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N-(2-biphenylenyl)-4-[2′-phenylethynyl]phthalimide—new monomer synthesis, cure and thermal properties of resulting high temperature polymer

Alexis Georgiades[a], Ian Hamerton[a], John N. Hay[a,*], Steve J. Shaw[b]

[a]*Department of Chemistry, School of Physics & Chemistry, University of Surrey, Guildford, Surrey GU2 7XH, UK*
[b]*Structures and Materials Centre, QinetiQ, Farnborough, Hampshire GU14 0LX, UK*

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Abstract

A synthetic route is described to a new monomer, *N*-(2-biphenylenyl)-4-[2′-phenylethynyl]phthalimide (BPP), which contains both phenylethynyl and biphenylene reactive functional groups. The monomer can be made either from *N*-(2-biphenylene)acetamide or 2-aminobiphenylene, by reaction with the phenylethynyl-containing anhydride. The monomer was characterised fully and the thermal cure of the material was studied by infrared (IR) spectroscopy and differential scanning calorimetry (DSC). The IR spectra showed that the phenylethynyl group reacted completely within 1 h at 370 °C. DSC showed the polymerisation exotherm of BPP centred at 379 °C, lower than two NASA-developed phenylethynyl-terminated imide (PETI) resins. In comparison with the PETI systems, the T_g of cured BPP was ca. 100 °C higher, making it a candidate for possible high temperature applications.

Keywords: Phenylethynyl; Biphenylene; High temperature

1. Introduction

The development of high temperature polymers over the last 30 years has been driven by the needs of aerospace applications for lightweight materials with outstanding combinations of mechanical and thermal properties. The high stiffness/weight and strength/weight ratios of polymer composites based on high performance thermosetting resins has allowed them to replace metals in a range of aerospace applications. While most such commercial activity has focussed on epoxy composites, the limitation on in-service use temperature (maximum ca. 150 °C in humid environments) imposed by the epoxy resin has hindered the extension of this technology to more temperature critical parts of an aircraft structure, for example in engine components. The requirement for composite resins with significantly higher temperature performance than even the best epoxies has led to the development of higher temperature systems such as cyanate ester (CE) resins, bismaleimides (BMIs) and other thermosetting polyimides such as the PMR (polymerisation of monomeric reactants) resins and benzocyclobutene (BCB) imides. The use temperatures of CE resins and BMIs are considered to be limited ordinarily to 150–250 °C [1]. The dominant composite matrix for use at high temperature (up to 300 °C short-term exposure) has long been PMR-15, which is proven in service in, for example, the bypass duct in the F404 engine used in the F18 fighter aircraft. In order to produce PMR resins with improved high temperature capability relative to PMR-15 [1,2], it is possible to change either the nature of the polymer backbone [3–7] or the end-caps/crosslinks or both simultaneously, although the observed improvements in thermo-oxidative stability relative to PMR-15 are not always significant. This approach is the basis of some promising systems such as PMR-II, V-CAP and AFR-700B [1,2].

Acetylene-terminated polyimides have been available commercially for some time, e.g. Thermid 600 manufactured by National Starch & Chemical Corporation [1]. Such materials have a narrow processing window, which is circumvented in part by use of an isoimide variant. In the 1990s, the technical requirements of the (now abandoned) US high-speed civil transport (HSCT) [8] programme highlighted the advantages of phenylethynyl-terminated resins and composites. The requirement for HSCT was for a resin that would survive for 60,000 h at 177 °C (Mach 2.4). One reason for the original study of these resins was an attempt

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* Corresponding author. Tel.: +44-1483-689586; fax: +44-1483-686851.
E-mail address: j.hay@surrey.ac.uk (J.N. Hay).

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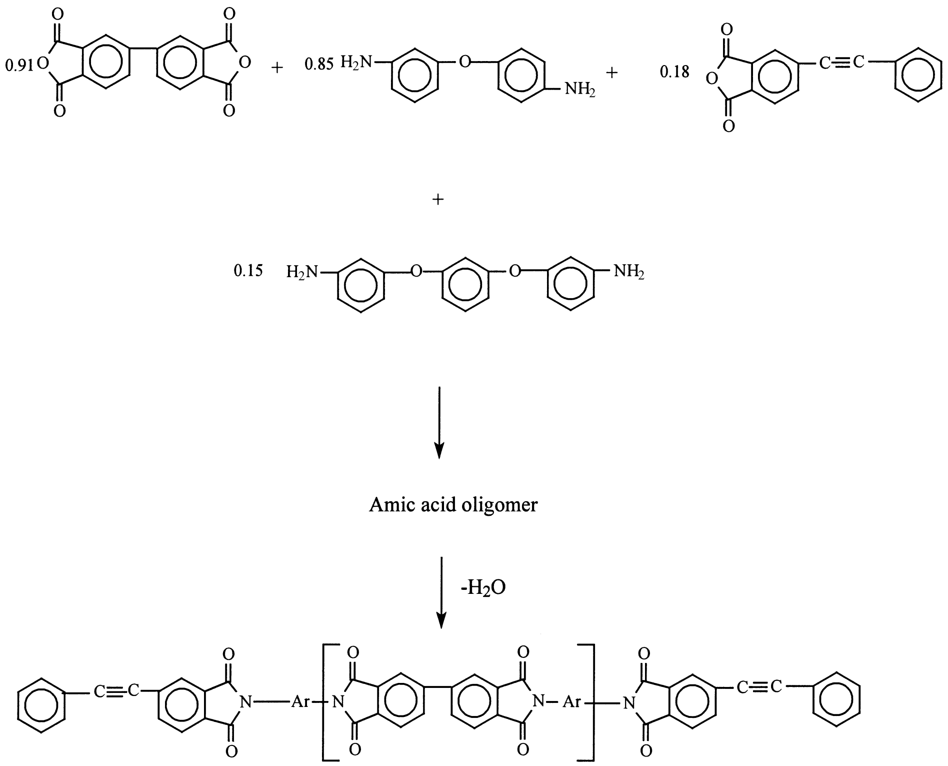


Fig. 1. Synthesis of PETI-5.

to overcome the narrow processing window of the acetylene-terminated systems. The resins have subsequently been studied extensively by workers at NASA, General Electric and elsewhere [9–15]. The chemistry of the phenylethynyl-terminated oligomer, PETI-5, is shown in Fig. 1. The end-cap can be introduced either via an amine-functional [9,10] or an anhydride-functional monomer [11,12].

The phenylethynyl groups cure without evolution of volatiles. The resins and their composites are characterised by excellent mechanical properties, in particular outstanding fracture toughness values (as high as 4.16 MPa $m^{1/2}$) [10], open hole compressive strength and compressive strength after impact (CAI). Although the glass transition temperature (T_g) values of the cured resins do not normally attain 300 °C, the resins exhibit moderate thermo-oxidative stability after 1500 h at 371 °C (weight losses of 13–23%) [14]. The anhydride-based end-caps resulted in cured resins with better thermo-oxidative stability than the amine-based end-caps. The thermo-oxidative stability of cured PETI at 371 °C has been found to be slightly less than the corresponding linear (thermoplastic) polyimide [13,14]. PETI/IM7 carbon fibre composites cured at 371 °C demonstrate the good processability of the resin system and confirm the excellent composite mechanical properties. Phenylethynyl groups have been co-reacted with BCBs via a Diels–Alder reaction [16]. Previously, thermally stable phenanthrene crosslinks have been shown to be formed by reaction of biphenylene groups with internal 1,2-diarylacetylene groups [17]. A related reaction between phenylethynyl groups and biphenylene groups might be expected to lead to a polymer with highly thermally stable phenanthrene linkages and no volatile evolution (Fig. 2). This is the rationale behind the synthesis of the novel monomer reported here. Synthesis and thermal cure of the monomer, *N*-(2-biphenylenyl)-4-[2′-phenylethynyl]phthalimide, is reported along with preliminary thermal properties of the resultant polymer.

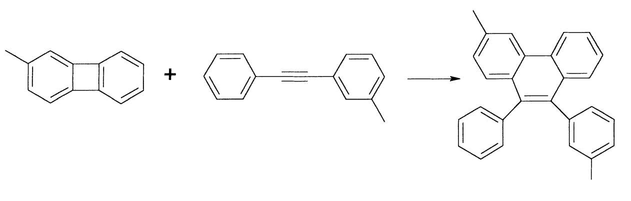


Fig. 2. Proposed reaction between phenylethynyl and biphenylene groups.

2. Experimental

2.1. Materials

Sodium azide, chloroacetic acid, phthalic anhydride (99%), anthranilic acid (all Lancaster), toluene, ammonium hydroxide, trichloroacetic acid, trifluoroacetic acid, phosphorus pentoxide (all Fisher Chemicals), hydrochloric acid, sodium hydroxide, sodium sulphate, petroleum ether (40–60), acetic acid (99.8%), magnesium sulphate, tetrahydrofuran (all BDH Laboratory Supplies), isoamyl

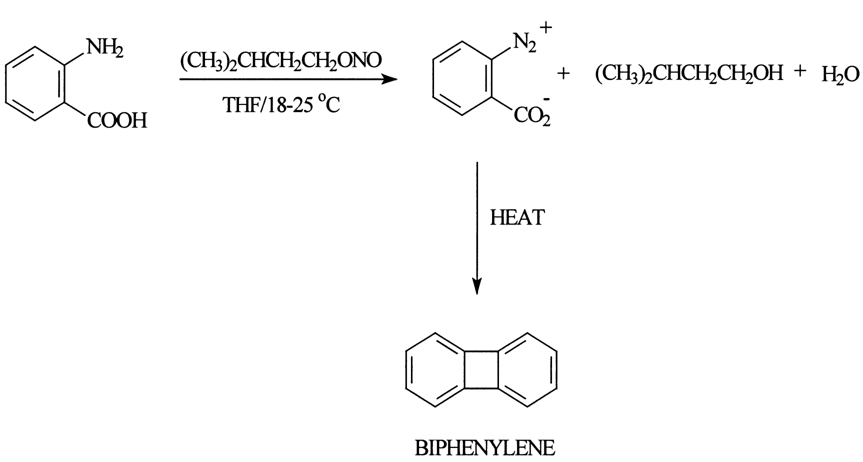


Fig. 3. Synthesis of biphenylene.

chloride, ethylene glycol, anhydrous diemethylacetamide (99.8%; DMAc) and *N*-methylpyrrolidone (99%; NMP) (Aldrich) were used as supplied. Diethyl ether (BDH) was dried overnight over sodium wire. When required, toluene was dried by distillation under nitrogen in the presence of sodium benzophenone ketyl. 4-Phenylethynylphthalic anhydride (4-PEPA) was provided by NASA Langley Research Centre, Virginia and used as supplied.

2.2. Techniques and instrumentation

Infrared (IR) spectroscopy was carried out using a Perkin Elmer System 2000 FT-IR Spectrometer, preparing the samples as KBr discs. Spectra were obtained at a resolution of 1 cm^{-1}. For cure studies, samples of BPP (15–20 mg) were placed under vacuum in small glass tubes for 5 min to remove all oxygen and the tubes then sealed with a Bunsen burner. The tubes were then placed in an oven at 370 °C for varying lengths of time. The IR spectra of the cured products were recorded as KBr discs. ^{1}H NMR spectroscopy was undertaken on a Bruker AC-300 spectrometer, operating at 300.13 MHz. Differential scanning calorimetry (DSC) measurements were made on samples of ca. 3–5 mg in sealed aluminium pans, using a TA Instruments MDSC 2920 calorimeter at a heating rate of 10 K min^{-1} under a nitrogen atmosphere with a flow rate of 40 cm^3 min^{-1}.

2.3. Synthesis of N-(2-biphenylenyl)-4-[2′-phenylethynyl]-phthalimide

Biphenylene was synthesised by the reaction of anthranilic acid (34.2 g; 0.25 mol) with isoamyl nitrite (55 cm^3, 48 g; 0.41 mol) in THF (250 cm^3) in the presence of trichloroacetic acid (0.3 g) [18] (Fig. 3). The resultant benzenediazonium-2-carboxylate was decomposed by *careful* addition to boiling, stirred 1,2-dichloroethane. *Note that the dry diazonium salt can detonate violently on impact, scraping or heating*. Work up gave biphenylene as white crystals, mp 105–109 °C (lit. [18] 109–112 °C). Over six preparations, the yield of biphenylene varied from 4.01 to 4.92 g (12–14%). ^{1}H NMR spectroscopy confirmed the structure of the biphenylene.

2-Acetylbiphenylene was synthesised by acetylation of biphenylene (6.3 g; 41 mmol) using acetic anhydride (4.6 cm^3; 5.0 g; 49 mmol) and aluminium(III) chloride (12.7 g) in dichloromethane (97 cm^3 total) [19] (Fig. 4). Recrystallisation of the crude product from aqueous ethanol yielded 2-acetylbiphenylene as bright yellow crystals, mp 131–135 °C (lit. [19] 134–136 °C). A typical yield was 4.09 g (64%). The structure of the product was confirmed by IR and ^{1}H NMR spectroscopies.

Attempts were made to synthesise 2-aminobiphenylene by the Schmidt rearrangement of 2-acetylbiphenylene [20] (Fig. 5). Using the reported method with trichloroacetic acid as solvent and catalyst, the yield of the amine was negligible. The intermediate *N*-(2-biphenylene)acetamide was formed by reacting 2-acetylbiphenylene with sodium azide in trifluoroacetic acid. For safety reasons, toluene was used in place of benzene during the extraction. To a solution of 2-acetylbiphenylene (4.0 g; 21 mmol) in trifluoroacetic acid (72 g) at 70 °C, sodium azide (2.0 g; 31 mmol) was added in one portion. Nitrogen evolution began at once. After 1 h, the nitrogen evolution had ceased and another portion of sodium azide (2.0 g) was added. The solution

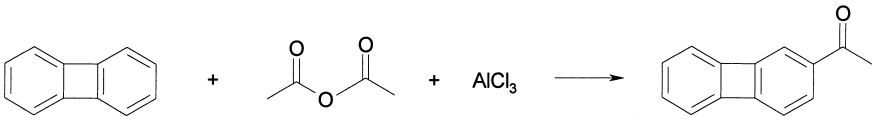


Fig. 4. Synthesis of 2-acetylbiphenylene.

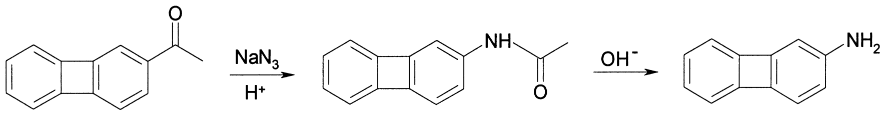


Fig. 5. Synthesis of 2-aminobiphenylene.

was maintained at 70 °C under static nitrogen atmosphere for 6 h, after which it was poured into ice (100 g) and extracted with toluene ($2 \times 200\ cm^3$). The toluene layer was washed with 10% aqueous hydrochloric acid ($100\ cm^3$), 10% aqueous sodium hydroxide ($2 \times 100\ cm^3$) and water ($200\ cm^3$) and dried over sodium sulphate. Removal of toluene and washing of the residue with petroleum ether (40–60) ($200\ cm^3$), afforded the crude *N*-(2-biphenylene)acetamide (2.5 g; 62% yield). The crude *N*-(2-biphenylene)acetamide was purified by recrystallisation from water to give a yellow solid (mp 118–120 °C).

^{1}H NMR ($CDCl_3$), δ: 2.1 (methyl H), 6.5–7.0 (7 aromatic H), 7.3 (N–H, disappears on shaking with D_2O).

IR ν_{max} (cm^{-1}): 3293–3072 (vs, N–H), 3071 (w, aromatic C–H), 1653 (vs, amide I), 1591 (s, amide II), 1550–1528 (s, aromatic C=C), 1490–1400 (s, CNH), 1377 (s/m, CH), 1042 (w, CH), 1015 (w, CH), 733 (vs, aromatic CH, out of plane bend). Calculated for $C_{14}H_{11}NO$: C, 80.3%, H 5.2%, N 6.69%. Found: C, 80.15%, H 4.98%, N 6.72%.

2-Aminobiphenylene was synthesised successfully from the crude *N*-(2-biphenylene)acetamide by the following route. A solution of the crude amide in ethanol ($200\ cm^3$) and conc. hydrochloric acid ($8\ cm^3$) was heated at the reflux temperature for 24 h. Ethanol was then removed under reduced pressure and the resulting solid was washed with dry ether. The solid was partially dissolved in hot water ($300\ cm^3$), filtered, and basified with ammonium hydroxide to give a cloudy, yellow solution. The product was removed from water by repeatedly extracting with ether. The solution was dried over magnesium sulphate. Removal of the solvent under reduced pressure and sublimation of the residue at 100 °C (0.05 mmHg) afforded 2-aminobiphenylene as bright yellow crystals having mp 118–120 °C (lit. [20]: 124–125 °C). The yield of 2-aminobiphenylene varied from 55 to 57% in repeat experiments.

δ($CDCl_3$): 3.5–3.7 (2H, NH_2, disappears when shaken with D_2O), 5.9–7.0 (7H; aromatic protons).

IR ν_{max} (cm^{-1}): 3400 (m, N–H asymmetric stretch), 3300 (m, N–H symmetric stretch), 1620 (m, N–H bending), 1263 (m/s, aromatic C–N stretching), 870–804 (m/s, C–H out of plane bending from 1,2,3 trisubstituted ring), 734 (s, C–H out of plane bending from 1,2 disubstituted ring).

N-(2-biphenylenyl)-4-[2′-phenylethynyl]phthalimide (BPP) was synthesised by two routes: (a) directly from the intermediate acetamide, and (b) from 2-aminobiphenylene.

(a) The route is shown in Fig. 6. To a solution of *N*-(2-biphenylene)acetamide (0.5 g, 2.4 mmol) in acetic acid ($5\ cm^3$), 4-phenylethynylphthalic anhydride (4-PEPA) (0.6 g, 2.4 mmol) was added together with chloroacetic acid (0.5 g). The solution was then heated under reflux for 30 h. The reaction mixture was then allowed to cool to room temperature overnight. *N*-(2-biphenylenyl)-4-[2′-phenylethynyl]phthalimide separated out (product started precipitating out during refluxing) as yellow crystals (0.20 g, 40% yield). The mixture was filtered on a Buchner funnel and *N*-(2-biphenylenyl)-4-[2′-phenylethynyl]phthalimide (mp 278 °C) was washed with water ($200\ cm^3$) several times.

^{1}H NMR ($CDCl_3$) (Fig. 7), δ: 6.6–6.8 (7H, biphenylene protons), 7.3–8.2 (8H, phenylethynyl + phthalimide protons).

IR ν_{max} (cm^{-1}): 3054 (w, aromatic CH), 2190 (w, C≡C), 1780 (m, C=O), 1708 (vs, C=O), 1611–1520 (s, aromatic C=C), 1265–1210 (m, C–N–C).

Raman ν_{max} (cm^{-1}) (Fig. 8): 3000 (w, aromatic CH), 2217 (vs, C≡C), 1776 (m, C=O), 1596 (m/s, aromatic C=C).

Electron impact (EI) mass spectrum: *m*/*z* 397 (M^+), 309, 291, 273, 165, 150, 140, 135, 123, 121, 119, 108, 105.

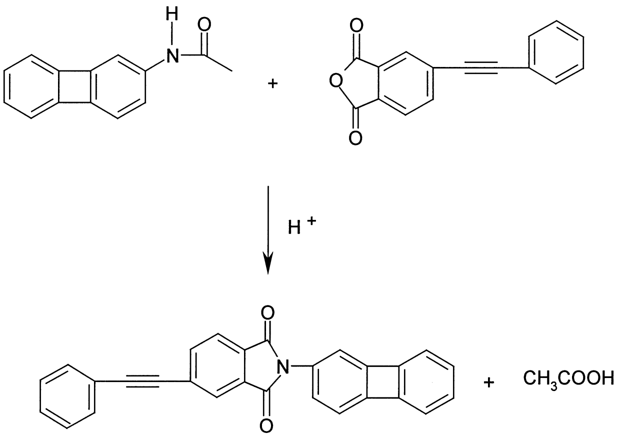


Fig. 6. Synthesis of BPP from the amide.

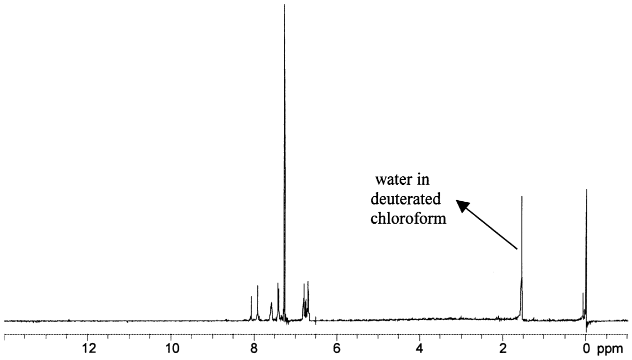


Fig. 7. ^{1}H NMR spectrum of BPP.

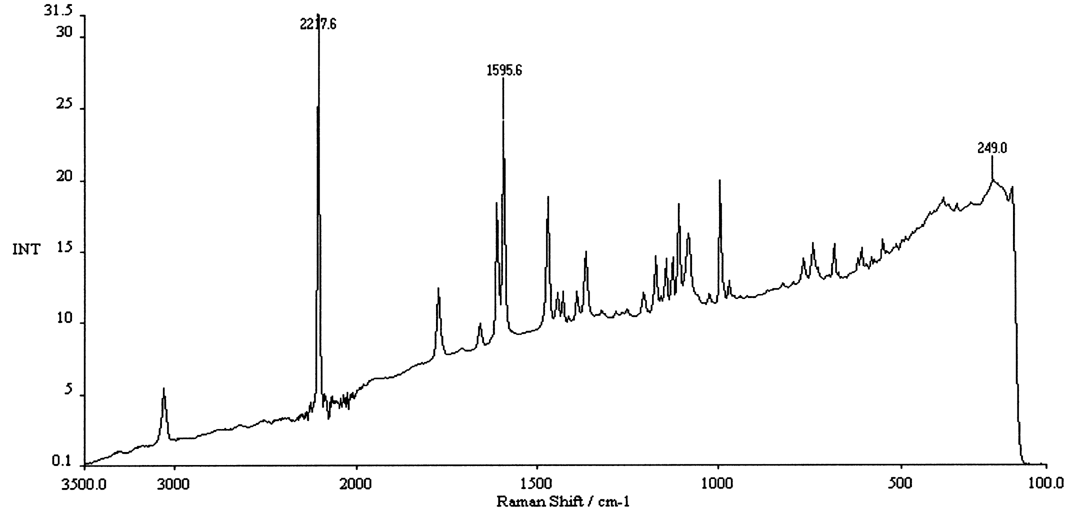


Fig. 8. Raman spectrum of BPP.

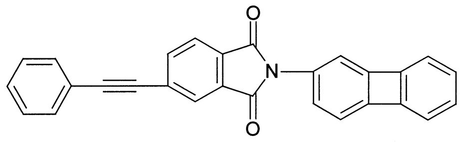
Calculated for $C_{28}H_{15}NO_2$: C, 84.6%, H 3.80%, N 3.52%. Found: C, 84.44%, H 3.36%, N 3.40%.

(b) BPP was also synthesised by reaction of 2-aminobiphenylene with 4-PEPA. 4-PEPA (2.17 g, 8.74 mmol) and 2-aminobiphenylene (1.46 g, 8.74 mmol) were added with DMAc (15 cm^3) and dry toluene (15 cm^3) to a one neck, round-bottom flask equipped with a magnetic stirrer, nitrogen inlet (bubbler), Dean and Stark trap and reflux condenser. The mixture was heated to 160 °C in a silicone oil bath, maintained at this temperature for 12 h and then allowed to cool to room temperature. The product precipitated out as a fine powder upon cooling. The product was then washed with excess anhydrous diethyl ether and allowed to dry (in air) for 6 h. The imide was then dried under vacuum at 120 °C for 24 h to afford yields greater than 90%, mp 278–280 °C (DSC). Calculated for $C_{28}H_{15}NO_2$: C 84.6%, H 3.80%, N 3.52%. Found: C 84.77%, H 3.33%, N 3.37%.

3. Results and discussion

The original observation that phenanthrene rings can be formed by the reaction of biphenylene groups with internal acetylene functionalities [17] suggests that such an approach could provide a route to formation of high temperature polymers with highly thermally stable aromatic crosslinks or chain extending units. To the best of our knowledge, this approach has not been extended to systems containing the phenylethynyl functional group (Fig. 2), as found in the NASA-developed PETI-5 resin. In the first of a series of studies aimed at developing new resin systems for ultra-high temperature composite applications, we describe here the synthesis and characterisation of a novel AB monomer containing both a biphenylene group and the phenylethynyl moiety. The thermally initiated polymerisation of this monomer is also investigated, along with the thermal properties of the resulting polymer system. Our ultimate aim is to develop composite resins with properties appropriate to continuous use at temperatures in excess of 350 °C. A continuous use temperature of 350–400 °C is believed to represent the maximum practicable for a wholly organic polymer system in oxidative environments. Beyond this temperature regime, inorganic or organic–inorganic hybrid system represent the only viable option, other than for short-term exposure.

The monomer selected for our initial study was *N*-(2-biphenylenyl)-4-[2′-phenylethynyl]phthalimide (**I**).



(I)

3.1. Monomer synthesis

The various stages in the synthesis of the BPP monomer are shown in Figs. 3–6. The first step involves synthesis of biphenylene (Fig. 3) by a reported route [18]. Anthranilic acid is converted to the internal diazonium salt, which is decomposed thermally, formally to the benzyne, which dimerises to form biphenylene. Caution must be exercised during this synthesis, because of the potential for explosive detonation of the diazonium salt, which should always be kept solvent-wet to help avoid this. This step represents the overall yield-limiting part of the process.

Although other possible routes exist to biphenylene, none is capable of producing the product in yields of more than a few percent. The anthranilic acid route was found to produce reasonably consistent yields of the biphenylene on repeat synthesis. Consistent with the literature, it was found that reducing the volume of 1,2-dichloroethane used resulted in reduction in yield.

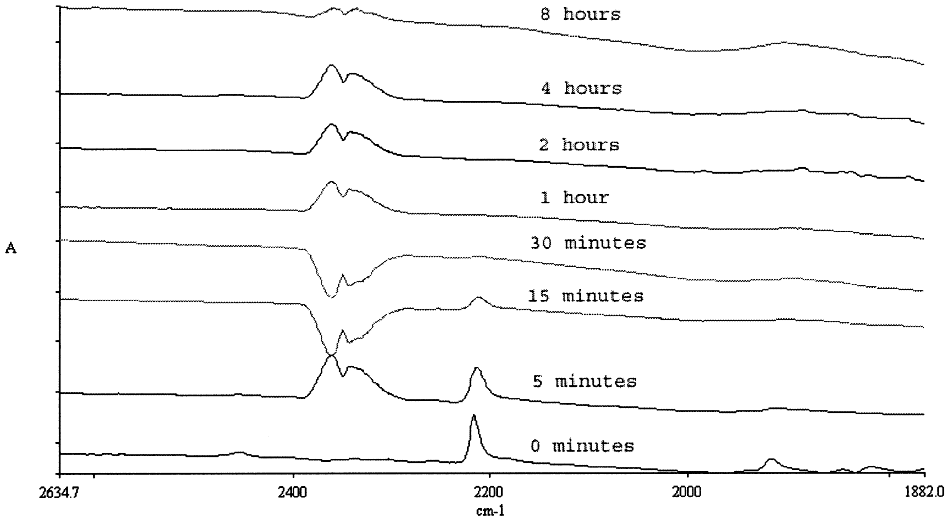


Fig. 9. IR spectra of BPP cured at 370 °C for different times, showing changes in the phenylethynyl absorption band.

The next stage involved Friedel–Crafts acylation of biphenylene to the 2-acetyl derivative (Fig. 4) which was obtained in a moderate yield. The product was purified by recrystallisation from aqueous ethanol [21], rather than by sublimation as reported in the literature [19]. All spectral data were consistent with the structure of the expected product, with a strong IR carbonyl absorption at 1667 cm^{-1}.

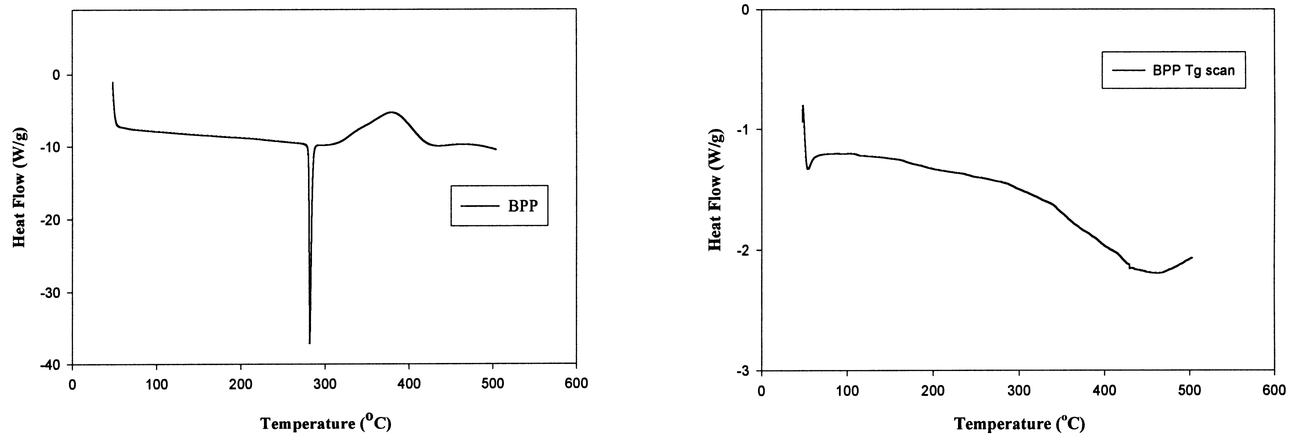
The original aim was to synthesise the monomer via 2-aminobiphenylene, itself prepared from the acetyl derivative via a Schmidt rearrangement using a literature method (Fig. 5) [20]. Although the only change to the literature method was replacement of benzene by toluene for the extraction of the acetamide, a negligible yield of the amine product was obtained, in contrast to a reported yield of 57%. As the amide hydrolysis step did not proceed in the same way as reported in the literature, it was suspected that this may have been the source of the problem, with the high sensitivity of the 2-aminobiphenylene to atmospheric oxidation being a further contributory factor [22]. For this reason, it was decided to synthesise the monomer directly from the acetamide, which was also synthesised in a purer form by using trifluoroacetic acid instead of trichloroacetic acid as solvent and catalyst. Use of the stronger acid resulted in formation of the acetamide as a fine, pale brown powder in contrast to the dark gummy product obtained when using trichloroacetic acid. A further advantage of the use of trifluoroacetic acid is that since it is a liquid (trichloroacetic acid is solid), the reactants can dissolve and react at room temperature. The acetamide product was purified by recrystallisation from water. It was subsequently found that 2-aminobiphenylene could be formed from this purer acetamide intermediate in yields comparable to those described in the literature [20]. It was thus possible to synthesise the BPP monomer in one of two ways, either from the acetamide or by conventional amine–anhydride reaction.

The BPP monomer was synthesised from *N*-(2-biphenylene)acetamide by reaction with 4-phenylethynylphthalic anhydride (4-PEPA) in acetic acid (Fig. 6), using a procedure similar to that used to synthesise *N*-substituted phthalimides from amines [23]. With acetic acid alone, however, the synthesis was unsuccessful and so a stronger acid, chloroacetic, was added to catalyse the reaction. In this way, a reasonable yield of the monomer BPP was obtained. Spectral data confirmed that reaction of the acetamide had occurred with the absence of the methyl resonance in the ^{1}H NMR spectrum (Fig. 7) and loss of the very strong amide IR band at 1653 cm^{-1}, to be replaced by the characteristic imide absorptions at 1708 and 1780 cm^{-1}. There are also obvious imide C–N–C stretching vibrations visible at 1210–1265 cm^{-1}. IR spectroscopy shows only a weak signal due to the triple bond. Although the Raman spectrum (Fig. 8) is less clear than the IR spectrum in many respects, because of fluorescence, it clearly shows a very strong signal at 2217 cm^{-1} due to the triple bond and is a sensitive method for detecting the presence of such a bond. The EI mass spectrum confirmed the presence of the expected product, showing a fairly strong parent ion at *m*/*z* 397. As shown later, DSC also shows a single sharp melting endotherm for the monomer, indicative of the purity of the compound.

BPP was also synthesised from 2-aminobiphenylene by a standard amine–anhydride reaction with 4-PEPA. The product obtained by this route was identical in every respect to that synthesised from the acetamide. Either product could thus be used in subsequent cure studies.

3.2. Monomer cure

This monomer contains two polymerisable functional groups, both of which are capable of ‘homopolymerisation’ as well as co-reaction with each other. The phenylethynyl



BPP (DSC scan)

BPP (T_g scan)

Fig. 10. DSC thermograms for BPP.

group polymerisation has been studied extensively, although there is still debate about the precise course of the reaction [11,24]. The normally accepted cure mechanism involves a complex combination of chain extensions, branching and crosslinking via a free radical process, leading to linear and crosslinked polyene structures [11,25,26]. Biphenylene-terminated imide oligomers undergo relatively inefficient thermal cure above 350 °C leading to cyclodimerisation and formation of a stable tetrabenzocyclooctatetraene structure [27]. Of particular interest is the possibility of co-reaction leading to formation of phenanthrene linkages [17]. Friedman and Rabideaux also demonstrated that reaction of biphenylene with a five-fold excess of diphenylacetylene at 350–375 °C under nitrogen led to formation of 9,10-diphenylphenanthrene in 50% yield [28]. If this were the only reaction occurring with BPP, then polymerisation would theoretically lead to a linear polymer, which would be expected to have high stability. The occurrence of other processes, such as phenylethynyl homopolymerisation, or a different type of reaction between the two groups might result in some degree of crosslinking taking place.

IR spectroscopy was used to monitor the cure of BPP at 370 °C over a range of curing times. The BPP was cured in vacuo in sealed glass tubes. Oxygen was excluded intentionally, since it has been noted that oxygen promotes homopolymerisation of the phenylethynyl group (10) and this reaction represents a competitive process to the desired co-polymerisation of the phenylethynyl and biphenylene groups. The progression of the cure was monitored by following the disappearance of the phenylethynyl absorption band at ca. 2210 cm^{-1} (Fig. 9). However, it should be noted that this provides no information on curing processes occurring subsequent to initial reaction of the triple bond. Nonetheless, the spectra show clearly that the triple bonds are consumed totally within 1 h at 370 °C, consistent with the work of others on PETI-5 [26,29,30]. The absorptions around 2350 cm^{-1} are due to carbon dioxide, hence their odd appearance. Little obvious change was apparent in the aromatic regions of the spectrum. Some changes might be expected if phenanthrene rings are formed, but as there is no increase in the number of aromatic protons as a result of this reaction, changes in the aromatic C–H bands might be insignificant.

An initial DSC scan of the BPP monomer shows no change in the monomer until a sharp melting endotherm is observed at 280 °C. This confirms the absence of lower melting temperature impurities such as starting materials (melting points for the acetamide and the PEPA are ca. 120 and 153 °C, respectively). Melting is followed at around 350 °C by the onset of an exothermic process, presumably arising from polymerisation, which is still continuing at 400 °C. A rescan shows a weak T_g at about 303 °C, but reaction is presumably incomplete under these conditions. A more detailed study of the cure was carried out, using PETI-5 and PETI-2.5 (oligomer molar masses of 5000 and 2500, respectively) for comparison with the BPP. Fig. 10 shows the DSC thermograms up to 500 °C for BPP, as a first scan and a subsequent T_g scan. The first and second (T_g) scans for PETI-2.5 and PETI-5 are shown in Fig. 11. The data represented in these scans are summarised in Table 1. The scans for the PETI systems are more complex than those for BPP, as would be expected from the oligomeric structures of the PETI molecules.

As expected for the semi-crystalline PETIs, two transitions are observed prior to polymerisation, the lower of which (ca. 220–230 °C) may represent the oligomer T_g, while the higher of the two is the melting temperature (T_m) denoted by an endotherm (at 347–357 °C). As a discrete small molecule, BPP shows no T_g, but only the melting endotherm at 280 °C. As expected, the T_g and T_m values are higher for PETI-5 than for the lower molar mass PETI-2.5, although the differences are relatively small. All three compounds show an exothermic peak between 330

Table 1
Summary of DSC data for PETI oligomers and BPP

Compound name	Initial		Range of exothermic peak (°C)	Exothermic peak maximum (°C)	Cured T_g (°C)
	T_g (°C)	T_m (°C)			
PETI-2.5	220	347	360–430	403	277
PETI-5	230	357	380–470	431	274
BPP		280	330–430	379	372

and 470 °C, resulting from polymerisation of the reactive functional groups. The reaction enthalpies were measured as 513, 94 and 35 J g^{-1} for BPP, PETI-2.5 and PETI-5, respectively. The higher enthalpy of reaction (in J g^{-1}) for PETI-2.5 compared to PETI-5 is expected because of the higher concentration of phenylethynyl groups in the former oligomer. BPP has the highest reaction enthalpy of all because of its high concentration of reactive groups compared to the oligomeric PETI compounds. The peak exotherm occurs at 403, 431 and 379 °C, respectively for PETI-2.5, PETI-5 and BPP. The temperature of the peak exotherm increases as the molar mass of the precursor increases and this is related to the melting temperature and differences in chain mobility. In the case of BPP, a variety of cure combinations is possible, including phenylethynyl–phenylethynyl, phenylethynyl–biphenylene, biphenylene–biphenylene, polyene–biphenylene and phenylethynyl–polyene, and this will also influence the polymerisation temperature range.

The rescan data show the T_g values for the polymers following curing in the DSC machine up to 500 °C. Cured PETI-5 and -2.5 show T_gs at 274 and 277 °C, respectively, consistent with a higher crosslink density for the cured PETI-2.5 [31]. The T_g of the cured BPP was not as distinct as those of the PETIs and occurred over a broad range, from about 330–430 °C. This could be explained by the presence within the cured BPP of a range of structures, with different T_g values arising from the different structural units. Nonetheless, the average T_g value of 372 °C for cured BPP is approximately 100 °C above those measured for the cured PETI polymers, indicative of a much more highly crosslinked or rigid structure. A cured resin T_g of this magnitude makes BPP a possible candidate for high temperature applications and thus a much more in depth study of BPP cure and thermal characterisation of the resulting polymer will be reported separately.

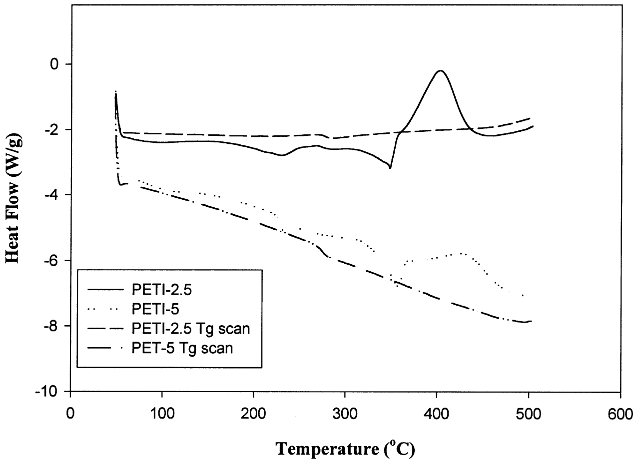


Fig. 11. DSC thermograms for PETI-2.5 and PETI-5 (first and second scans).

4. Conclusions

A new monomer (BPP) containing both phenylethynyl and biphenylene groups has been synthesised. Thermal cure of the monomer leads to formation of a polymer by reaction of both polymerisable groups, potentially involving a number of different reactions. The triple bond is consumed entirely within 1 h at 370 °C. In comparison with the PETI resins, the cured BPP has a T_g value about 100 °C higher. This material is therefore a possible candidate for use in high temperature aerospace applications.

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