N,N'-bis(4-ethynyl phenyl) 1,4,5,8-naphthalimide: a new monomer for a high T_g, heat-resistant polymer

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A new 4-ethynyl-substituted monomer, bis(4-ethynyl phenyl) 1,4,5,8-naphthalimide (EPNI) was synthesized and characterized. EPNI is a crystalline material which, when thermally polymerized under N_2 in the solid state, yielded a highly crosslinked resin. The progress of polymerization was followed by Fourier transform i.r. spectroscopy, differential scanning calorimetry and wide-angle X-ray diffraction. It was found that EPNI reacted completely thermally to yield an extended polyene structure. Polymer plates were made by solid-state polymerization of EPNI under 4.8 MPa for 1.5 h at 300°C. Because EPNI is ordered and polymerized in the crystalline state, it showed zero polymerization shrinkage (EPNI had the same density as the well consolidated polymer, $1.40\,\mathrm{g\,ml^{-1}}$). EPNI polymerized to high conversion in spite of its very rigid matrix, probably because of the localization of its polymerizable ethynyl groups. A plate of polymeric EPNI (PEPNI) with 10% voids had a storage modulus of 2.2 GPa at room temperature, a glass transition temperature, T_g, of 309°C and a linear coefficient of thermal expansion of $4.28 \times 10^{-5}\,\mathrm{K^{-1}}$. PEPNI has excellent thermal and thermooxidative stabilities since it retained over 83% of its initial weight after 105 h at 427°C in air.

(Keywords: thermal polymerization; heat resistance; polyimide)

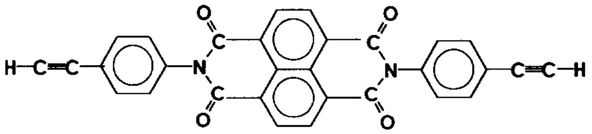
INTRODUCTION

Polyimides have been developed for applications such as coating, adhesives and thermosetting laminates where stability at temperatures up to 400°C is required. They have also been used in the microelectronics industry as interlayer dielectrics, passivation layers and structural resins. A variety of crosslinking sites have been used to improve the properties of readily processible thermally stable polymers. Acetylene as an end group is currently being used in some commercially available imide prepolymers[1]. Acetylene-terminated benzimide oligomers[2,3] were first reported in 1974. Harris *et al.*[4] synthesized ethynyl-terminated oligoimides. Some were crystalline and polymerized in the solid state. Our recent research in the area of ethynyl-terminated monomers[5–10] has also included an imide, bis(4-ethynyl phenyl) pyromellitimide[11].

The objective of this research was to develop a new ethynyl-terminated monomer, bis(4-ethynyl phenyl) 1,4,5,8-naphthalimide (EPNI) which could be thermally polymerized. It has been reported that imide oligomers end-capped with 4-ethynyl aniline failed to cure properly, presumably because of decreased molecular mobility arising from the rigidity of 4-ethynyl aniline *versus* the 3-isomer[12]. (Also, thermal cyclodehydration of the amic acids produced water which hydrated the 4-ethynyl groups[13].) We proposed that EPNI should polymerize to high conversion in spite of its rigid matrix because the molecules pack in lamelli, which brings the polymerizable ethynyl groups close to each other. Because the monomer is crystalline, it should not shrink much during the polymerization reaction and cooling. Interfacial stresses with the reinforcing fibre should thus be very low. It should be noted that 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) has been used for the synthesis of polyimides[14–16] and polyimidoaroylenebenzimidazole copolymers[17]. No processing data are reported, owing to insolubility problems. Despite the reported problems, we decided to develop a new 4-ethynyl-terminated polyimide based on NTDA because (1) the condensed naphthalene ring should have very high thermal and thermooxidative stability, and (2) the formerly serious disadvantage (very poor solubility and high melting points of naphthalimides) is less important since we have been able to process insoluble rigid-rod monomers in the solid state[7].

RESULTS AND DISCUSSION

The chemical structure of EPNI is shown below:



Monomer preparation and characterization

EPNI was synthesized by a two-step reaction: NTDA (1 mol) was reacted with 4-ethynyl aniline (2 mol) in

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N-methylpyrrolidinone (NMP). Chemical cyclodehydration was carried out with acetic anhydride and pyridine. Thermal cyclodehydration could not be used; it was reported that the 4-ethynyl group is hydrolysed to an acetyl group by the water evolved during thermal imidization of the amic acid[13].

The chemical structure of EPNI was confirmed by Fourier transform i.r. spectroscopy (*FT*i.r.), and by ^1H and ^{13}C nuclear magnetic resonance (n.m.r.). The i.r. spectrum of EPNI (*Figure 1a*) exhibited a sharp absorption band at 3261 cm^{-1} due to the ethynyl group (C(sp)–H stretch). The absence of a broad absorption band around 3400–3300 cm^{-1} (attributable to hydroxyl groups of the corresponding diamic acid) demonstrated that EPNI is completely imidized. The ^1H n.m.r. and ^{13}C n.m.r. spectra of EPNI could not be recorded because of its very low solubility in polar aprotic solvents. The ^1H n.m.r. and ^{13}C n.m.r. spectra (*Figure 2*) of its diamic acid (DMSO-d_6, 60°C) agree with the proposed structure (see Experimental section).

Study of monomer polymerization

EPNI was thermally polymerized in a pellet form between glass plates in a hot stage by heating (15°C min^{-1}) to 295°C and holding at 295°C for 1.3 h. The curing behaviour of EPNI was examined by differential scanning calorimetry (d.s.c.) (15°C min^{-1} in N_2) (*Figure 3a*). The d.s.c. thermogram showed a major polymerization exotherm between 138 and 307°C centred at 258°C, and a minor exotherm centred at 345°C. The total enthalpy of polymerization was 129 kJ mol^{-1} (276 J g^{-1}). The glass transition temperature, T_g, of polymeric EPNI (PEPNI) could not be detected by d.s.c. This is attributed to the fact that resin was highly crosslinked and the change in heat capacity was very small.

EPNI polymerization was followed by *FT*i.r., d.s.c. and wide-angle X-ray diffraction (WAXD). *Figures 1* and *4* show the i.r. spectra of EPNI (*Figure 1a*), after heating for 40 min at 270°C (*Figure 1b*) and after heating for 1.3 h at 295°C (*Figure 1c*). The d.s.c. thermograms and WAXD spectra of the same samples are shown in *Figures 3* and *5*, respectively. The absorption band at 3261 cm^{-1}, due to the C(sp)–H stretch vibrations of the acetylenic groups in *Figure 1a*, appears with lower intensity in *Figure 1b* (it corresponds to 83% polymerization based on *Figure 3b*) and has completely disappeared in *Figure 1c* (completely polymerized resin based on *Figure 3c*). An absorption band at 3041 cm^{-1}, which appears in *Figures 1b* and *c* (olefinic C–H stretch), is absent in *Figure 1a.* This was attributed to the thermal polymerization of the acetylenic groups to yield a polyene system. The band at 3080 cm^{-1} in *Figure 1* is associated with the aromatic C–H stretch mode of EPNI; the increase in absorption

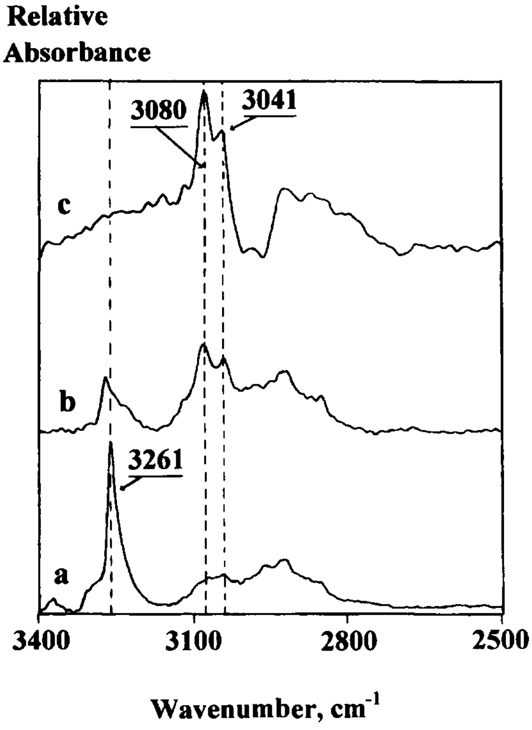

Figure 1 I.r. spectra of EPNI (a), after heating for 40 min at 270°C (b) and after heating for 1.3 h at 295°C (c)

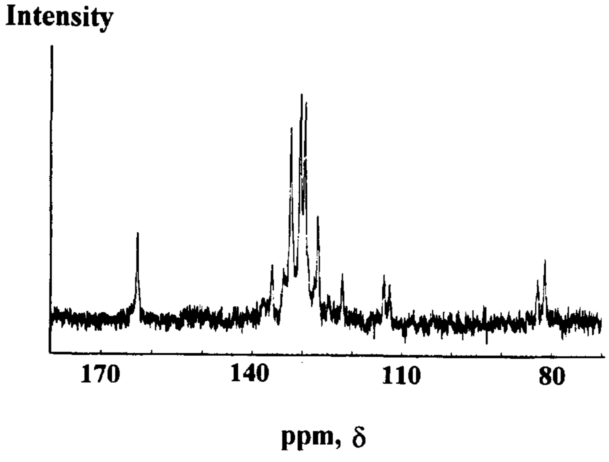

Figure 2 ^{13}C n.m.r. spectrum of EPNI

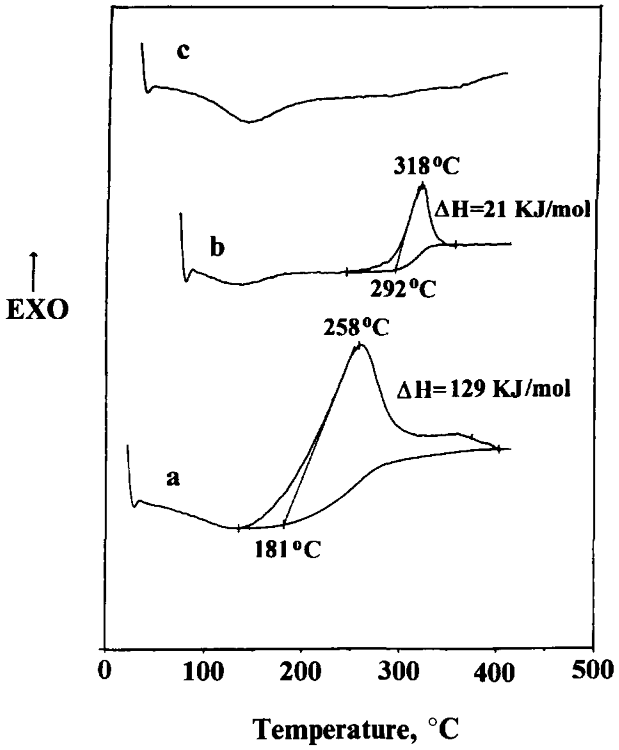

Figure 3 D.s.c. thermograms of EPNI (a), after heating for 40 min at 270°C (b), and after heating for 1.3 h at 295°C (c). The d.s.c. thermograms were recorded in N_2 (15°C min^{-1} heating rate)

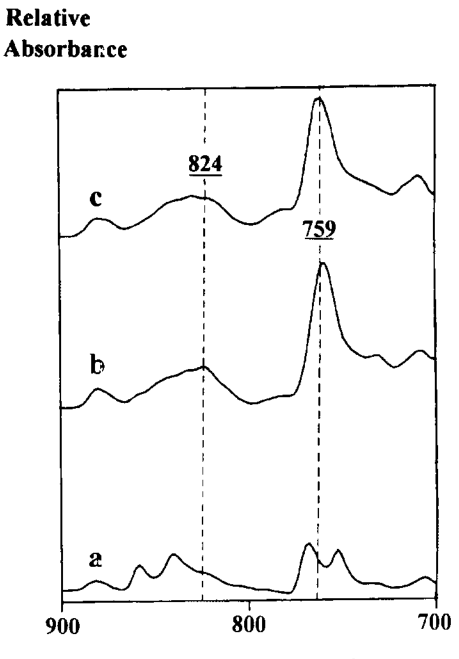

Figure 4 I.r. spectra of EPNI (a), after heating for 40 min at 270°C (b), and heating for 1.3 h at 295°C (c). Spectra were normalized to the 1647 cm^{-1} absorption band, which remains unchanged during polymerization

could indicate that some aromatic structures have formed. However, polyene systems can also absorb at this wavelength.

The question of the polymerization mechanism can be answered better by looking at the 700–900 cm^{-1} region of the i.r. spectra in *Figure 4*. Two new bands appear at 759 and 824 cm^{-1} (*Figures 4b* and *c*). The band at 759 cm^{-1} is due to coalescence of the two bands at 752 and 767 cm^{-1} (*Figure 4a*). (These arise from crystal field splitting of the vibration mode[18] at 759 cm^{-1}.) The band at 824 cm^{-1} was seen in the polymerization of other ethynyl benzene monomers[10,11], and was identified as arising from a trisubstituted ethylene C–H bend mode. The generation of 1,3,5-triphenyl-substituted benzenes (by cyclotrimerization in this case) was studied by Nguyen *et al.*[19]. They identified a specific band at 800 cm^{-1} attributed to the C–H bend mode of these materials. *Figure 4* shows no absorption band at 800 cm^{-1} at any stage from the monomer to post-cured polymer. Therefore, the main polymerization route cannot be cyclotrimerization to aromatic rings, but must be polyene formation.

The WAXD spectra of an EPNI disc before polymerization, and polymerized EPNI discs, were recorded. EPNI is a highly crystalline material (*Figure 5a*) that polymerized in the solid state (*Figure 3a*) to 83% conversion (based on $\Delta H_{\text{polym.}}$ of *Figure 3b*). The sample plate (*Figure 5b*) exhibits the same peaks as the EPNI monomer plate (*Figure 5a*) but with a lower intensity, except for the peak at 27.6°, which remains unchanged (*Figure 5b*). The intensity of this peak does not reduce much even at 100% conversion (*Figure 5c*); at 100% conversion (based on *FT*i.r. and d.s.c., *Figures 1c* and *3c*) the WAXD scan of the polymer plate (*Figure 5c*) shows mainly amorphous scattering with sharp small peaks at 11.85, 22.40, 23.70 and 27.60°. The fact that these peaks are sharp indicates that there are regions in the amorphous polymer matrix that remain crystalline. These sharp peaks appear in the same position as in the WAXD spectrum of the monomer (*Figure 5a*). Because the corresponding *FT*i.r. and d.s.c. graphs (*Figures 1c* and *3c*) show complete polymerization, the crystalline phase cannot be residual monomer. It should not be the isoimide form because the reaction dehydration temperature was high enough to convert all the product to imide[20]. It is possibly a residual impurity.

Density

The densities of EPNI and PEPNI (well consolidated plate) were found to be the same (1.40 g ml^{-1}). Since EPNI was polymerized in the solid state this demonstrates that EPNI exhibits zero polymerization shrinkage. This is unusual, since the well known epoxy–aromatic amine systems[21] have shrinkages of 9–10% and the acrylate networks[22,23] between 11 and 15%. Zero polymerization shrinkage suggests that this monomer may be a candidate for high temperature composites, as the interfacial stresses between matrix and reinforcement will be minimized. Some *p*-ethynyl benzoyl esters[5] and the bis(*p*-ethynyl phenyl)pyromellitimide[11], which were synthesized and studied in our laboratory, similarly had zero polymerization shrinkage.

Polymer plate fabrication and thermomechanical properties

EPNI polymer plates were made by a solid-state processing technique[7] developed in our laboratory. EPNI powder was compression moulded under 69 MPa pressure for 5 min at 90–100°C, heated at 295–300°C for 1.5 h under 4.8 MPa and cooled to room temperature (r.t.) gradually. These plates were not uniform: some areas were dark brown with a reflective surface and others (larger portion) were tan and dull. Scanning electron microscopy (SEM) photographs of fracture surfaces were taken to gain insight into the morphology of these plates (fracture surface); they are shown in *Figure 6*. These SEM

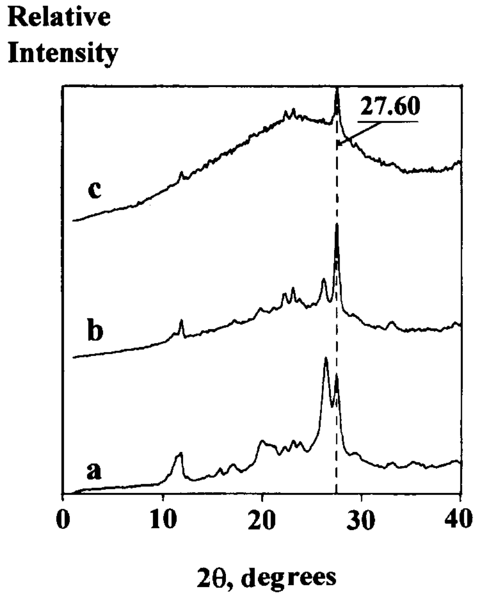

Figure 5 WAXD spectra of a plate (1.2 mm thick) of EPNI before polymerization (a), after heating for 40 min at 270°C (b), and after heating for 1.3 h at 295°C (c)

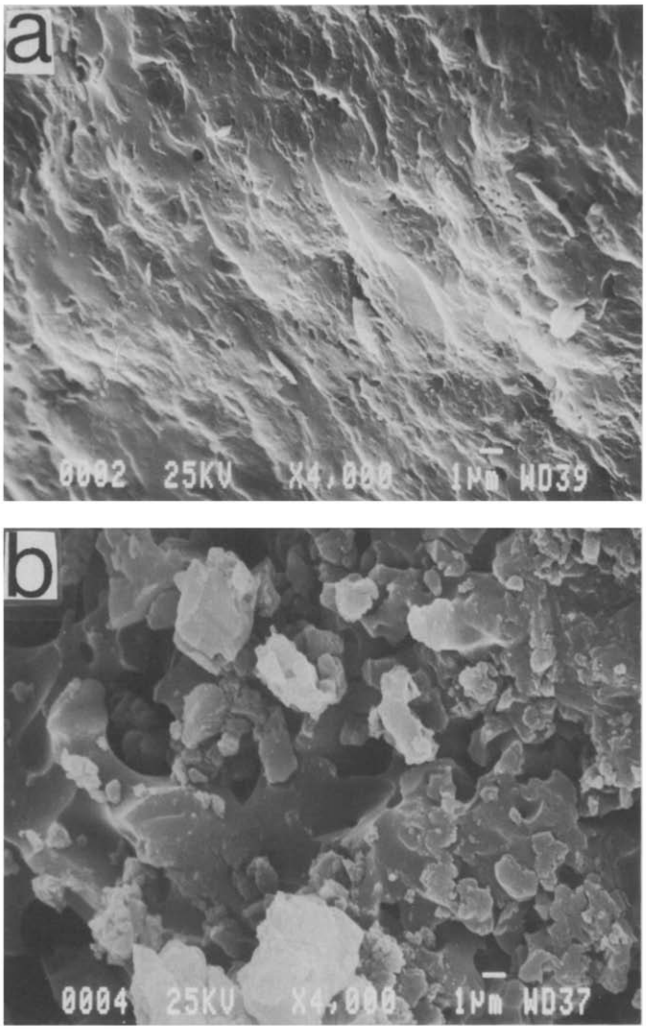

Figure 6 SEM photographs (fracture surface) of a well consolidated PEPNI (a) and of a poorly consolidated PEPNI (b)

photographs were taken from different areas of the same specimen. *Figures 6a* and *b* show SEM photographs of well consolidated PEPNI (dark brown, reflective surface) and poorly consolidated PEPNI (light tan, dull surface), respectively. There are almost no voids (or the voids occupy less than 1% of the volume in the fracture surface) in *Figure 6a*. It can also be seen that this polymer retains a certain amount of order. However, many large voids exist in the fracture surface of poorly consolidated PEPNI (*Figure 6b*). The surface of this part of PEPNI is tan and dull because the voids scatter light. The densities of PEPNI plates that were dark brown and reflective and others with tan, dull surfaces were measured in order to determine the void percentage. The density for PEPNI with tan, dull surface was found to be 1.26 g cm^{-3} while well consolidated PEPNI had a density of 1.40 g cm^{-3}. This datum indicates that there is about 10% void volume in the measured PEPNI specimen.

Dynamic mechanical analysis (d.m.a.) (5°C min^{-1}, 1 Hz frequency in N_2) was used for the evaluation of the thermomechanical properties of PEPNI. Its r.t. storage modulus, E', was found to be 2.2 GPa. This low value was attributed to the existing voids. It is known that these voids are stress concentrators and are responsible for the inferior mechanical and thermomechanical properties of polymers. E' of void-free PEPNI is expected to be 4–5 GPa at r.t. When *p*-ethynyl benzoyl esters were initially processed in our laboratory, plates with 6–10% voids had E' values between 2.3 and 2.8 GPa at r.t. After processing conditions were improved and void-free plates were obtained, the E' values increased to 4.5–4.8 GPa at r.t.[7].

Thermomechanical analysis (t.m.a.) (5°C min^{-1} in static air) showed that PEPNI has a linear coefficient of thermal expansion of 4.28×10^{-5} K^{-1}, which is one half that of most crosslinked systems. The T_gs of both unpost-cured and post-cured PEPNI samples were between 304 and 309°C. The t.m.a. thermogram of the unpost-cured sample showed a 1% expansion between 304 and 322°C, followed by a decrease in the 322–340°C range. This was attributed to the evolution of trapped solvent at the T_g since the t.m.a. thermograms of post-cured samples did not show this feature. This was also confirmed from the t.g.a. data (see below) which showed some weight loss after 310°C.

Thermal properties

PEPNI was polymerized as a pellet at 270°C for 1 h and at 295°C for further 1.3 h in the absence of air. Dynamic thermogravimetric analysis (t.g.a.) (15°C min^{-1}) showed that PEPNI lost about 28% of its initial weight by 500°C and pyrolysed completely after 620°C in air. The t.g.a. thermogram is bimodal and shows a gradual weight loss between 310 and 520°C, followed by a dramatic weight loss around 550°C. The gradual weight loss between 310 and 470°C was attributed to evolution of trapped NMP. By post-curing at 320–330°C in the absence of air the initial decomposition temperature is expected to shift to about 500°C. PEPNI started losing weight at about 310°C in N_2; the temperature of its maximum decomposition rate was found to be 602°C. The anaerobic char yield at 800°C was 53%.

Since this polymer could be used as a structural polymer or matrix composite in air, the long-term thermooxidative stability for PEPNI (polymer discs) was estimated using isothermal ageing. PEPNI retained up to 83% of its initial weight after 105 h at 427°C in air. This indicates that this crosslinked polyimide has outstanding thermooxidative stability and can be used as a load-bearing material at temperatures over 316°C in air.

EXPERIMENTAL

Materials

NTDA was received from Aldrich and used without further purification. 4-Ethynyl aniline was synthesized in our laboratory in high yield and purity by a new, economical route[9]. NMP (Aldrich) was distilled over phosphorus pentoxide at reduced pressure. Acetic anhydride and pyridine (Fisher) were used without further purification.

Analytical methods

Proton (^{1}H) and carbon (^{13}C) n.m.r. spectra were taken on XL-200, 200 MHz FT-NMR. Chemical shifts (δ) are given in parts per million, with tetramethylsilane as internal standard. *FT*i.r. spectra of powdered materials in KBr pellets were recorded on a Bio-Rad Digilab FTS-60 spectrometer. Monomer and polymer densities were measured using a density gradient column containing chloroform-hexanes solution. Pellets (1 mm thick) were made from the monomer by compression moulding. For the corresponding polymer, plates of similar thickness polymerized in the solid state under moderate pressure were used for density measurements. X-ray scans were recorded using a Phillips APD 3520 automatic diffractometer using nickel-filtered Cu$K\alpha$ radiation. Scans were run from 1° to 40° with a goniometer speed of $2^\circ\,\mathrm{min}^{-1}$. D.s.c. was run on a Du Pont 2000 Thermal Analyzer with a heating rate of $15^\circ\mathrm{C\,min}^{-1}$ at $50\,\mathrm{ml\,min}^{-1}$ gas flow rate (N_2 or air). D.m.a. experiments were conducted on a Du Pont 983 DMA and analysed with a 2000 Thermal Analyzer. A ramp of $5^\circ\mathrm{C\,min}^{-1}$, $50\,\mathrm{ml\,min}^{-1}$ flow rate (N_2), 1 Hz frequency, 0.5 mm length correction, 0.15 mm amplitude and a 0.38 Poisson's ratio were used. The t.g.a. measurements were performed on a Du Pont 2000 Thermal Analyzer with a heating rate of $15^\circ\mathrm{C\,min}^{-1}$ and a gas flow rate of $50\,\mathrm{ml\,min}^{-1}$. SEM photographs were taken using a GEOL 840A. T.m.a. experiments were carried out on a Seiko Instruments Inc. thermomechanical analyser with a heating rate of $5^\circ\mathrm{C\,min}^{-1}$ in static air.

Neat resin processing

A cylindrical stainless steel mould of 5.5 cm diameter equipped with a thermocouple was sprayed with a high temperature release agent (Frekote 44™) and dried at r.t. for 1 h. The mould was charged with approximately 4.5 g of monomer (powder) and pressed for 5 min under 69 MPa at 90–100°C. The mould was then placed into a preheated (processing temperature 300°C), manually operated press (F. Carver, Inc.) under very low pressure (345 kPa). The mould was heated at a rate of $20^\circ\mathrm{C\,min}^{-1}$. When the temperature of the mould reached 220–240°C, 4.8 MPa pressure was applied. After heating for 1.5 h at 300°C under pressure, the pressure was released and the mould was cooled within 1–1.3 h. When the mould was below 60°C, the plate was removed.

Isothermal ageing

Isothermal weight loss studies of PEPNI were conducted on five disc-shaped post-cured specimens of 13 mm diameter and 1.4 mm thickness. PEPNI discs were pressed under 69 MPa at r.t. for 5 min. They were gradually heated in the absence of air from r.t. to 280°C within 30 min, followed by further heating at 300°C for 45 min; they were post-cured for 1.5 h at 330°C. During the heating (polymerization) and post-curing, 0.69 MPa pressure was applied. The isothermal ageing took place at 427°C in an oven under 0.1 MPa (static air).

Synthesis of EPNI

NTDA (18.98 g, 70.79 mmol) was dissolved in NMP (1.1 l) at 90–100°C. A clear brown solution was obtained. The solution was gradually cooled to 50°C and 4-ethynyl aniline[9] (17.02 g, 145.47 mmol) in NMP (100 ml) was added at once. The solution was stirred at 50°C for 30 min and for 50 min at 75°C. It was divided into two portions: 40 ml of this solution (solution A) was used for isolating the diamic acid of EPNI, while the remaining solution (solution B) was chemically cyclodehydrated (see later). The mixture obtained by pouring solution A into crushed ice (1 l) was filtered and the residue was stirred with water (1 l), filtered and dried at 60°C under vacuum. The diamic acid was obtained as a tan crystalline solid. *FT*i.r. ($\mathrm{KBr, cm^{-1}}$) 3500–3350 (hydroxyl stretch of carboxylic group); 3350–3230 (NH stretch of amido group); 3271 (C(sp)–H stretch of acetylene group); 1722 (carbonyl stretch); 1543 (NH deformation); 1515 (C═C stretch of aromatic ring). ^{1}H n.m.r. (DMSO-d_6) 4.1 (s, 2H, acetylenic); 7.4–7.65 (m, 8H, aromatic *ortho* to acetylenic and *ortho* to –NHCO– groups); 8.7 (s, 4H, aromatic of the naphthalene ring); 8.25 (s, 2H, –NHCO–). ^{13}C n.m.r. (DMSO-d_6) 81.3 (s, 2C, C(sp)–H); 82.7 (s, 2C, C(sp)–C(sp)–H); 113.59 (2C), 124.83 (4C) and 135.89 (2C) are attributed to the aromatic carbons which are attached, *ortho*, *meta* and *para* to the acetylenic groups; 112.42 (2C), 121.82 (2C), 126.84 (4C), 129.38 (4C) and 133.21 (2C) are attributed to the aromatic carbons of the naphthalene ring; 162.63 (4C) are attributed to two carboxylic and two carbamido carbons. The assignments for the ^{13}C n.m.r. spectrum are based on the ^{13}C n.m.r. data of naphthalene derivatives[24,25].

Acetic anhydride (50 ml) and pyridine (5 g) were added to the remaining solution B. The solution was stirred for 1 h at 110°C and for 3 h at 130°C. After completion of the reaction the flask was cooled to r.t. and the mixture was poured into crushed ice (9 l) and allowed to stand overnight. It was stirred for 40 min and filtered. The residue was stirred with H_2O (1.2 l) three times, filtered and dried at 100°C under vacuum. EPNI was obtained as a dark brown crystalline solid (30.87 g) in 97% yield. *FT*i.r. ($\mathrm{KBr, cm^{-1}}$) 3261 (C(sp)–H stretch of acetylenic group); 3080 (C(sp^2)–H stretch); 1786, 1718 (C═O stretch of imide linkage); 1510 (C═C stretch). The absence of a broad absorption band around $3400–3250\,\mathrm{cm}^{-1}$ shows that the monomer was completely imidized.

SUMMARY AND CONCLUSIONS

N,N'-bis(4-ethynyl phenyl) 1,4,5,8-naphthalimide (EPNI) was thermally polymerized to yield a highly crosslinked resin. EPNI polymerized to high conversion in spite of its rigid matrix, probably because of the localization of the polymerizable ethynyl groups. Cohesive polymeric plates were made by a processing technique developed in our laboratory. EPNI had the same density as its polymer (polymeric plate) which implies zero polymerization shrinkage. SEM photographs showed that the dark brown, reflective portions of PEPNI plates had no voids and kept orientational order. PEPNI had a T_g of 309°C and a linear coefficient of thermal expansion of $4.28 \times 10^{-5}\,\mathrm{K}^{-1}$. This is the first time that a rod-like polynaphthalimide has been processed to a polymer plate.

Because EPNI can polymerize and process readily, shows zero polymerization shrinkage, has a low linear coefficient of thermal expansion and is a very thermostable polymer (based on isothermal ageing results), it is expected to be a good candidate for high temperature composites. Its zero polymerization shrinkage and low expansion coefficient should minimize interfacial stresses.

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