Processable heat-resistant resins based on novel monomers containing *o*-phenylene rings: 2. Ordered benzoxazole– and benzthiazole–imide copolymers*

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Highly processable heat-resistant resins containing *o*-phenylene rings have been prepared with high molecular weight from the reaction of simple aromatic dianhydrides with aromatic diamines containing preformed bisbenzoheterocyclic groups connected by an *o*-phenylene ring. Thus, 2,2′-*o*-phenylene-bis(5-aminobenzoxazole) was polycondensed with 3,3′4,4′-benzophenone dianhydride to yield a polyamic acid precursor, which was converted to an ordered benzoxazole–imide copolymer via cyclodehydration. Polymers can be prepared from diamines that are structural isomers, e.g. the amino groups can be in the 6-position instead of the 5-position. Additionally, polymers have been prepared from diamines, e.g. 2,2′-*o*-bis(6-aminobenzothiazole), having structurally similar heterocyclic units such as benzothiazole in place of benzoxazole rings. The preparation of the dinitro precursors to the bisbenzoheterocyclic diamines and their reduction is described along with nuclear magnetic resonance data. Polymers were characterized by differential scanning calorimetry, thermogravimetric analysis and inherent viscosity measurements of the polyamic acid precursors.

(Keywords: heat-resistant resins; ordered benzoxazole–imide copolymers; ordered benzothiazole–imide copolymers; *o*-phenylene rings)

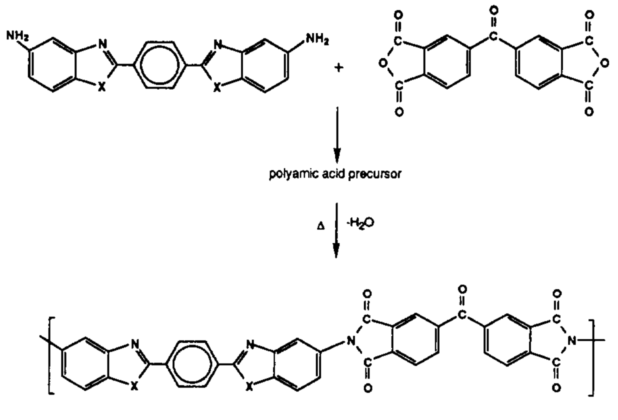
INTRODUCTION

Previous work[1] reported data on very thermo-oxidatively stable fibres from ordered benzoxazole–imide copolymers (*Scheme 1*) derived from bisbenzoxazole diamines containing *para*-oriented rings bridging the heterocyclic rings.

In the present work, the focus is on highly processable heat-resistant resins containing *ortho*-phenylene rings. These polymers have been prepared with high molecular weight from the reaction of simple aromatic dianhydrides with aromatic diamines containing preformed bisbenzoheterocyclic groups connected by an *o*-phenylene ring followed by cyclodehydration. For example, 2,2′-*o*-phenylene-bis(5-aminobenzoxazole) (*o*-P5ABO) was polycondensed (*Scheme 2*) with 3,3′4,4′-benzophenone dianhydride (BPDA) to yield a polyamic acid precursor, which was converted to an ordered benzoxazole–imide copolymer via cyclodehydration. (Note that this particular polymer was reported[2] previously, but very little information was available at that time. It was reported, however, that drastic softening of a film occurred at 280°C. But if annealed at 300°C, strong, flexible films were obtained that exhibited only a 10% weight loss in air to 550°C by t.g.a. at a heating rate of 15°C min^{-1}.)

In addition to the polymer from *o*-P5ABO and BPDA (*Scheme 2*), other polymers containing *o*-phenylene rings can be prepared (*Scheme 3*) from bisbenzoheterocyclic diamines that are structural isomers of *o*-P5ABO, e.g. 2,2′-*o*-phenylene-bis(6-aminobenzoxazole) (*o*-P6ABO). Additionally, a diamine containing benzothiazole units has been prepared, e.g. 2,2′-*o*-phenylene-bis(6-aminobenzothiazole) (*o*-P6ABT), and polymerized with dianhydrides.

Unlike the diamine *o*-P5ABO, which can be synthesized[3,4] directly from 2,4-diaminophenol and phthalic anhydride, *o*-P6ABO and *o*-P6ABT have been obtained



Scheme 1

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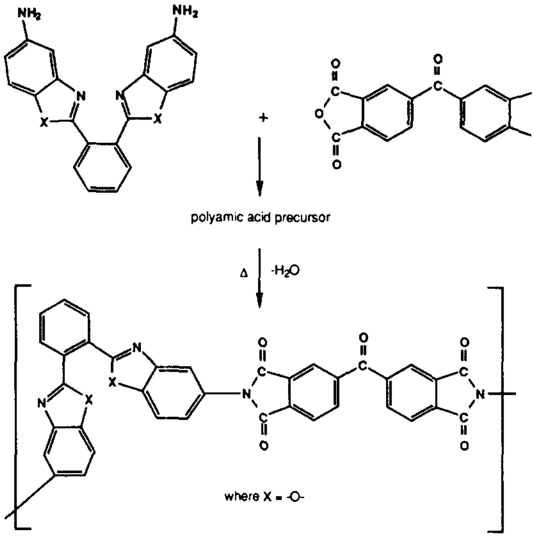
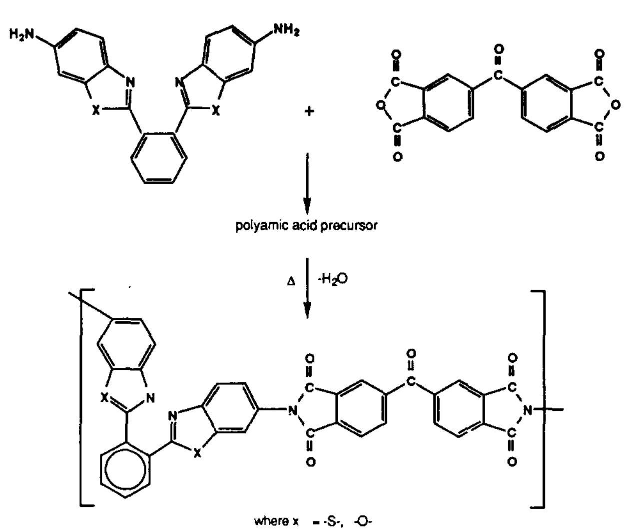
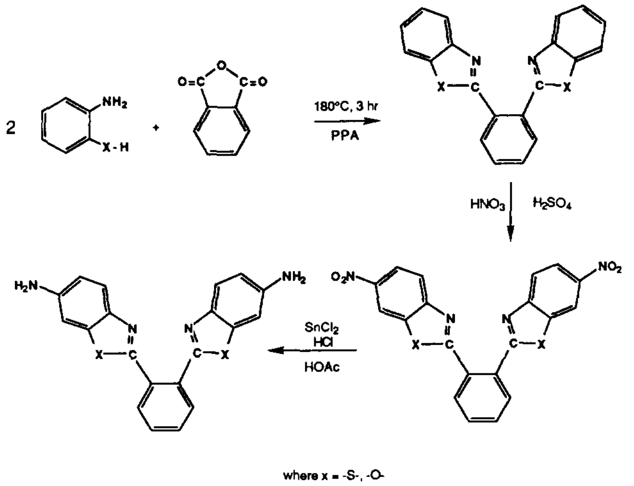


Scheme 2



Scheme 3



Scheme 4

via reduction of their dinitro precursors. The latter were prepared via nitration (*Scheme 4*) of unsubstituted 2,2′-*o*-phenylene-bisbenzoxazole (*o*-PBO) and 2,2′-*o*-phenylene-bisbenzothiazole (*o*-PBT). It is significant to note that nitration of *o*-PBT leads to virtually quantitative substitution in the 6-position, while nitration of *o*-PBO leads mostly to substitution in the 6-position. Additionally, there appears to be strong conjugation through *o*- and *p*-phenylene rings bridging PBOs, which prevent nitration on them, whereas an *m*-phenylene ring bridging PBO is nitrated to a significant extent[6].

Details of the preparation of the various dinitro precursors to bisbenzoheterocyclic diamines and their reduction are given below.

EXPERIMENTAL

Monomer synthesis

o-PBO and *o*-PBT were prepared by procedures that were similar to published ones[3–5]. The nitration and reduction procedures are standard ones and are similar to a previously published one[6]. N.m.r. spectra were obtained in deuterated dimethylsulphoxide (DMSO-d_6).

*2,2′-*o*-Phenylene-bisbenzothiazole* (o-*PBT*). 2-Aminothiophenol (12.5 g, 0.1 mol) was added to a 250 ml, three-necked tapered flask containing polyphosphoric acid (90 g). The mixture was mechanically stirred under nitrogen and phthalic anhydride (7.4 g, 0.5 mol) was added. The temperature was raised to 180°C and maintained for 3 h. The solution was cooled to 100°C and precipitated into a blender containing ice–water (600 ml). The damp cake was suspended in water and neutralized with sodium carbonate (2 g), filtered, washed with water and refiltered. The dried cake was dissolved in 100% ethanol (500 ml) and Norite (2 g) was added. After refluxing for 2 h, the product was collected, dried, recrystallized from ethanol, and sublimed to yield white crystals. Yield, 81%; m.p., 115°C. ^{13}C n.m.r. (DMSO-d_6) ppm: C2, 165.68; C3a, 152.76; C4, 123.15; C5, 126.52; C6, 125.61; C7, 172.24; C7a, 135.93; C8, 130.98; C9, 132.82; C10, 130.80.

*2,2′-*o*-Phenylene-bis(6-nitrobenzothiazole)* (o-*P6NBT*). *o*-PBT (4 g, 0.0058 mol) was added to a 50 ml, three-necked round-bottom flask containing concentrated sulphuric acid (11 ml). An ice bath was used to keep the temperature below 50°C. The nitration mixture (fuming nitric acid, 2 ml, and concentrated sulphuric acid, 2.4 ml) was added slowly via a dropping funnel over a 10 min period, but stirring was continued for 1 h. The reaction mixture was poured into a blender containing ice–water (250 ml). The crude product was filtered, suspended in water, neutralized with sodium carbonate (pH 9), washed again with water, and collected on filter paper. Crude yield, 5 g; m.p., 243°C. The crude product was twice refluxed in ethanol (500 ml), filtered, and recrystallized from tetrahydrofuran (THF) to yield light yellow crystals. Yield, 60%; m.p., 275°C. ^{13}C n.m.r. (DMSO-d_6) ppm: C2, 172.23; C3a, 156.38; C4, 123.60; C5, 121.84; C6, 144.62; C7, 119.5; C7a, 136.40; C8, 131.34; C9, 132.16; C10, 131.69.

*2,2′-*o*-Phenylene-bis(6-aminobenzothiazole)* (o-*P6ABT*). *o*-P6NBT (1 g, 0.0017 mol) was added to a 1 litre flask containing glacial acetic acid (100 ml) while stannous chloride (7 g) was dissolved in concentrated HCl (8 ml). Both solutions were brought to boil, the glacial acetic acid solution removed from the heat and then slowly added to the stannous chloride solution. Stirring was continued for 15 min, the solution cooled in an ice bath to 5°C, and filtered. The bright orange compound was dissolved in water (200 ml), neutralized with sodium carbonate, filtered, washed with water, and dried. Yield, 0.81 g; m.p., 199°C. The crude product was dissolved in ethanol, refluxed with Norite (1 g), filtered, and sublimed to yield light yellow crystals. Yield, 42%; m.p., 248°C. ^{1}H n.m.r. (DMSO-d_6) ppm: N–H, 5.4. ^{13}C n.m.r. (DMSO-d_6) ppm: C2, 158.79; C3a, 138.00; C4, 123.40; C5, 115.01; C6, 144.46; C7, 103.28; C7a, 147.43; C8, 130.54; C9, 133.08; C10, 129.85.

*2,2′-*o*-Phenylene-bisbenzoxazole* (o-*PBO*). The molar amounts and procedure used to synthesize *o*-PBT were also used successfully to produce *o*-PBO. Yield, 83%; m.p., 174°C. ^{13}C n.m.r. (DMSO-d_6) ppm: C2, 161.49; C3a, 141.19; C4, 120.02; C5, 125.76; C6, 124.80; C7, 110.795; C7a, 150.35; C8, 126.72; C9, 131.83; C10, 181.01.

*2,2′-*o*-Phenylene-bis(6-nitrobenzoxazole)* (o-*P6NBO*). Conditions used to synthesize *o*-P6NBT were suitable for the oxygen analogue to give *o*-P6NB. Yield, 76%; m.p., 233°C. ^{13}C n.m.r. (DMSO-d_6) ppm: C2, 165.83; C3a, 146.71; C4, 120.41; C5, 120.86; C6, 145.13; C7, 107.79; C7a, 149.91; C8, 125.86; C9, 132.82; C10, 131.44.

*2,2′-*o*-Phenylene-bis(6-aminobenzoxazole)* (o-*P6ABO*). Again, reduction of the oxygen analogue was similar to that previously described for *o*-P6ABT. Yield, 37%; m.p., 215°C. ^{13}C n.m.r. (DMSO-d_6) ppm: N–H, 5.4. ^{13}C n.m.r. (DMSO-d_6) ppm: C2, 158.48; C3a, 130.23; C4, 119.78; C5, 112.43; C6, 147.97; C7, 93.88; C7a, 152.06; C8, 126.84; C9, 131.62; C10, 130.74.

Polymerization and film curing

Polymerizations were carried out as reported previously[3]. The polyamic acid solutions were cast into films and converted to the polyheterocycle–imides by heating of the polyamic acid precursor at 100–110°C to remove solvent, followed by gradual increase in temperature to about 150°C over a period of 4–6 h and holding at this temperature for about 3 h. The temperature was raised to 170°C and the films heated overnight. At this stage and until they are fully imidized, the films were brittle and had to be handled carefully in order not to break them as is the case for most polyimides not containing a so-called hinge group, e.g. an ether group. The temperature was raised slowly to about 200°C and the films were held at this temperature for 2–4 h. Films so prepared were highly flexible. Small portions of the film were exposed to 300°C to see if any bubbles appeared. If none did, the larger portions of the films were cured for about 5 min and removed from the oven. If bubbles appeared, the films were heated longer at 200°C and then at about 220°C until no bubbles appeared when test specimens were heated at 300°C. (Note that the higher the glass temperature of the polyheterocycle–imide, the longer the time and the higher the temperature necessary prior to the 300°C cure in order to obtain a bubble-free test specimen.)

Measurements

Thermogravimetric analyses (t.g.a.) were conducted under helium at a heating rate of 20°C min^{-1} using a Perkin–Elmer TGA-1 analyser. Differential scanning calorimetry (d.s.c.) measurements were made with a Perkin–Elmer DSC-2 at a heating rate of 20°C min^{-1} under nitrogen.

Viscosities were determined on 0.5% (0.5 g in 100 ml *N*-methylpyrrolidinone, NMP) solutions of the polyamic acid solutions at 25 ± 0.1°C in an Ubbelohde viscometer.

RESULTS AND DISCUSSION

Polymerizations

Polymerizations were carried out in the usual manner for the preparation of polyimides and for ordered heterocycle–imides in particular[3]. For the materials of the present study, it was much easier to dissolve the bisheterocyclic diamines bridged by *o*-phenylene rings than it was for similar diamines bridged by, for example, *p*-phenylene rings. Thus, diamines of the former type were readily soluble to 60% solids or more whereas a diamine of the latter type, e.g. *p*-phenylene-2,2′-bis(5-aminobenzoxazole), was soluble to the extent of only about 6% solids. (In the latter case, high-solids polymer solutions can be achieved because the polyamic acid formed is rather soluble, especially compared with the starting diamine, which, despite its low solubility, enters solution as polymer is formed. However, this is inconvenient for processing when using the polyamic acid as a precursor. But in the case of the formation of polyimides via formation from diamine plus a diester–diacid derivative of the dianhydride chosen, highly insoluble diamines cannot be used because the diamine will not enter solution and polymerize stoichiometrically, leaving pockets of unreacted diamine.)

The polyamic acids formed by the reaction of *o*-P6ABT and benzophenonetetracarboxylic dianhydride (BTDA) or pyromellitic dianhydride (PMDA) were prepared at about 18% solids in solution. The inherent viscosity (*IV*) values of the two polymers formed were 0.61 and 0.40, respectively. (By contrast, the benzophenone polyamic acid precursor of the *para* analogue of *o*-P5ABO shown in *Scheme 1* typically has an *IV* of about 1.5[1].) The two solutions of polymer had rather low viscosities despite the high solids content and the fair *IV* values. Nevertheless, excellent films could be cast from the solutions and, following cure at 300°C, the films were highly flexible. The low viscosities of the high-solids solutions actually should be a plus for processability when making composites.

In view of the large ‘bend’ in the diamine moieties produced by the *o*-phenylene rings, it is conceivable that, in addition to linear chains, there may be some macrocyclic rings present, as is well known for certain aromatic polyesters (e.g. polyisophthalates) and polycarbonates. Should such macrocyclic rings be present, it could well account for the low viscosities observed despite good mechanical properties of the films obtained.

Film curing

Typically, polyimide films are obtained by stepwise heating of polyamic acid precursors. Thus, after solvent removal and cyclodehydration at about 150–170°C, most polyimides can be heated rapidly to 300°C to effect full ring closure and to rearrange any isoimide groups to imide ones. The present polyimides are no exception, but curing in the range 170–300°C must be carried out with more care than is usual in order not to degrade the films by too rapid an evolution of water, which produces blisters in the films. The order of difficulty in curing and the order of increasing care that must be taken during curing is directly related to the T_g of the several polymers. (For T_g values, see below.) With increasing T_g, the time at which a film is held at a given temperature increases and the higher the intermediate temperature (from 170 to 220°C) that is necessary before carrying out final cure at 300°C. Although it is speculation at this point, the above observations are consistent with the view that there may be macrocyclic rings present which become linear upon heat treatment, especially above 170°C. It should be noted that the polyimides of the *para* analogues (see *Scheme 1*), which are rather rod-like, can be cured rather easily by heating to 150°C followed by raising the temperature immediately to 300°C.

The fully cured (5 min or more at 300°C or more) ordered heterocycle–imide copolymers reported here are designated for the discussions to follow by taking the symbols for the diamines and combining them with the designation for the appropriate dianhydride, using I for pyromellitimide and ICO for benzophenoneimide. Since only the 5-amino isomer of the benzoxazole diamine and the 6-amino isomer of the benzothiazole diamine were used to make polyimides, it is not necessary to indicate 5A or 6A in the various symbols for diamines. Consequently, benzoxazole and benzothiazole diamine moieties can be represented by, respectively, *o*-PBO, *p*-PBO and *o*-PBT. Thus, the polymer of *Scheme 1* can be designated as *p*-PBO-ICO, the polymer of *Scheme 2* is designated as *o*-PBO-ICO and the ordered benzothiazole–imide copolymer of *Scheme 3* is designated as *o*-PBT-ICO.

When clamped at the bottom and thrust into an oven at 450°C, films of *o*-PBO-ICO, *p*-PBO-ICO and *o*-PBT-ICO that had been cured at 300°C (for 5 min or more) showed distinctly different behaviour. Thus, the former bent slightly and then froze in position, usually at a 45° angle, and the other films showed no movement. This behaviour probably is related to the phenomena reported[7] earlier concerning the ability to press films of *o*-PBO-ICO, but not *p*-PBO-ICO, together at about

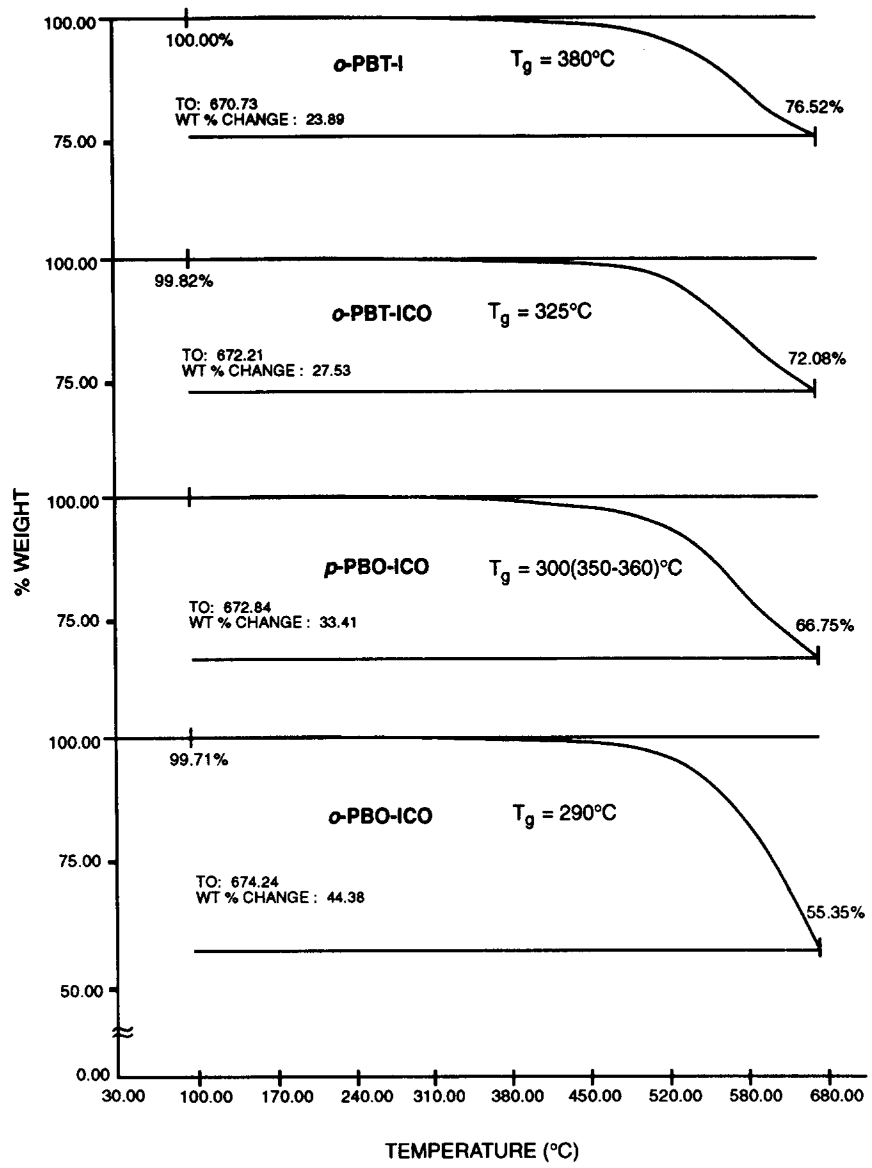


Figure 1 Thermogravimetric analysis (t.g.a.) curves for ordered heterocycle–imide copolymers in helium (rate = 20°C min^{-1})

310°C. Consolidated films of *o*-PBO-ICO can be placed in an oven at 450°C without distortion when suspended between bars set about 5–6 cm apart. Such behaviour possibly augurs well for pressing of such a resin in a composite because of the possibility of good consolidation at a reasonable temperature (e.g. 300–310°C) followed by 'setting', which then allows the resin to be used at a much higher in-use temperature, e.g. to 450°C.

The glass transition temperature (T_g) of the several polymers as determined by d.s.c. are as follows:

o-PBO-ICO	290°C
p-PBO-ICO	300 and 350–360°C
o-PBT-ICO	325°C
o-PBT-I	380°C

In addition to the T_g values determined by d.s.c. for *o*-PBO-ICO, the same value was determined by torsion braid analysis (t.b.a.)[7]. The value obtained indicates that the *o*-PBO moiety is relatively non-rigid and that the T_g is controlled by the benzophenoneimide moiety, which typically contributes a T_g value of about 289°C to polyimides having non-rigid diamine moieties.

For *p*-PBO-ICO, an initial transition is shown in the d.s.c. curve at 300°C (due to the benzophenoneimide moiety) but another higher transition is shown at 350–360°C, which is attributable to the relatively rod-like diamine moiety. The T_g of *o*-PBT-ICO indicates that the *o*-PBT moiety is intermediate in rigidity to the *o*-PBO and the *p*-PBO moieties. The very high T_g of *o*-PBT-I is due to the high rigidity of the pyromellitimide moiety.

The weight-loss curves determined by t.g.a. curves of the several polymers are shown in *Figure 1*. All of the polymers have a 5% weight loss at about 550°C. To 673±1°C, the weight retention values were remarkably high and they varied according to structure:

o-PBT-I	76.58%
o-PBY-ICO	72.08%
p-PBO-ICO	66.75%
o-PBO-ICO	55.355%

Because the several polymers would probably not be used long-term at a temperature in excess of about 400°C, they are all seen to be comparable to this temperature. The greater stability to 673°C *may* be an indication of long-term stability at a lower in-use temperature, e.g. 350°C, but this is by no means assured. Long-term stability tests in air are planned for the future.

CONCLUSIONS

Some very thermally stable ordered heterocycle–imide copolymers have been produced, all of which can be made into excellent films. One of the polymers, *o*-PBO-ICO, prepared from the reaction of 2,2′-*o*-bis(5-aminobenzoxazole) and BTDA, would appear to hold particular promise as a resin for the moulding of composites because the fully imidized polymer (hence, no volatiles of water or solvent used in the preparation of the precursor) in film form appears to coalesce with itself during moulding to produce a consolidated film, which can be used at an in-use temperature much higher than that used for moulding. *o*-PBO-ICO possibly derives its useful moulding property from the fact that it does not have a rod-like diamine moiety, and hence it initially 'flows' during moulding. The other polymers, having more rod-like diamine moieties, appear to have T_g values too high for moulding in a useful range.

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REFERENCES

1 Preston, J., Black, W. B. and DeWinter, W. *Appl. Polym. Symp.* 1969, **9**, 145
2 Preston, J., DeWinter, W. F. and Black, W. B. *J. Polym. Sci.* 1969, **6**, 283
3 Preston, J., DeWinter, W. F. and Hofferbert, Jr, W. L. *J. Heterocyclic Chem.* 1968, **5**, 169
4 Nyilas, E. and Pinter, I. L., US Pat. 3314894, 1967
5 Rai, C. and Braunworth, J. B. *J. Org. Chem.* 1961, **26**, 3434
6 Petitcolas, P. and Goupil, R. *Soc. Chim. Fr.* 1949, 103
7 Preston, J., Trexler, Jr, J. W. and Tropsha, Y. 'Polymer and Fiber Science: Recent Advances' (Eds. R. E. Fornes and R. D. Gilbert), VCH Publishers, New York, 1992, p. 233