal expansion coefficient. This feature is considered important in the fabrication of low stress multilayer polyimide components on rigid substrates. These desirable mechanical properties result from their liquid crystalline or crystalline morphology, as described by Takahashi *et al.*[1] and Russell[2]. However, poor planarization, melt processability and self- or auto-adhesion (i.e. the adhesion of polyimide to itself) are some of the drawbacks associated with the retention of this ordered structure to high temperatures and the absence of a glass transition temperature (T_g). Conversely, other rigid heterocycle containing thermally stable polymers such as poly(oxadiazoles), poly(phenylquinoxalines) and others all, possess a T_g, thus circumventing many of the problems with the semi-rigid and rigid polyimides. Consequently, it is of interest to combine the desirable characteristics of polyimide with those possessed by other heterocycle containing polymers.

Preston and coworkers[3,4] prepared polyimides containing phenylquinoxaline, benzothiazole, benzimidazole, benzoxazole, oxadiazole and other heterocycles, where the heterocycle was introduced as the diamine monomer. A wide variety of morphologies and properties were made possible by this approach. Likewise Augl and Duffy[5] reported the synthesis of such copolymers in which the quinoxaline ring formation was the polymer forming reaction. A bis(dicarbonyl) monomer containing a preformed imide linkage, prepared by the reaction of aminobenzil with the appropriate dianhydride, was reacted with various bis(*o*-diamines). In addition, Korshak *et al.*[6] have reported imide-phenylquinoxaline copolymers which were prepared by the melt polycondensation of bis(aminophenyl)-quinoxaline with 1,4,5,8-naphthalenetetracarboxylic dianhydride. These materials displayed excellent thermal stability and could be melt fabricated.

Alternatively, we have reported the synthesis of imide-aryl ether phenylquinoxaline statistical copolymers by the co-reaction of PMDA with various compositions of ODA, and bis(amino) monomers with preformed phenylquinoxaline moieties, 1,4-bis-2-[[3-phenyl-6-(3-aminophenoxy)]quinoxalinyl]benzene, **1** and 1,4-bis-2-[[3-phenyl-6-(4-aminophenoxy)]quinoxalinyl]benzene, **2** (*Scheme 1*). These diamines were prepared by a novel halodisplacement reaction of an appropriately substituted halophenylquinoxaline with either 3- or 4-aminophenol, respectively. Facile displacement of the fluoride was demonstrated from either the 6- or 7-positions of the quinoxaline heterocycle, affording the desired diamines in high yield. Due to the nonselectivity of the quinoxaline ring formation, three isomers were possible, similar to those generated in the synthesis of poly(phenylquinoxaline) (PPQ). This random isomer mixture imparts solubility and processability to an otherwise intractable polymer. Copolymers of various phenlyquinoxaline compositions were prepared, and those containing the high phenylquinoxaline composition displayed T_g values

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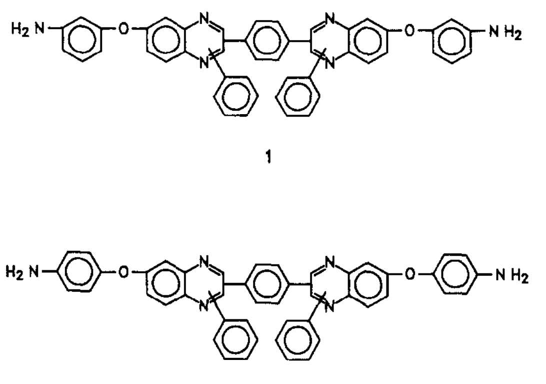


1

2

Scheme 1

in the 300°C range, while retaining the desired thermal stability. Ordering characteristics of the polyimide were found to be retained and even refined in some cases. At high compositions of phenylquinoxaline in the copolymer, however, the interchain packing was sufficiently hampered to disrupt this ordering and variation in the ordering of the PMDA/ODA sequences ultimately defined the properties of the copolymers. The net result was that auto-adhesion characteristics of the polyimides were significantly improved by the incorporation of the PPQ[7].

We have recently found that in addition to the demonstrated activity of aromatic nucleophilic displacement of the 6- and 7-positions of the quinoxaline benzo ring[8] the quinoxaline heterocycle also activates the 4-positions of appended 2- and 3-phenyl rings. This reaction was used to prepare poly(aryl ether phenylquinoxalines) by the polymerization of bisphenols with 2,3-bis(4-fluorophenyl)quinoxaline in aprotic dipolar solvents in the presence of base[8]. In this synthetic approach, the constitutional isomers characteristic of the previous system are not possible, and consequently the resulting poly(aryl ether phenylquinoxalines) were not as processable or soluble[9–11]. Due to the interesting properties of the poly(aryl ether phenylquinoxalines) without isomers, it was of interest to use this reaction to prepare new diamines and the resulting polyimides. In this article we will discuss the use of the quinoxaline activated fluorodisplacement to prepare new diamines and the subsequent imide homopolymers and copolymers.

Experimental

Materials. PMDA (Chriskev Company), 4-aminophenol (Aldrich) and 3-aminophenol (Aldrich) were sublimed prior to use. ODA and 4,4'-difluorobenzil were obtained from Davos Chemical Co., and were used without further purification.

Monomer synthesis. *2,3-Bis(4-fluorophenyl)quinoxaline,* **3**. Into a 1000 ml round bottom flask equipped with a reflux condenser, nitrogen inlet and stirbar was placed 4,4'-difluorobenzil, **2** (19.69 g, 80 mmol), *o*-phenylenediamine (8.65 g, 80 mmol), and 150 ml of acetic acid. The solution was gradually warmed to 110°C and allowed to stir for 2.5 h. After cooling, water (700 ml) was added dropwise to give a white solid which was isolated by suction filtration and washed repeatedly with water. Recrystallization from ethanol and water gave 24.3 g (95%) of white fluffy crystals in two crops: m.p. 133.5–134.0°C; ^1H n.m.r. (DMSO) δ 8.20–8.13 (*m*, 2H), 7.93–7.87 (*m*, 2H), 7.58–7.50 (*m*, 4H), 7.29–7.18 (*m*, 4H); ^{13}C n.m.r. ($CDCl_3$) δ 163.10 ($d, J = 249.8$ Hz), 152.05, 141.07, 134.90, 131.73, 130.09, 129.03, 115.41 ($d, J = 21.8$ Hz). Analyt. Calcd for $C_{20}H_{12}N_2F_2$: C, 75.45; H, 3.81; N, 8.80. Found: C, 75.42; H, 3.90; N, 8.79. *2,3-Bis-[(3-aminophenoxy)phenyl]quinoxaline,* **4**. A three-neck flask equipped with a nitrogen inlet, overhead stirrer and Dean–Stark trap was charged with **3** (25.00 g, 0.0478 mol) and 1,3-aminophenol (11.3500 g, 0.1029 mol), which were carefully rinsed in the flask with 150 ml of NMP and 25 ml of toluene. Next, an excess of anhydrous K_2CO_3 (30 g 0.021 mol) was added. The reaction was heated at the reflux temperature (≈ 140–150°C) for 6 h to dehydrate the system. The temperature was increased to 180°C and monitored for 40 h to effect the displacement reaction, and toluene was removed through the Dean–Stark trap. The product was isolated in water and recrystallized (chloroform/methanol) to yield a crystalline a light yellow powder: m.p. 187–190°C; ^1H n.m.r. δ ($CDCl_3$) 8.13–8.17 (*m*, 2H), 7.73–7.79 (*m*, 2H), 7.53 ($d, J = 9$ Hz, 4H), 7.12 ($t, J = 8$ Hz, 2H), 7.01 (*m*, 4H), 6.42–6.47 (*m*, 4H), 6.37 ($t, J = 2$ Hz, 2H), 3.72 (*br s*, 4H); ^{13}C n.m.r. δ ($CDCl_3$) 157.97, 157.60, 152.74, 147.96, 141.04, 133.66, 131.26, 130.34, 129.76, 128.99, 118.41, 110.42, 109.15, 105, 79. Analyt. Calcd for $C_{32}H_{24}N_4O_2$: C, 77.39; H, 4.87; N, 11.93. Found: C, 77.37; H, 4.71; N, 11.16. *2,3-Bis-[(4-aminophenoxy)phenyl]quinoxaline,* **5**. A three-neck flask equipped with a nitrogen inlet, overhead stirrer and Dean–Stark trap was charged with **3** (5.061 g, 0.01589 mol) and 1,4-aminophenol (3.8475 g, 0.03497 mol) and rinsed in the flask with 35 ml of NMP and 25 ml of toluene. Approximately 3 g of K_2CO_3 was added to the flask and the reaction mixture was heated to the reflux temperature (~ 140–150°C) for 6 h to dehydrate the system. Toluene was then removed through the Dean–Stark trap and the temperature was increased to 180°C and monitored for 20 h to effect the displacement reaction. The product was isolated in water and recrystallized from chloroform/methanol mixture to yield a light brown crystalline powder: m.p. 220–222°C; ^1H n.m.r. δ (DMSO-d_6) 8.05–8.11 (*m*, 2H), 7.79–7.84 (*m*, 2H), 7.43 ($d, J = 8$ Hz, 4H), 6.82 ($t, J = 8$ Hz, 8H), 6.63 ($d, J = 8$ Hz, 4H), 5.05 (*s*, 4H); ^{13}C n.m.r. δ (DMSO-d_6) 159.62, 152.44, 145.86, 144.99, 140.36, 132.30, 131.35, 130.11, 128.69, 121.15, 115.89, 114.95. Analyt. Calcd for $C_{32}H_{24}N_4O_2$; C, 77.39; H, 4.87; N, 11.93. Found: C, 77.42; H, 4.85; N, 11.41.

Polymer synthesis. The copolymers were prepared according to a published literature procedure[12]. A three-neck flask equipped with an overhead stirrer and nitrogen outlet was charged with the diamines (ODA and **4** or **5**), which were rinsed in with NMP and cooled to −10°C under a strong nitrogen flow. To this solution, solid PMDA was added with slow stirring, and the reaction mixture was allowed to return to room temperature, affording a viscous polymer solution (24 h). The solution was filtered (0.5 μm) and stored cold until used.

Characterization

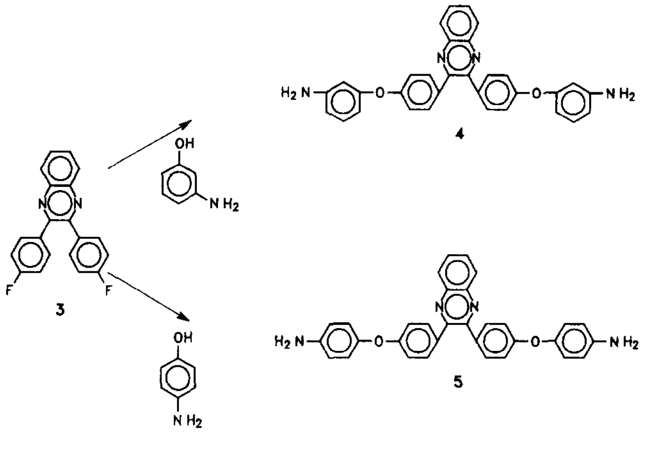
Films for thermal and mechanical analysis were cast from NMP and heated to 350°C ($5^{\circ}C\,min^{-1}$ heating rate), and held for 30 min. T_gs, taken as the mid point of the change in slope of the baseline, were measured on a DuPont 1090 instrument with a heating rate of $10^{\circ}C\,min^{-1}$. The dynamic mechanical measurements were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyser (DMTA) at 10 Hz and a heating rate of $10^{\circ}C\ min^{-1}$, in the tension mode. Isothermal and variable temperature ($5^{\circ}C\,min^{-1}$ heating rate) thermal gravimetric analysis (t.g.a.) were performed on a Perkin-Elmer model TGA-7.

Wide angle X-ray diffraction (WAXD) 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 reaction utilized for the synthesis of bis(amino)-phenylquinoxaline monomers was the nucleophilic aromatic substitution on a fluoride at the *para* positions on the phenyl groups attached to the 2- and 3-positions of quinoxaline by 1,3- or 1,4-aminophenol. The rationale for the nucleophilic aromatic substitution on the pendent phenyl groups of the quinoxaline was similar to that described before the halide on the 6- or 7-positions of the heterocycle[8]. First, the electron-poor pyrazine ring would have the effect of an electron-withdrawing group, and secondly, due to resonance of the negative charge in the pyrazine ring, a Meisenheimer complex would form as a stabilized intermediate during the transformation. The electronic effect of the pyrazine ring on the 2-phenyl group was evaluated by ^{1}H n.m.r., as the deshielding of the protons *ortho* to a substituent is indicative of an electron-withdrawing group. The deshielding of the *ortho* protons of the 2-phenyl group on the phenylquinoxaline to the *ortho* protons of 4,4'-difluorobenzophenone, a conventional activated dihalide[13,14] showed them to be comparable with respect to nuclear correlation with electron affinity. Furthermore, this reaction was used to successfully prepare high molecular weight poly(aryl ether phenylquinoxalines)[9].

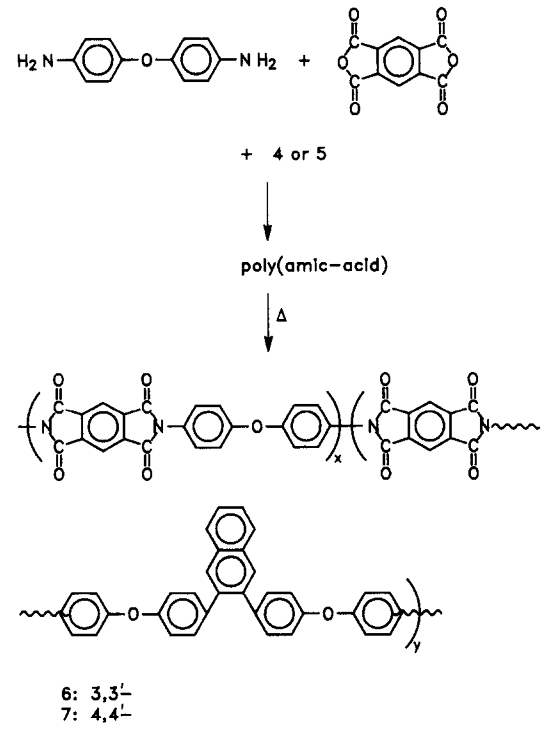
The requisite 2,3-bis(4-fluorophenyl)quinoxaline, **3**, was prepared in good yield by reaction of 1,2-phenylenediamine with 4,4'-difluorobenzil, as described previously. The main distinction between this monomer and those previously reported[15] is the absence of the constitutional isomers due to the unsymmetrical substitution at the 6- and 7-positions. The preference for reactivity at these positions is unknown, but the resulting isomer content significantly influences the solubility characteristics of PPQ by disrupting the chain packing precluding an ordered or semi-crystalline morphology. Likewise, in the previously reported poly(aryl ether phenylquinoxalines) derived from 1,4-bis[2-(3-phenyl-6-fluoroquinoxalinyl)]benzene, three distinct isomers were generated in the monomer forming reaction and retained in the polymer as is analogous to the multiple isomeric phenylquinoxaline moieties formed in the PPQ synthesis[15]. In contrast, 2,3-bis(4-fluorophenyl)quinoxaline does not have the isomers and poly(aryl ether phenylquinoxalines) derived from such materials are only marginally soluble and appear to be partially crystalline[9,10].



Scheme 2

Two new phenylquinoxaline-based diamines were prepared by the nucleophilic aromatic substitution reaction of the bis-2,3-(4-fluorophenyl)quinoxaline with either 3- or 4-aminophenol (*Scheme 2*). The first example involved the preparation of 2,3-bis-[(3-aminophenoxy)-phenyl]quinoxaline **4**, synthesized by the reaction of **3** with 3-aminophenol in NMP-containing base (*Scheme 2*). Quantitative conversion of **3** was observed with the formation of a single product peak (thin layer chromatographical (t.l.c.) analysis, ethyl acetate/hexane). The resulting monomer was isolated in 90% yield and recrystallized to produce polymer grade monomer. The spectral characteristics and C, H and N values were consistent with the assigned structure. The second example involves the synthesis of 2,3-bis-[(4-aminophenoxy)phenyl]quinoxaline **5**, which was prepared in an analogous fashion to **2** except that **1** was reacted with 4-aminophenol (*Scheme 1*). Once again the reaction was mediated in NMP in the presence of potassium carbonate. Quantitative conversion of **3** was observed with the formation of a single product peak (t.l.c.). The light brown product was recrystallized from chloroform/methanol, and showed the spectral characteristics and C, H and N values of the expected **5**. It is important to note that this synthetic approach is analogous to the preparation of sulfone[14], ketone[16], phenylquinoxaline[7], and benzoxazole[17] based diamines previously reported.

The imide–aryl ether phenylquinoxaline copolymers were prepared via the amic-acid route in NMP. Monomers **4** or **5** were co-reacted with various compositions of PMDA and ODA to afford copolymer series **6a–c** and **7a–c**, respectively (*Scheme 3*). The copolymer synthesis involved the incremental addition of PMDA to a solution of ODA and either **4** or **5** (−10°C) in NMP. The solids composition was generally maintained at approximately 10%. PMDA is only marginally soluble in NMP at low temperatures, and upon dissolution, near perfect stoichiometry is generated with the diamines affording high molecular weight polymer early in the polymerization similar to an interfacial synthesis[12]. The polymerizations were allowed to return to room temperature and stirred for 24 h. High molecular weight poly(amic-acid) solution was obtained as judged by the dramatic increase in viscosity. It is interesting to note that the incorporation of the phenylquinoxaline containing diamines produced lower viscosity solutions than



Scheme 3

those typically encountered in polyimide syntheses, allowing many of the polymerizations to be performed in solutions with solid contents as high as 20% (w/v). This effect was also observed on earlier reports of imide phenyl quinoxaline copolymers[7]. This is not entirely unexpected because NMP is a non-solvent for many PPQ homopolymers.

Copolymer compositions were prepared so as to vary the weight percent of **4** or **5** (denoted as **a**–**c** in each copolymer series), the phenylquinoxaline component, relative to the total weight of ODA and PMDA, the polyimide component. The phenylquinoxaline compositions ranged from 25 to approximately 75 wt%, with the latter sample being **4** or **5** chain extended with PMDA (copolymers **6c** and **7c**) (*Table 1*). A blocky chain microstructure is avoided in these copolymerizations since poly(amic acid) solutions are known to undergo transimidization yielding random or statistical copolymers[12]. The copolymer solutions were filtered and cured (350°C) to effect imide formation.

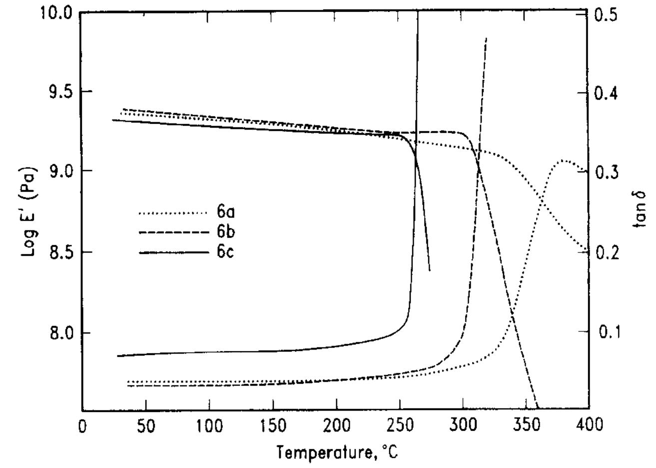


Figure 1 Dynamic mechanical behaviour for copolymer series **6**

The thermal analysis for the copolymers prepared and PMDA/ODA polyimide to facilitate comparison are shown in *Table 1*. The polyimide homopolymer shows no detectable T_g up to 400°C. Conversely, copolymers **6b** and **6c** show T_gs by differential scanning calorimetry (d.s.c.) measurements, which were in the 300°C range. Likewise, copolymers **7a**–**c** displayed T_gs in the 370°C range. Copolymer **6a** shows similar behaviour to that of PMPA/ODA polyimide, with no detectable T_g up to 400°C. These values are somewhat higher than those of copolymer series **6**, consistent with the *para*-linkages. The thermal stability, as judged by polymer decomposition temperature and isothermal weight loss upon ageing at both 350 and 400°C for 8 h, for the copolymers was good, yet not comparable to that for PMDA/ODA polyimide (*Table 1*). The decomposition temperatures were in the 480°C range and approximately 0.20 wt% h^{-1} weight loss was observed upon ageing at 400°C.

The dynamic mechanical behaviour for copolymers **6** and **7** are shown in *Figures 1* and *2*. The 'liquid crystalline' or 'crystalline' ordering manifested by the polyimide homopolymer significantly influences the modulus–temperature profile[1,2]. The modulus is essentially invariant up to 400°C, except for a small drop at ~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 reflects an

Table 1 Characteristics of imide phenylquinoxaline copolymers

Sample entry	Phenylquinoxaline composition (wt%)	T_g (°C)	Polym. decomposition temperature (°C)	Isothermal wt. loss 400°C N_2 (wt% h^{-1})	Isothermal wt. loss 350°C N_2 (wt% h^{-1})
6a	10	–^{a}	465	0.32	0.02
6b	50	300	460	0.26	0.02
6c	75	266	460	0.18	0.01
7a	25	378	455	0.19	0.04
7b	50	370	460	0.25	0.01
7c	75	355	450	0.17	001
PMDA/ODA polyimide		^{a}	480	0.04	–

^{a} Not detectable by d.s.c.

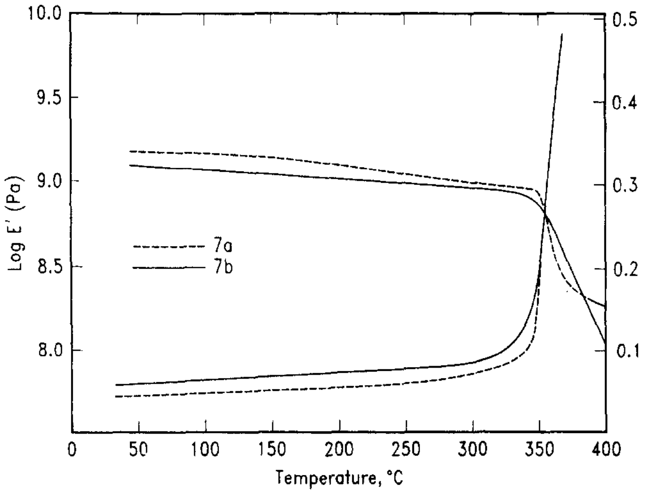


Figure 2 Dynamic mechanical behaviour for copolymer series **7**

enhancement in ordering in the PMDA/ODA segments with thermal cycling.

The modulus–temperature profiles of the copolymers containing the low phenylquinoxaline compositions are somewhat similar to that of PMDA/ODA polyimide. T_gs, as characterized by a large sharp modulus drop, were not observed for either of the copolymer series[7]. Instead, the copolymers showed large and broad transitions between 300 and 400°C. These spectra are somewhat similar to those observed for imide–aryl either benzoxazole 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[17,18]. Copolymers **6a** and **7a** showed a similar modulus–temperature profile to that of PMDA/ODA polyimide with a modulus invariance up to ~370°C with only a small drop (~half decade) at this temperature. The modulus then levels out analogously to PMDA/ODA polyimide, suggesting that the ordered morphology is retained in this copolymer. At higher phenylquinoxaline compositions (**6b** and **c**, **7b** and **c**), a larger drop in modulus was observed, indicative of a T_g, consistent with the calorimetry measurements. Wide angle X-ray diffraction measurements showed no evidence of crystallinity, and the ordered liquid crystalline morphology of the PMDA/ODA segments rapidly diminished with increasing phenylquinoxaline compositions.

Summary

Imide–aryl ether phenylquinoxaline random copolymers were prepared and their thermal and mechanical properties investigated. Phenylquinoxaline-containing diamines were prepared via a novel nuclephilic aromatic substitution reaction, where the phenylquinoxaline heterocyclic activated an aryl fluoride towards displacement with amine-substituted phenoxides. The diamines were coreacted with various compositions of PMDA and ODA, producing poly(amic acid) solutions, which were subsequently cast and cured to the imide form. The copolymers showed both good thermal and dimensional stability to high temperatures. This represents another example of an aryl–ether-containing diamine based on nucleophilic aromatic substitution of aryl fluorides activated by a heterocyclic ring. Furthermore, heterocyclic-activated nucleophilic displacement should prove effective with monomers derived from other ring systems.

References

1 Takahashi, N., Yoon, D. Y. and Parrish, W. *Macromolecules* 1984, **17**, 583

2 Russell, T. P. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **22**, 1105

3 Preston, J., Dewinter, W. F. and Black, W. B. *J. Polym. Sci. (A-1)* 1969, **7**, 283

4 Preston, J., Dewinter, W. F., Black, W. B. and Hofferbert, W. L. Jr. *J. Polym. Sci. (A-2)* 1969, **7**, 3027

5 Augl, J. M. and Duffy, J. V. *J. Polym. Sci. (A-1)* 1971, **9**, 1334

6 Korshak, V. V., Berestneva, G. L., Aksenova, T. S., Krongauz, E. S., Belomonia, N. M., Babich, S. A., Slonimskii, G. L. and Dubovik, I. I. *Vysokomol. Soedin. Ser. A* 1987, **29**, 1609

7 Hedrick, J. L., Russell, T. P. and Labadie, J. W. *Polymer* 1991, **32**, 950.

8 Hedrick J. L., Twieg, R., Matray, T. and Carter, K. *Macromolecules* 1993, **26**, 4833

9 Connell, J., Smith, J. and Hergenrother, P. M. *Polymer* 1993

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

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

12 Johnson, R. N., Farnham, A. G., Clendinning, R. A., Hale, W. F. and Merrian, C. N. *J. Polym. Sci., Polym. Chem. Edn* 1967, **5**, 2375

13 Atwood, T. E., Barr, D. A., Faasey, G. G., Newton, V. J. and Rose, A. B. *Polymer* 1977, **18**, 354

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

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

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

17 Hedrick, J. L., Russell, T. P., Labadie, J. W., Hilborn, J. G. and Palmer, T. D. *Polymer* 1990, **31**, 3284