N,N'-Bis(p-ethynylphenyl)pyromellitimide: A New Processable, High-T_g, Rigid Rod Heat-Resistant Polymer Precursor with No Polymerization Shrinkage

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ABSTRACT: A new p-ethynyl-substituted rigid rod monomer, bis(p-ethynylphenyl)pyromellitimide (EPPI), was synthesized and characterized. EPPI is a crystalline material which thermally polymerized under N_2 in the solid state to yield a highly cross-linked resin with a low crystallinity. However, it retained its overall molecular orientation. The progress of polymerization was followed by FTIR, DSC, and WAXD. It was found that EPPI reacted easily (thermally) to yield an extended polyene structure. Tough polymeric plates were made by solid-state polymerization of EPPI under 1000 psi for 1 h at 600 °F (315 °C). Because EPPI is ordered and polymerized in the crystalline state, it showed zero polymerization shrinkage (EPPI had the same density as the well-consolidated polymer, 1.29 g/mL)! EPPI 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 EPPE (PEPPI) with over 6% voids showed a storage modulus of 2.6 GPa at room temperature and 750 MPa at 400 °C, with a T_g over 400 °C. After heating to 480 °C, the polymer had a T_g over 440 °C and a storage modulus of 900 MPa at 400 °C. PEPPI showed 1.95% elongation at break at room temperature, even though the specimen had over 6% voids!

Introduction

Recently, interest and investment in carbon-based composite materials has outstripped all unbiased projections made in the past decade. Mainly, this has been a marketing phenomenon in which new niches have been identified and successfully filled by tailoring existing systems or by the development of new materials. One such "niche" is the use of composite materials in extreme environments, such as large static or fluctuating stresses at either very high or very low temperatures. In such situations, the venerable (but still only partially understood) epoxy resin-based composites are often unable to meet specifications for strength, stiffness, or durability. Much attention has focused on the development of alternative high-performance resin systems.

Polyimides have been developed for applications as coatings, 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; the polymer properties required for these applications generally include high thermal and dimensional stability, low thermal expansion coefficient and residual stress upon thermal cycling, planarization, low dielectric constant, and good mechanical properties. Aromatic polyimide derived from pyromellitic dianhydride and 4,4'-oxydianiline have been used extensively in the microelectronics industry. The good mechanical properties and low thermal expansion coefficient can be attributed, in part, to the liquid crystalline or crystalline order exhibited by these materials.[1,2] Although the rigid and semirigid polyimides fulfill many of the material requirements for structural or functional applications, their poor processability and autoadhesion (i.e., the adhesion of the polyimide to itself) have plagued these systems.

The acetylene-terminated systems offer a viable alternative to the polyimide and other high-performance systems which cure via condensation processes through a

resin cure based on thermal (catalyst free) polymerization of terminal acetylene functionalities attached to a stiff, thermally stable resin backbone. This process has been shown to proceed through a free radical intermediate and to involve the formation of an oligomeric polyene whose reactivity decreases with length, presumably due to a progressive delocalizaton of the propagating free radical.[3] In addition, reactions of this type do not produce volatiles, so void formation in the product is not a problem. The reaction can proceed in the absence of added catalyst; catalyst often contributes to long-term instability in the cured resin. Cross-linking improves the thermal and mechanical properties of heat-resistant polymers; highly cross-linked polymers show desirable properties such as excellent dimensional stability with low creep rates, high resistance to solvents, increased softening temperatures, and improved thermal stability compared to the analogous un-cross-linked polymers. Oligomers and polymers containing acetylenic groups[4-8] have excellent shelf lives and, when cured, provide resins with solvent resistance and a favorable combination of physical and mechanical properties.

The first reports on acetylene-terminated imide oligomers (ATIs) were from Bilow et al.[9,10] The synthesis of these ATIs entails the reaction of an aromatic tetracarboxylic acid dianhydride (2 mol) with an aromatic diamine (1 mol) to yield an anhydride-terminated amic acid oligomer. Subsequent reaction with an ethynyl-substituted aromatic amine followed by chemical or thermal cyclodehydration converts the amic acid to an ATI. The early work on ATIs led to the development of a material called HR-600 (Thermid-600 is the trademark for HR-600). This polymer precursor was cured at 250 °C for 2 h and at 316 °C for 16 h under 2000 psi. In spite of the properties reported for HR-600, major processing problems have plagued this system. The ethynyl groups generally begin to react and inhibit flow and wetting prior to the formation of a complete melt or soft state. Other acetylene-terminated oligoimides have been synthesized and polymerized by Stille et al.[11] and Hergenrother.[12] N,N'-Bis(3-ethynylphenyl)pyromellitimide has been synthesized and

is included in a patent of National Starch Co.[13]

An effort has started in our laboratory to synthesize and polymerize new *p*-ethynyl-terminated esters[14,15] and benzyl ethers.[16] Solid-state polymerization of the rigid rod *p*-ethynyl-terminated monomers under low pressure yields good, tough, void-free polymeric plates.[17] The objective of this research was to develop a new ethynyl-terminated rigid rod monomer, bis(4-ethynylphenyl)-pyromellitimide (EPPI), which could be polymerized at moderately elevated temperatures to yield a highly cross-linked thermally stable resin suitable as a matrix for high-temperature composites. It has been reported that imide oligomers end-capped with 4-ethynylaniline failed to cure properly,[12,18] presumably due to decreased molecular mobility arising from the rigidity of 4-ethynylaniline. We proposed that EPPI should polymerize to high conversion in spite of its rigid matrix because the molecules pack in lamellae, 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 fiber should thus be very low.

Results and Discussion

The chemical structure of bis(*p*-ethynylphenyl)pyro-mellitimide (EPPI) synthesized is shown below. EPPI
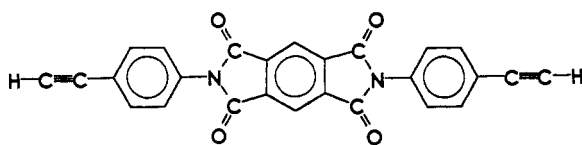
was synthesized by a two-step reaction: pyromellitic dianhydride (1 mol) was reacted with *p*-ethynylaniline (2 mol) in NMP. (*p*-Ethynylaniline was synthesized in our laboratory in 93% overall yield and 99% purity by a new simple synthetic route using the inexpensive reagent 2-methyl-3-butyn-2-ol.[19]) The solution was stirred at room temperature for 30 min and then at 80 °C for 1 h more. A small aliquot of the solution was poured into crushed ice to isolate the bis(*p*-ethynylphenyl)pyromellitic diamic acid, which was used for characterization. Chemical cyclodehydration was carried out by adding acetic anhydride and pyridine to the solution. The system was stirred in 140 °C for 2 h and poured into crushed ice. During the heating, the color of the mixture changed from light yellow to olive-brown. EPPI was obtained as an olive–brown crystalline solid in 99% yield.

The chemical structure of EPPI was confirmed by FTIR, ^{1}H-NMR, and ^{13}C-NMR. The IR spectrum of EPPI (Figure 1) exhibited a sharp absorption band at 3298 cm^{-1} due to the ethynyl group (C(sp)–H stretch). The absorption bands at 1790 and 1730 cm^{-1} (Figure 2) were attributed to the C=O stretch of the imide linkage. The absence of a broad absorption band around 3500–3300 cm^{-1} (attributable to hydroxyl groups of the corresponding diamic acid) demonstrated that EPPI is completely imidized.

The ^{1}H-NMR spectrum of EPPI could not be recorded because of its very low solubility in polar aprotic solvents. The ^{1}H-NMR (Figure 3) and ^{13}C-NMR (Figure 4) spectra of the diamic acid of EPPI (soluble in polar aprotic solvents) were recorded in DMSO-*d₆* to confirm its chemical structure and estimate the molar ratio of the two possible isomers as well. The ^{1}H-NMR spectrum of the diamic acid (Figure 3) showed a strong singlet at 3.96 ppm attributable to the acetylenic protons. The multiplets at 7.28 and 7.73 ppm were associated with the aromatic protons ortho to C(sp) and ortho to NHCO. These peaks
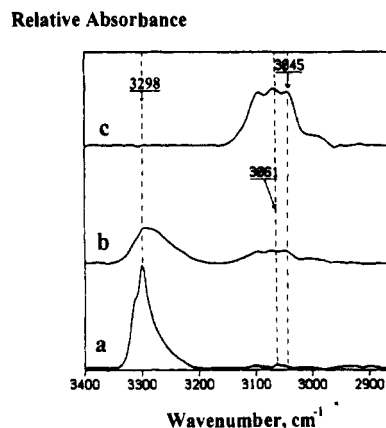
Figure 1. IR spectra of EPPI (a), after heating for 20 min at 218 °C (b), and after heating for 20 min at 270 °C (c).
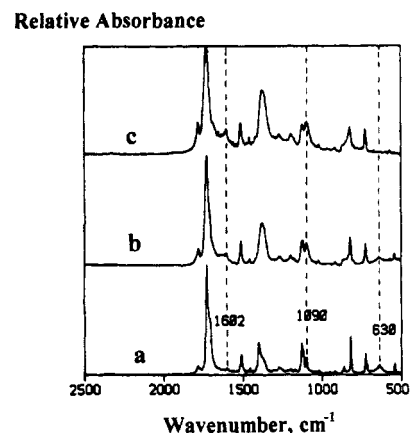
Figure 2. IR spectra of EPPI (a), after heating for 20 min at 218 °C (b), and after heating for 20 min at 270 °C (c).
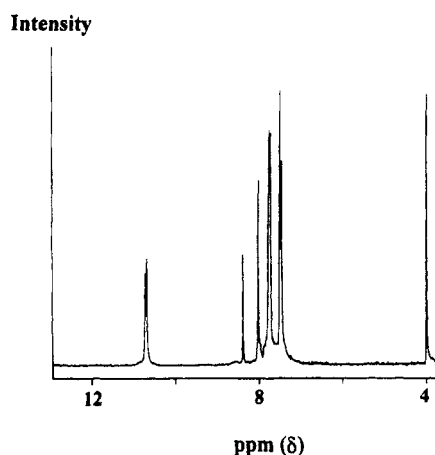
Figure 3. ^{1}H-NMR spectrum of EPPI.

appeared as multiplets instead of doublets because of the existence of the two isomeric cis and trans structures. The singlet at 7.99 ppm was attributed to the two aromatic protons of the pyromellitic ring (trans configuration), and the singlet at 8.37 ppm was associated with the aromatic proton of the pyromellitic ring ortho to two carboxylic groups (cis configuration). The other aromatic proton of the cis configuration pyromellitic ring overlapped at 7.73 ppm with the aromatic protons ortho to NHCO. It can be said that the cis and trans isomers were formed in a 1/1 molar ratio as the intensity ratio of the singlets at 7.99 and 8.37 ppm was 2/1. The ^{13}C-NMR spectrum of the diamic acid of EPPI (Figure 4) showed two singlets at 80.1 and 83.6 ppm that were attributed to the C(sp) carbons attached to the aromatic ring and C(sp)–H, respectively. The singlet at 114.5 ppm was associated with the carbons
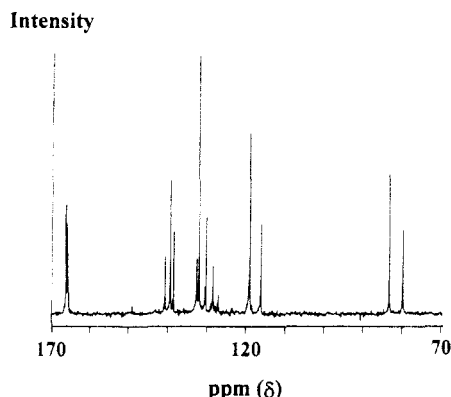
Intensity

ppm (δ)

Figure 4. ^{13}C-NMR spectrum of EPPI.

of the aromatic ring attached to the acetylenic groups, and the singlet at 118.1 ppm was associated with the aromatic carbons ortho to the acetylenic groups. The singlet at 131.6 ppm was attributed to the aromatic carbons meta to the acetylenic group. The aromatic carbons of the pyromellitic ring appeared between 128 and 140 ppm. The peak at 164.5 ppm, after local expansion of the spectrum, was found to be a quartet and was attributed to the carbons of the carboxyl and amido groups of both of the isomers. The cis and trans isomers formed in equimolar amounts as the quartet at 164.5 ppm consisted of four equal-area peaks.

The FTIR, ^{1}H-NMR, and ^{13}C-NMR spectra (Figures 1-4) show that no byproducts were present in the material. First, studies in our laboratory showed that *p*-ethynylaniline[19] and *p*-ethynylbenzoic acid[15] were stable in solution and when stored as solids at -20 °C. Second, high-purity *p*-ethynylaniline (99%)[19] was synthesized, stored, and used under conditions where it could not self-react. This is best shown in Figure 3; the proton NMR spectrum has no trace of vinyl hydrogens that would be expected if there were any self-reaction of the *p*-ethynylaniline.

EPPI was thermally polymerized by heating at 220 °C for 30 min and subsequently at 280 °C for 1.5 h (postcuring) in N₂. It is noteworthy that the polymerization went to completion by heating even for 1 h at 228 °C (reaction of all ethynyl groups). However, postcuring is necessary to get a highly cross-linked resin with improved thermal and thermomechanical properties. The curing behavior of EPPI was examined by DSC (Figure 5). The DSC thermogram showed a polymerization exotherm between 155 and 350 °C with a temperature of maximum polymerization rate, T_{max}, of 268 °C (heating rate of 15 °C/min) and with a 415 J/g (172 kJ/mol) enthalpy of polymerization. EPPI exhibited a low initial polymerization temperature comparable to that of ethynyl-terminated esters[14] synthesized in our laboratory. It has been reported[12,18] that acetylene-terminated oligoimides (ATIs) terminated with *p*-ethynylaniline failed to cure properly, while ATIs terminated with *m*-ethynylaniline cured completely. This behavior was rationalized by the hypothesis that para substitution (acetylene group) decreased the molecular mobility of the oligomers. The lower diffusion rates resulted in slower polymerization. Even though EPPI is much more rigid than the ATIs previously reported, we believe that it polymerized at low temperatures because its molecules in the solid state are packed in a way which facilitates the polymerization. The T_g of its cross-linked resin could not be detected by DSC. This was attributed to the fact that the resin was highly cross-linked and the change in C_p was very small.

The progress of the polymerization of EPPI was followed by FTIR, DSC, and X-ray diffraction. Figures 1 and 2
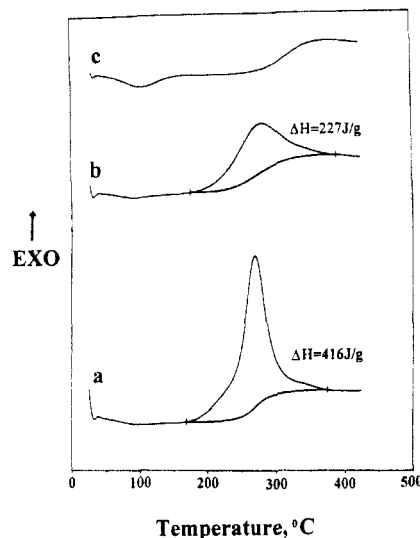

Temperature, °C

Figure 5. DSC thermograms of EPPI (a), after heating for 20 min at 218 °C (b), and after heating for 20 min at 270 °C (c). (The DSCs were carried out in N₂.)

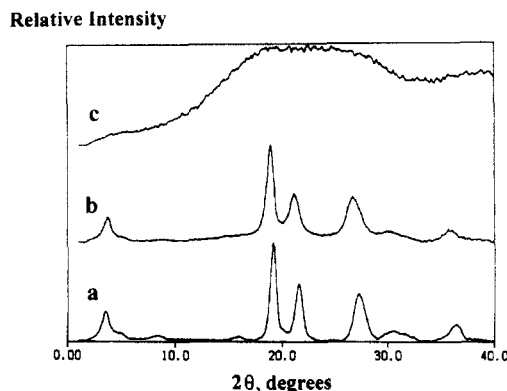Relative Intensity

2θ, degrees

Figure 6. WAXD spectra of EPPI (a), after heating for 20 min at 218 °C (b), and after heating for 20 min at 270 °C (c).

show the IR spectra of EPPI (Figures 1a and 2a), after heating for 20 min at 218 °C (Figures 1b and 2b), and after heating for 20 min at 270 °C (Figures 1c and 2c). The DSC thermograms and WAXD spectra of the same samples are shown in Figures 5 and 6. Figures 1a and 2a show absorption bands at 3298 and 630 cm⁻¹ due to the C(sp)-H stretch and bending vibrations of the acetylene groups. The same bands with lower intensity appear in Figures 1b and 2b (which correspond to 48% polymerized resin based on Figure 5b) and have completely disappeared in Figures 1c and 2c (completely polymerized resin based on Figure 5c). The weak band at 3061 cm⁻¹ in Figure 1a is associated with the aromatic C-H stretch mode of EPPI. The new absorption band at 3045 cm⁻¹ which appears in Figure 1b (olefinic C-H stretch) is absent in Figure 1a and becomes more intense in Figure 1c. This was attributed to the thermal polymerization of the acetylene groups to yield a polyene system. Figure 2a shows a weak band at 1602 cm⁻¹ attributable to the aromatic C=C stretch. However, this band keeps increasing in Figure 2b (1602 cm⁻¹) and Figure 2c (1604 cm⁻¹); this was attributed to the olefinic C=C stretch of the generated conjugated polyene structure. Figure 2a shows an absorption band at 1090 cm⁻¹ attributable to a 1,4-disubstituted aromatic system (aromatic C-H bend in plane). This band becomes more intense in Figure 2b (1092 cm⁻¹) and much more intense in Figure 2c (1091 cm⁻¹) due to the formation of an extended aromatic system.

EPPI is a highly crystalline material (Figure 6a) which is polymerized in the solid state (Figure 5a). Up to 50%
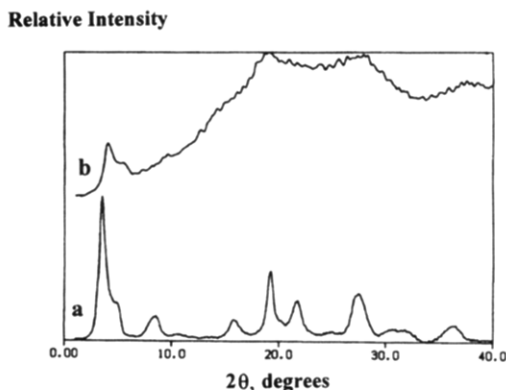
Relative Intensity

2θ, degrees

Figure 7. WAXD spectra of a plate (1 mm thick) of EPPI before polymerization (a) and after heating for 1.5 h at 300 °C under 1000 psi (b).

conversion (based on ΔH_{polym} of Figure 5b), the (half-polymerized) monomer powder exhibits the same crystal pattern (Figure 6b) as EPPI (powder) (Figure 6a) with no amorphous scattering. At 100% conversion (Figure 5c) the WAXD scan of the powder shows no crystallinity. Since this material could be used as a coating (film or polymeric plate) and for composite fabrication, the WAXD spectra of pressed plates of EPPI and PEPPI were recorded and are shown in Figure 7a. From these it can be seen that the polymer (Figure 7b) keeps a certain amount of crystallinity as its WAXD spectrum exhibits four peaks.

Optical microscopy was used to elucidate changes in the morphology of EPPI during its polymerization. A few drops of an EPPI solution in DMAc were evaporated on a glass plate. The thin film of EPPI was covered with a cover glass plate and heated (absence of air) in the hot stage at 15 °C/min to 295 °C, followed by isothermal heating at this temperature for 1 h more. The final polymer had almost the same birefringence as the monomer. This indicates that the EPPI polymer keeps its overall orientation.

The densities of EPPI and its polymer (PEPPI) (well-consolidated plate) were found to the same (1.29 g/mL)! Since EPPI was polymerized in the solid state, this demonstrates that EPPI exhibits zero polymerization shrinkage! These data are unusual, as the well-known epoxy–aromatic amine systems have shrinkages of 9–10%[20] and the acrylate networks have shrinkage, of 11–15%.[21,22] Zero polymerization shrinkage means that this monomer is a candidate for high-temperature composites, as the interfacial stresses between matrix/reinforcement will be minimized. p-Ethynylbenzoyl esters which were synthesized and studied in our laboratory similarly had a polymerization shrinkage between 0 and 2.3%[14]!

Films could not be made by casting a solution of EPPI and heating to the polymerization temperature because the monomer is highly crystalline. Much effort has gone into finding the appropriate conditions for making good polymeric plates with no voids. A processing technique[17] for making cohesive disks or plates using solid-state polymerization has been developed in our laboratory. This was applied to the polymerization of EPPI. Polymer plates were made by compression molding of EPPI (powder) under 10000-psi pressure for 3 min at 90–100 °C, heating at 600 °F (315 °C) for 1 h under 1000 psi, and cooling to room temperature gradually. These plates were not uniform; there were areas which were dark brown and with a reflective surface and others (larger portion) which were tan and dull. SEM microphotographs were taken to gain insight into the morphology of these plates (broken surface); they are shown in Figure 8. These SEM
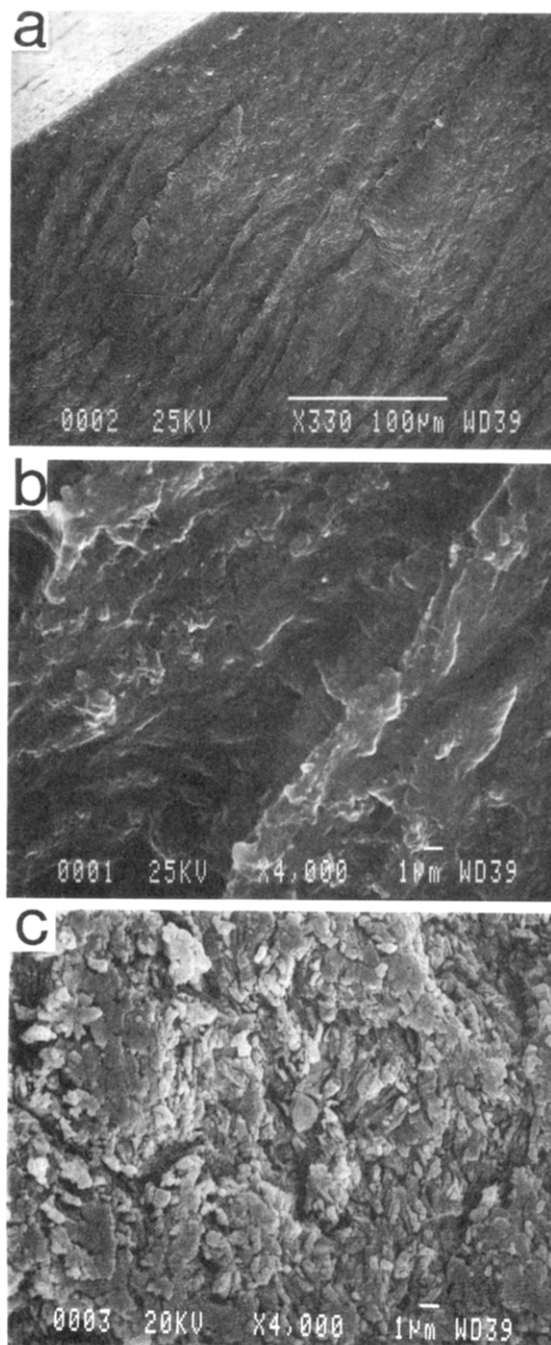

Figure 8. SEM microphotographs (broken surface) of a well-consolidated PEPPI under 330 × magnification (a), of a well-consolidated PEPPI under 4000 × magnification (b), and of a poorly consolidated PEPPI with 6% voids under 4000 × magnification (c). The micrographs are reproduced at 65% of their original size.

photographs have been taken from different areas of the same specimen. Figures 8a and 8b show SEM photographs of well-consolidated PEPPI (dark brown, reflective surface), and Figure 8c shows a SEM photograph for PEPPI which was light tan and had a dull surface. There are no voids in the broken surface of the plate in Figures 8a and 8b. It can also be seen that this polymer retains a certain amount of order (Figure 8a). However, many voids exist in the broken surface of PEPPI which did not consolidate well (Figure 8c). The surface of this part of PEPPI is tan and dull because the voids scatter light. These voids are stress concentrators and are responsible for the inferior mechanical and thermomechanical properties of the polymers. The densities of EPPI polymeric plates which were dark brown and reflective and others with tan, dull
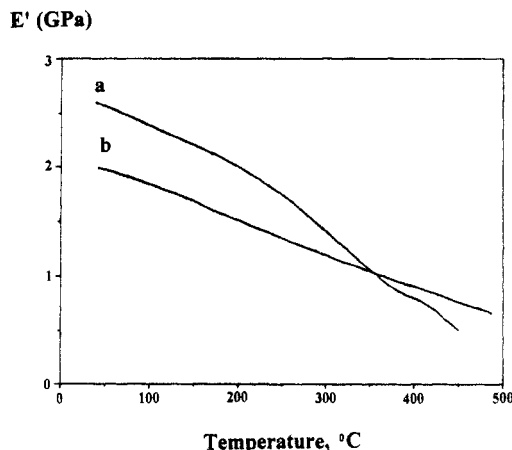
E' (GPa)

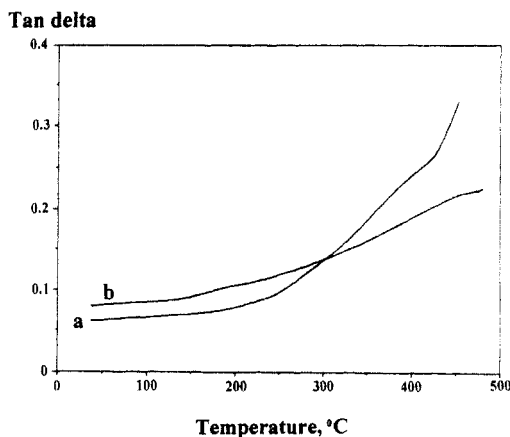**Figure 9.** DMA thermograms (temperature dependence of E') for PEPPI (a) and second run (b).

Tan delta

Figure 10. DMA thermograms (temperature dependence of tan δ) for PEPPI (a) and second run (b).

Weight, %

Temperature, °C

Figure 11. TGA thermogram of PEPPI (powder) prepared by polymerizing EPPI for 2 h at 270 °C in N_2.

Table I. TGA Data for PEPPI Cross-Linked Polymers

	in nitrogen			in air	
sample	$T_{5\%}{}^a$ (°C)	PDT^b (°C)	$Y_c{}^c$ (%)	$T_{5\%}$ (°C)	PDT (°C)
1^d	461	609	53	425	565
2^e	454	611	53	431	570
3^f	480	649	63	464	640

^{a} Temperature where the polymer shows 5% weight loss. ^{b} Maximum decomposition temperature. ^{c} Char yield at 700 °C. ^{d} EPPI polymerized for 2 h at 270 °C in N_2. ^{e} EPPI polymerized for 5.5 h at 270 °C in N_2. ^{f} EPPI polymerized for 2 h at 270 °C in N_2 and for 2 h at 290 °C in air.

surfaces were measured to determine the void percentage. The density for PEPPI with the tan, dull surface was found to be 1.21 g/cm³, while well-consolidated PEPPI had a density of 1.29 g/cm³. This datum indicates that there are ca. 6% voids in the PEPPI specimen with the tan, dull surface.

Dynamic mechanical analysis (DMA) was used for the evaluation of the thermomechanical properties of PEPPI. The temperature dependence of its flexural storage modulus E', for the first and second runs is shown in Figure 9. The temperature dependence of the tan δ's of PEPPI (first and second runs) is shown in Figure 10. PEPPI has an E' of 2.6 GPa at room temperature and 750 MPa at 400 °C (Figure 9a). From Figure 9b it can be seen that the PEPPI (rerun) has an E' of 2 GPa at room temperature and over 900 MPa at 400 °C. These data indicate that E' drops to one-third of its room temperature value at 400 °C. It should be noted that the E' of PEPPI is expected to be between 4 and 5 GPa at room temperature when the processing conditions are optimized. When p-ethynyl-benzoyl esters were initially processed in our laboratory, their E' values were between 2.5 and 3 GPa at room temperature. After processing conditions were improved, void-free plates were obtained, and their E' values increased to 4.5–4.8 GPa at room temperature with T_g's between 350 and 440 °C.[17]

tan δ (Figure 10a) changes from 0.06 to 0.32 from room temperature to 450 °C. It shows a very broad transition between 350 and 450 °C with a broad "maximum" around 400 °C, which can be considered as its T_g. In the second heating, tan δ was flatter than in the first heating, and possible transitions which might be related to the T_g were
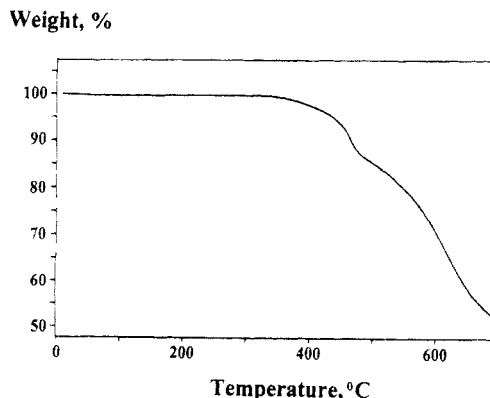
pushed to ca. 440 °C. It should be noted that these T_g's are much higher than previously reported for acetylene-terminated systems. Those polymers, derived from bis-(4-(3-ethynylphenoxy)phenyl) sulfone and acetylene-terminated quinoxalines, had T_g's from 300 to 365 °C.[18]

Stress–strain tests were carried out to evaluate the tensile modulus and elongation at break for PEPPI. The tensile modulus and elongation at break of these pressed plates were found to be 1.71 GPa and 1.95% at room temperature. The existence of voids in sections of PEPPI plates was probably responsible for the low values of tensile modulus and elongation at break as it is well known that the voids are stress concentrators. It was pointed out earlier in this paper that the tested PEPPI specimens had ca. 6% voids. The 1.95% elongation at break is very high for such a highly cross-linked rigid rod system. It is doubly unusual in samples with a high void content. It is expected that these values will be significantly increased when optimum processing conditions for EPPI are developed. As was expected, the stress–strain curve was a straight line up 0.8% elongation. Afterward, the slope dropped slightly up to 1.95% elongation (break).

Dynamic thermogravimetric analysis (TGA) was used for the rapid evaluation of the thermal stability of polymerized EPPI. EPPI was polymerized and postcured under different conditions to help understand the relationship between the reactions of the acetylene groups as a function of curing conditions and the thermal stability of the cross-linked resins. A TGA thermogram representative of this series is shown in Figure 11. The TGA data of resins cured for 2 and 5.5 h at 270 °C in N_2 and of a PEPPI cured for 2 h at 270 °C in N_2 and for 2 h at 290 °C in air are listed in Table I. This table shows that EPPI cured in N_2 for 2 h showed the same thermal stability as the resin postcured for 5.5 h. Thus, curing is complete after 2 h at 270 °C in N_2. When EPPI is polymerized in N_2 (2 h at 270 °C) and postcured in air (2 h at 290 °C), the resulting PEPPI had a much higher thermal and thermoxidative stability than the EPPI resins cured only under N_2 (Table I). These results agree with previously

reported data[18,23,24] that the thermal polymerization of ethynyl-terminated systems (ETS) in air rather than in N_2 afforded resins with better thermal and thermomechanical properties. Those ETS were cured at high temperatures (350–370 °C) for 5–20 h in air to yield highly cross-linked resins with outstanding properties. When p-ethynylbenzoyl esters (EBEs)[14] were polymerized in air, it was found that the obtained resins had higher short-term thermal and thermooxidative stability (TGA analysis) than resins cured in N_2. However, for long-term thermal and thermooxidative stability, isothermal aging[25] of EBEs at 550 °F (288 °C) in air for 250 h showed that the resins which were polymerized and postcured in N_2 exhibited only 5–6% weight loss instead of the 30–35% found for resins postcured in air. These data imply that polymerization of EBEs in the absence of air dramatically improved their long-term performance. Isothermal studies showed that the PEPPI retained 97% of its initial weight after isothermal heating for 500 h at 550 °F (288 °C) in a circulating air atmosphere. The decomposition analysis and isothermal aging studies for these polymers are reported elsewhere.[25]

Experimental Section

Materials. Pyromellitic dianhydride was received from Aldrich and recrystallized from acetic anhydride. p-Ethynylaniline was synthesized in our laboratory in 93% overall yield and 99% purity by a new route.[19] N-Methylpyrrolidinone (NMP) was obtained from Aldrich and distilled over phosphorus pentoxide at reduced pressure. Acetic anhydride and pyridine were received from Fisher and used without any further purification. Polymeric EPPI plates were made by the following processing technique developed and reported from our laboratory.[17]

Neat Resin Processing. A cylindrical stainless steel mold of 5.5-cm diameter equipped with a thermocouple was sprayed with a high-temperature release agent (Frekote 44) and dried at room temperature for 1 h. The mold was charged with ca. 4.5 g of monomer (powder) and pressed for 3 min under 10000 psi at 90–100 °C. The mold was then placed into a preheated manually operated press (F. Carver, Inc.) under very low pressure (50 psi). The mold was heated at 20 °C/min. When the mold temperature reached 220 °C, 1000-psi pressure was applied. After 1 h of heating and pressing, the pressure was released and the mold was cooled within 1–1.3 h to <60 °C. The polymer plate was then removed.

Analytical Methods. Proton (^{1}H-NMR) and carbon (^{13}C-NMR) nuclear magnetic resonance spectra were taken on an XL-200, 200-MHz FT-NMR. Chemical shifts (δ) are given in parts per million, with tetramethylsilane as an internal standard. Infrared spectra (FTIR) 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 a chloroform–hexanes solution. Twenty-mil-thick pellets were made from the monomer by compression molding. For the corresponding polymer, films of similar thickness polymerized in the solid state under moderate pressure were used for these measurements. X-ray scans were recorded using a Phillips APD 3520 automatic diffractometer. Nickel-filtered copper Kα radiation was used. Scans were run from 1 to 40° with a goniometer speed of 2°/min. Hot stage cross-polarized photographs were taken on a Carl Zeiss optical olarizing microscope equipped with a Mettler FP-82 hot stage and a Mettler FP80 central processor. DSC was performed on a DuPont 2000 thermal analyzer with a heating rate of 15 °C/min in nitrogen at a 50 mL/min flow rate. The DMA experiments were conducted on a DuPont 983 DMA and analyzed with a 2000 thermal analyzer. A ramp of 5 °C/min, a flow rate of 50 mL/min (N_2), a frequency of 1 Hz, a length correction of 0.5 mm, an amplitude of 0.15 mm, and a Poisson ratio of 0.38 were used. The tested samples had a 24-mm clear length distance, a 10.28-mm width, and a 1.36-mm thickness. The DMA tests represent the average value based on three tests. Instron testing for PEPPI

was carried out on an Instron 1125 at room temperature with dog bone specimens with a 23- or 29-mm reduced length, a 5.7-mm width, a 1.7-mm thickness, and a 0.05 mm/min crosshead speed. The stress–strain tests were performed in duplicate. TGA measurements were performed on a DuPont 2100 thermal analyzer with a heating rate of 15 °C/min and a gas flow rate of 50 mL/min. SEM microphotographs were taken in a JEOL 840A.

Synthesis of EPPI. To a vigorously stirred solution of p-ethynylaniline (55.11 g, 471 mmol) in NMP (400 mL) at 5 °C was added granular pyromellitic dianhydride (PMDA) (51.36 g, 235.5 mmol) in portions. The stirred solution was allowed to warm to room temperature. After the dissolution of PMDA, within 30 min, the solution was further stirred for 1 h at 75 °C. It was separated into two portions; 40 mL of this solution (solution A) was used for isolating the diamic acid of EPPI, while the remaining solution (solution B) was chemically cyclodehydrated. 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 light yellow crystalline solid (10.35 g) in 98% yield. FTIR (KBr, cm^{-1}): 3600–3350 (hydroxyl stretch of carboxylic group), 3350–3300 (NH stretch of amido group), 3290 (C(sp)–H stretch of acetylene group), 1720 (carbonyl stretch), 1540 (NH deformation), 1514 (C=C stretch of aromatic ring). ^{1}H-NMR (DMSO-d_6): 3.96 (s, 2H, acetylenic), 7.28 (d, 4H, aromatic ortho to acetylenic group), 7.73 (d, 4H, aromatic ortho to NHCO), 7.99 (s, 2H, aromatic of PMDA ring; cis configuration), 8.37 (s, 1H, aromatic of PMDA ring ortho to two carboxylic groups of trans configuration), 10.67 (s, 2H, NHCO, 10.70 (s, 2H, COOH). The proton NMR spectrum is very clean with no trace of vinyl hydrogens that could result from attack on the ethynyl groups. ^{13}C-NMR (DMSO-d_6): 80.1 (s, 2C, C(sp)–H), 83.6 (s, 2C, C(sp)–C(sp)–H), 114.5 (s, 2C, aromatic attached to acetylenic group), 118.1 (s, 4C, aromatic ortho to acetylenic group), 131.6 (s, 4C, aromatic meta to acetylenic group), 126.5 (1C, aromatic of PMDA ring ortho to carboxyl groups of cis configuration), 128.9 (2C, aromatic of PMDA ring, ortho carbonyls of trans configuration), 132.4 (4C, aromatic meta to acetylenic group), 131.6 (2C, aromatic of PMDA ring attached to carbonyl group), 139.4 (2C, aromatic attached to NHCO, 164.5 (4C, two of NHCO and two of COOH).

Acetic anhydride (150 mL) and pyridine (15 g) were added to the remaining solution B (360 mL). Within a few minutes the system became heterogeneous. NMP (150 mL) was added and the mixture was stirred for 2 h at 135 °C. The color of the mixture changed gradually from light yellow to olive-brown. After the completion of the reaction the flask was cooled to room temperature, and the mixture was poured into crushed ice (7 L). The mixture was stirred for 40 min and filtered. The residue was stirred with H_2O (3 L), filtered, and dried at 100 °C under vacuum. EPPI was obtained as an olive-brown crystalline solid (86.8 g) in 99% yield. FTIR (KBr, cm^{-1}): 3298 (C(sp)–H stretch of acetylenic group), 1790, 1730 (C=O stretch of imide linkage), 3061 (C(sp^2)–H stretch, 1512 (C=C stretch). It should be noted that the absence of a broad absorption band around 3500–3300 cm^{-1} shows that the monomer is completely imidized. Its ^{1}H-NMR or ^{13}C-NMR spectra could not be recorded due to its low solubility in all solvents tested.

Conclusions

N,N'-Bis(p-ethynylphenyl)pyromellitimide (EPPI) was thermally polymerized to yield a highly cross-linked resin. EPPI 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. This technique involves the solid-state polymerization of EPPI under moderate pressure. The polymeric plates kept a certain amount of crystallinity. EPPI had the same density as its polymer (polymeric plate) which implies zero polymerization shrinkage! It was postulated that EPPI is properly organized so that it can be easily polymerized in the solid state. SEM microphotographs showed that the dark brown, reflective PEPPI plates had no voids and were

semicrystalline. PEPPI had a T_g over 400 °C, which is over 80 °C higher than its polymerization (processing) temperature.

We demonstrated that void-free, completely polymerized disks can be made. The fact that we have not been able to make large void-free disks is because our apparatus was primitive.

Because EPPI can be polymerized and processed easily, showed zero polymerization shrinkage, and is a very thermostable polymer, it is expected to be a good candidate for high-temperature composites as the matrix/reinforcement interfacial stresses will be minimized.

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