

## High Modulus and High $T_g$ Thermally Stable Polymers from *p*-Ethynyl-Terminated Rigid-Rod Monomers. 2

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**ABSTRACT:** Novel *p*-ethynyl-substituted rigid rod monomers were studied by pressure differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), isothermogravimetric analysis (IGA), and TGA-IR. These monomers, 4,4'-bis[[(4-ethynylphenyl)carbonyl]oxy]biphenyl, designated **1**, 1,5-bis[[(4-ethynylphenyl)carbonyl]oxy]naphthalene, designated **2**, and bis(4-ethynylphenyl)pyromellitimide, designated **3**, were polymerized in the solid state. Thermal polymerization in  $N_2$  or air produced highly cross-linked resins with polymerization exotherms centered between 212 and 276 °C. The  $\Delta H$ 's of polymerization of these resins in air were found to be double those in  $N_2$ . When monomers **1** and **2** were heated in air from 23 to 750 °C at 10 °C/min, the main decomposition product was carbon dioxide, evolving at a maximum rate between 500 and 600 °C; water was also detected as a decomposition product. Void-free neat resin moldings, designated **1p** to **3p**, were made by compression molding the monomers and then heating them. The resulting polymers were highly cross-linked, and their glass transition temperatures ( $T_g$ ) were much higher than their polymerization temperatures. Using thermomechanical analysis (TMA), we found that polymers **1p** to **3p** had  $T_g$ 's of 422, 329, and 380 °C, respectively. The thermal and thermooxidative stabilities improved when **1p** to **3p** were postcured in  $N_2$  (the postcured polymers were designated **1pp** to **3pp**). The linear thermal expansions (LTE) for **1p** and **3p** were 1% between 23 and 420 °C. Using rheological analysis, we could not clearly detect the  $T_g$ 's of **1p** to **3p** because their moduli dropped only slightly between 23 and 490 °C and the changes in  $\tan \delta$  were very low. Because of high cross-link density, their moduli changed little as the resins went from a glassy to a rubbery state. Their shear storage moduli in air ranged from 0.82 (**3p**, **3pp**) to 1.6 GPa (**1pp**) at 23 °C, from 0.16 (**2p**) to 0.7 GPa (**1pp**) at 380 °C, and from 0.18 (**1pp**) to 0.6 GPa (**2p**) at 490 °C. Finally, these novel *p*-ethynyl polymers exhibited an excellent combination of high  $T_g$ , low LTE, and high thermooxidative stability. Most notably, **3pp** lost only 3% of its initial weight when it was aged for 500 h at 288 °C in air.

### Introduction

Structural resins with a favorable combination of properties such as long-term environmental durability from -50 to +220 °C, damage tolerance, and solvent resistance are required for use in high-temperature areas of advanced and commercial aircraft. Epoxy systems, especially the new, toughened epoxies, exhibit excellent properties, but their short-term operating temperatures are limited to 177 °C. This paper describes our efforts to develop materials that could extend a composite's service life at temperatures greater than 177 °C by using acetylene-endcapped monomers as matrices.

Acetylene compounds, especially terminal arylacetylenes, are important intermediates in the syntheses of

several high-performance polymeric resins.<sup>1</sup> They have generated much interest as candidates for high-performance matrix resins for aircraft and aerospace applications. This interest hinges on several attractive features of these materials: an addition-curing mechanism that produces no volatiles and generates void-free laminates;<sup>2</sup> a thermally initiated cure requiring no added catalyst or hardener, which implies long shelf lives and batch-to-batch homogeneity approaching that of the thermoplastics;<sup>3</sup> high  $T_g$ 's;<sup>4-8</sup> and thermal stabilities made possible by incorporating wholly aromatic precursors into a heavily cross-linked polyene network. Furthermore, cross-linking improves the thermal and mechanical properties of cured ethynyl-terminated polymers (ETP's). Highly cross-linked ETP's show such desirable properties as excellent dimensional stability with low creep rates, high resistance to solvents, increased softening temperatures, and better thermal stability than linear polymers. These high-temperature properties, coupled with their moisture insensitivity, make ETP's promising thermosetting polymers. The cured

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Table 1. Processing Conditions for Monomers 1–3

monomer	pressure (psi)	temp (°C)	time (h)
1	1000	290	1
2	500	290	1
3	1000	325	1

resins are useful as both functional (films and coatings) and structural (adhesives and composite matrices) resins.<sup>6</sup>

In previous studies<sup>6</sup> meta-substituted ethynyl endcaps have been incorporated into high-temperature resins for several reasons: (a) the meta-substituted monomers (*m*-ETM's) polymerized completely, whereas para-substituted monomers (*p*-ETM's), because of their rigidity, did not; (b) the *m*-ETM melt temperatures were low compared to those of the *p*-ETM's; and (c) the *m*-ETM's had lower melting points, enabling them to flow and consolidate to yield void-free specimens. These monomers polymerized completely in spite of their rigid matrix, presumably because the acetylene groups<sup>5</sup> are closely interdispersed. Recent work in our labs<sup>5,7</sup> demonstrated that para-substituted acetylene monomers polymerized completely in the solid state and yielded high modulus, void-free resin moldings that retain some degree of crystallinity, as shown by X-ray diffraction. Furthermore, the *p*-ETP's were more rigid than the *m*-ETP's, thereby yielding both higher  $T_g$ 's and lower coefficients of thermal expansion than the *m*-ETP's. Some of the *p*-ETP's had zero polymerization shrinkage,<sup>5,7</sup> and these postcured resins decomposed before they softened. Moreover, they had flexural moduli  $E'$  of up to 4.8 GPa at 23 °C.<sup>5</sup>

One goal of this research was to demonstrate that three *p*-ETM's could be polymerized into neat resin moldings by heating. We were also interested in determining the effects of curing and postcuring on the thermomechanical properties of 4,4'-bis[[(4-ethynylphenyl)carbonyl]oxy]biphenyl, 1,5-bis[[(4-ethynylphenyl)carbonyl]oxy]naphthalene, and bis(4-ethynylphenyl)pyromellitimide. Isothermogravimetric analysis (IGA) was to be used to study their long-term thermooxidative stability. Additionally, we wanted to define the predominant decomposition routes during thermal and thermooxidative degradation of the systems.

### Experimental Procedure

4,4'-bis[[(4-ethynylphenyl)carbonyl]oxy]biphenyl, designated 1, 1,5-bis[[(4-ethynylphenyl)carbonyl]oxy]naphthalene, designated 2, and bis(*p*-ethynylphenyl)pyromellitimide, designated 3, were synthesized in our laboratory,<sup>5,7</sup> as previously reported. Rheological measurements were performed on a Rheometrics, Inc., RMS 800 mechanical spectrometer using a torsion rectangular mode at 0.5% strain with a temperature sweep up to 450 °C and a heating rate of 5 °C/min. Thermomechanical analysis (TMA) was recorded on a DuPont 943 TMA using a 5-g expansion probe at a scan rate of 10 °C/min in static air. The TMA experiments were conducted in duplicate. Differential scanning calorimetry (DSC) was performed in N<sub>2</sub> and in air under 200 psi pressure on a DuPont 910 calorimeter at a scan of 10 °C/min and recorded on a PL Thermal Sciences analysis system. Thermogravimetric analyses (TGA) were carried out in N<sub>2</sub> and air (50 mL/min flow rate) on a Perkin-Elmer TGS-2 at a scan rate of 10 °C/min.

**Neat Resin Processing.** Cylindrical D2 hardened steel molds with a diameter of either 2.5 or 5.5 cm that were equipped with a thermocouple and sprayed with a release agent (Frekote 44) were used to process neat resin disks. For example, the mold (5.5-cm diameter) was charged with 4.5 g of monomer (powder) and pressed for 3 min under 8–10 kpsi at 23 °C. The mold was then placed into a preheated press (processing temperature, Table 1) under low pressure (50 psi).

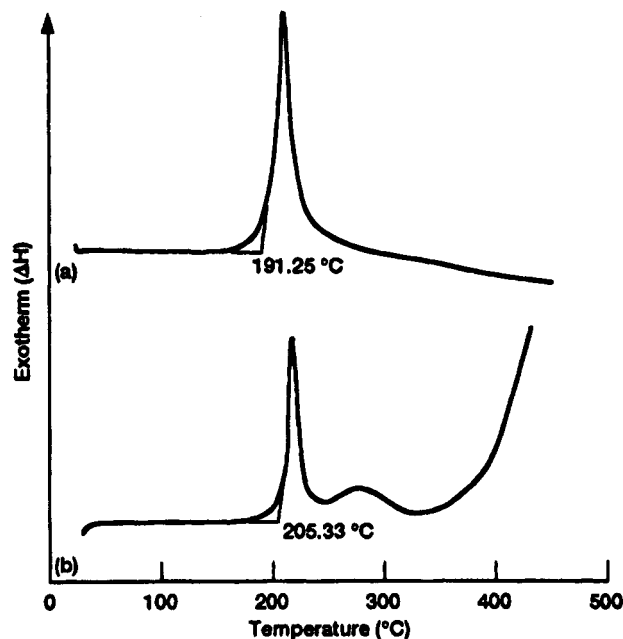


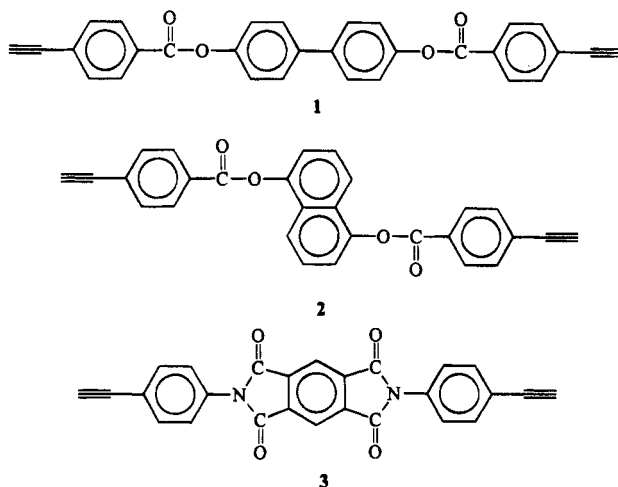
Figure 1. Pressure (200 psi) DSC thermograms of 1 (a) in N<sub>2</sub> and (b) in air.

Typically, the mold was heated at a rate of 20 °C/min. When the temperature of the mold reached 220–240 °C, pressure was applied according to the settings listed in Table 1. After 1 h in the press, the mold was cooled to 140 °C, whereupon the pressure was released. The resins were removed from the mold at 23 °C.

**Isothermal Aging.** Isothermal weight loss studies were conducted on postcured neat resin samples (five specimens per resin type; 0.4 cm by 0.4 cm by 1.5 mm) at 288 °C in a Blue M forced-hot-air oven under 1-atm flowing air. The oven temperature fluctuated  $\pm 7$  °C over the 500-h study.

### Results and Discussion

The chemical structures of *p*-ETM's 1–3 are shown as follows:



We denote their polymers by appending **p** to the monomer numbers (i.e., 1**p**–3**p**) and the postcured resins by appending a second **p** to the polymer abbreviation (i.e., 1**pp**–3**pp**). The synthesis and characterization of monomers 1–3 were done in our laboratory and have been reported elsewhere.<sup>5,7</sup> The curing behavior of these monomers was examined by pressure differential scanning calorimetry (DSC) at 200 psi in N<sub>2</sub> and air. Representative thermograms are shown in Figure 1, and the DSC data for 1–3 are listed in Table

Table 2. DSC and TGA Data for Monomers 1–3

mono- mer	DSC						TGA	
	N <sub>2</sub>			air			N <sub>2</sub>	air
	<i>T</i> <sub>ons</sub> <sup>a</sup> (°C)	<i>T</i> <sub>max</sub> <sup>b</sup> (°C)	Δ <i>H</i> (kcal/mol)	<i>T</i> <sub>ons</sub> (°C)	<i>T</i> <sub>max</sub> (°C)	Δ <i>H</i> (kcal/mol)	IDT <sup>c</sup> (°C)	IDT <sup>c</sup> (°C)
1	191	212	45	205	220	123	479	485
2	235	251	42	229	243	119	419	469
3	200	261	39	236	276	79	486	502

<sup>a</sup> Onset temperature of polymerization derived by extrapolation.

<sup>b</sup> Temperature at maximum polymerization rate. <sup>c</sup> Initial decomposition temperature derived by extrapolation.

2. Monomers 1–3 polymerized in the crystalline (solid) state. Their polymerization exotherms peaked between 212 and 276 °C, whether in N<sub>2</sub> or air. And their temperatures at maximum polymerization rate in N<sub>2</sub> and air were similar (Table 2). Although monomer 1 had the lowest temperature at maximum polymerization rate, it had the highest Δ*H* of polymerization. All three monomers showed one polymerization exotherm when they polymerized in N<sub>2</sub> and two exotherms [one major (Table 2) and one minor, centered at approximately 300 °C] when they polymerized in air (Figure 1). The Δ*H* of polymerization in air was double that in N<sub>2</sub> (Table 2).

These polymerization rate differences imply that air (oxygen) does not slow down the thermal polymerization of monomers 1–3. Previous literature on this issue has been confusing: one report suggested that oxygen slows down the polymerization of acetylenes;<sup>8</sup> another stated that acetylene-terminated monomers can be cured better in air than in N<sub>2</sub>.<sup>6</sup> Our data (Table 2) show that air (oxygen) did not slow down the initiation and the main polymerization step of monomers 1–3, since the onset and maximum rate temperatures (*T*<sub>onset</sub> and *T*<sub>max</sub>) for polymerization in N<sub>2</sub> and air are similar. The doubling of the Δ*H* of polymerization in air compared to that in N<sub>2</sub> could be explained by postulating that at higher temperatures oxygen initiates and participates in further reactions of the polyene system, thus generating a more highly cross-linked resin.

The thermal and thermooxidative stability of monomers 1–3 were evaluated by using TGA to determine whether monomers 1–3 polymerize to highly cross-linked resins in powder form when they are heated gradually (10 °C/min) to their decomposition temperature. If the thermal and thermooxidative stabilities of these monomers and their polymers were found to be similar, that would indicate that they polymerize readily to yield highly cross-linked resins. All monomers had higher initial decomposition temperatures (IDT) in air than in N<sub>2</sub> (Table 2). Notably, 2 had an IDT 50 °C higher in air than in N<sub>2</sub>. We attribute the higher IDT to the presence of oxygen, which could react with the polyene system to increase the polymer weight and thus counteract any loss due to volatility. Of all the monomers, 3 had the best thermal and thermooxidative stability.

Molding powders of 1–3 were analyzed in air by using TGA-IR<sup>9,10</sup> to determine the decomposition mechanisms of the three monomers. Examples of monomer 2's TGA thermogram and its derivative are shown in Figure 2. The IR spectra were recorded at specific times. Spectra taken at 57.7, 78.8, and 89.6 min and temperatures of 320, 530, and 640 °C, respectively, are shown in Figure 3. The weight losses measured at these times and temperatures were 2, 17, and 57%, respectively. From the derivative shown in curve b of Figure 2, the highest

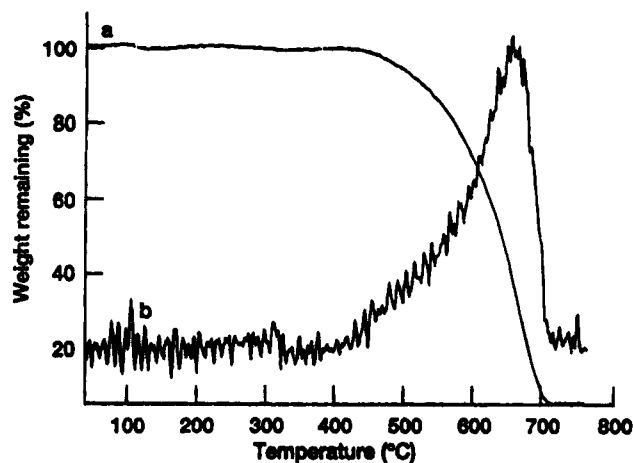


Figure 2. TGA thermogram (10 °C/min) (a) of 2 in air and (b) its derivative.

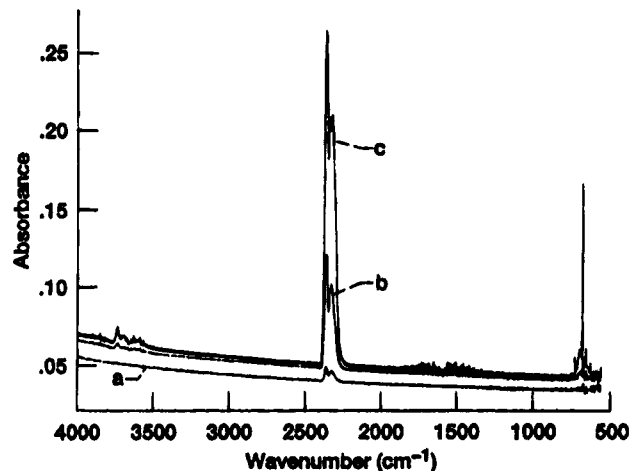


Figure 3. FTIR spectra for decomposition products (gas phase) of 2 corresponding to TGA curve a in Figure 2 at (a) 320, (b) 530, and (c) 640 °C.

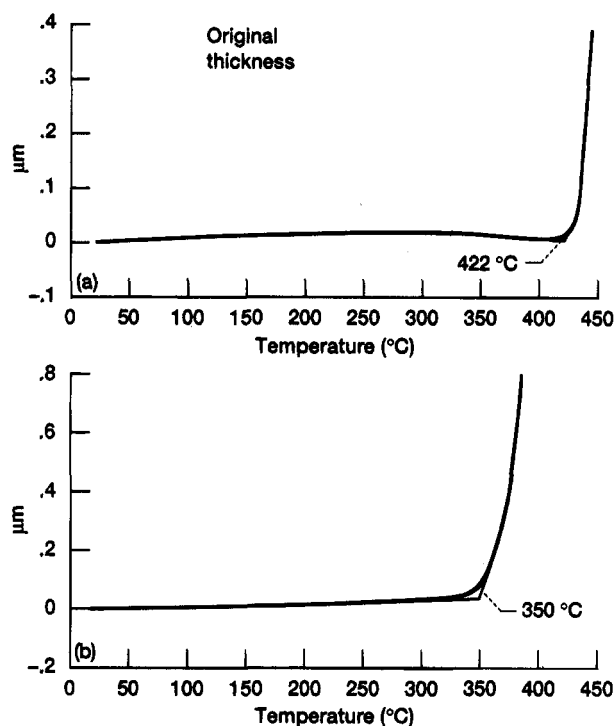
rate of weight loss for 2 occurred between 500 and 630 °C, with CO<sub>2</sub> being the primary decomposition product, accompanied by a small, yet detectable, amount of water. These products are associated with the absorption bands at 2335 and 3300–3600 cm<sup>-1</sup> in curve b of Figure 3 and probably result from dissociation of the ester bonds and oxidation of the polymer. The maximum decomposition rate for 2 occurs at 640 °C, where CO<sub>2</sub> and water were identified as decomposition products. Monomer 1 followed the same decomposition pattern, which suggests that the thermooxidative decomposition of *p*-ethynylbenzoyl esters is independent of the chemical structure of the aromatic group. However, 3 decomposed in a slightly different way: the onset for decomposition (IDT) was 15–30 °C higher than the IDT's for 1 and 2. The primary decomposition products for 3 were also CO<sub>2</sub> and a small amount of water. Unlike 1 and 2, however, 3 produced small amounts of phenyl-substituted isocyanate (Ph–N=C=O), which began to appear after 530 °C.

Films could not be made by casting a monomer solution and evaporating the solvent, because the monomers are highly crystalline and precipitate as powders. Therefore, processing conditions that involved solid state compaction and polymerization of 1–3 were developed. First, good polymer plates were made by compression molding 1–3; then these were heated (see conditions in Table 1). To understand how postcuring affects the thermal and thermomechanical properties,

**Table 3. Results of TMA and TGA of 1p–3p and 1pp–3pp in Air and in N<sub>2</sub>**

polymer	air		N <sub>2</sub>	
	TMA <sup>a</sup>		TGA	
	<i>T<sub>g</sub></i> (°C)	LTE <sup>c</sup> (%)	IDT <sup>c</sup> (°C)	IDT (°C)
1p	422	0.8	464	477
1pp	430	1.1	493	502
2p	329		418	412
2pp	350	2.1	440	431
3p	380	0.9	491	483
3pp	>400	0.6	503	510

<sup>a</sup> In static air; heating rate, 10 °C/min. <sup>b</sup> LTE from 23 °C to the *T<sub>g</sub>*. <sup>c</sup> Initial decomposition temperature.

**Figure 4.** TMA thermograms for (a) 1p and (b) 2p (static air; ramp, 10 °C/min).

1–3 were processed to polymer plates 1p–3p. The latter were postcured for 2 h at 315 °C in N<sub>2</sub>, yielding 1pp–3pp.

Dynamic TGA was used to evaluate the short-term thermal and thermooxidative stability of both the unpostcured and postcured neat resins (Table 3). The IDT's for 1–3 and 1p–3p are similar (see Tables 2 and 3), which demonstrates that monomers 1–3 readily polymerize (even by gradual heating at 10 °C/min from 23 to 350 °C) to yield highly cross-linked thermally stable resins. The IDT's of 1pp–3pp increased as a result of postcuring in air or N<sub>2</sub> (Table 3), although resins 2p and 2pp had the lowest IDT's of all the unpostcured and postcured resins. We also found that in N<sub>2</sub>, the IDT's of 1p and 3p were similar to those of 1pp and 3pp.

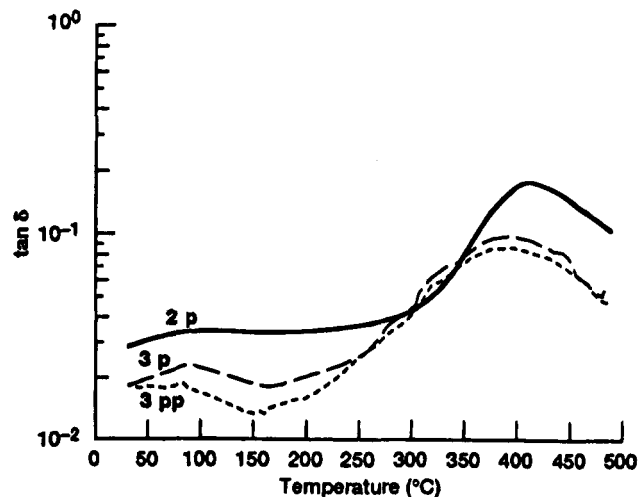
The *T<sub>g</sub>*'s of 1p–3p and 1pp–3pp could not be detected by DSC, presumably because the polymers were highly cross-linked and any change in heat capacity *C<sub>p</sub>* would be very small. Therefore, TMA was used to determine the *T<sub>g</sub>*'s as well as the thermal expansion of the polymers (Table 3). Figure 4 shows TMA thermograms representative of this series of polymers.

Based on the TMA thermogram, the *T<sub>g</sub>* was defined as the intersection of the two lines drawn by extrapolat-

**Table 4. Shear Storage Modulus of Polymers 1p–3p and Their Postcured Resins 1pp–3pp**

polymer	<i>G'</i> (GPa)			
	10 °C	200 °C	380 °C	490 °C
1p	1.3	0.7	0.2	0.2
1pp	1.6	1.5	0.7	0.18
2p	1.5	0.9	0.16	0.6
2pp <sup>a</sup>	0.45	0.39	0.23	<sup>b</sup>
3p <sup>c</sup>	0.8	0.6	0.4	0.27
3pp <sup>c</sup>	0.82	0.7	0.4	0.5

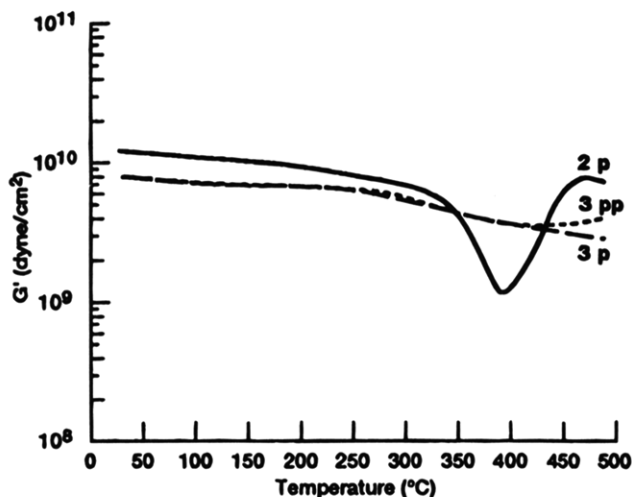
<sup>a</sup> Sample had 8% voids. <sup>b</sup> Sample broke at 400 °C. <sup>c</sup> Sample had 6% voids.

**Figure 5.** Temperature dependence of tan δs for 2p, 3p, and 3pp.

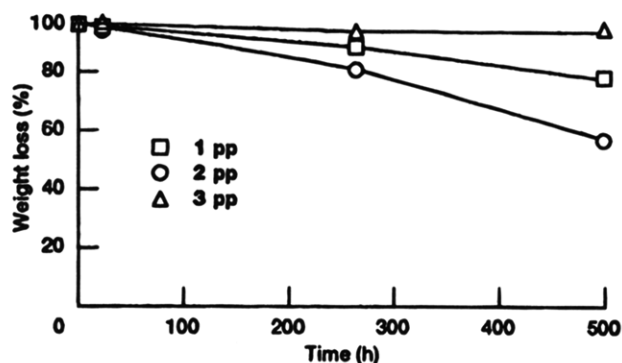
ing the horizontal and vertical parts of the TMA curve (Figure 4). The unpostcured resin with the highest *T<sub>g</sub>* was 1p; it was significantly higher (over 90 °C higher) than that of 2p. We presume this corresponds to the higher  $\Delta H$  of 1 versus that of 2, which suggests that the cross-link density of 1p is higher than that of 2p. When 1p–3p were postcured for 2 h at 315 °C in N<sub>2</sub>, there was only a slight increase in their *T<sub>g</sub>*'s (Table 3). In summary, the trend for the *T<sub>g</sub>*'s of the postcured polymers was 1pp > 3pp > 2pp.

Thermomechanical analysis was also used to evaluate the linear thermal expansion (LTE) of 1p–3p and 1pp–3pp. The LTE's of polymers 1p and 3p were less than 1% when they were heated from 23 to 420 °C (Table 3). Earlier studies<sup>5,7</sup> demonstrated that 1p and 3p had the same density as 1 and 3; there was zero polymerization shrinkage. Because these polymers had zero polymerization shrinkage and low LTE values, we feel that monomers 1 and 3 may potentially be used as matrices in composites.

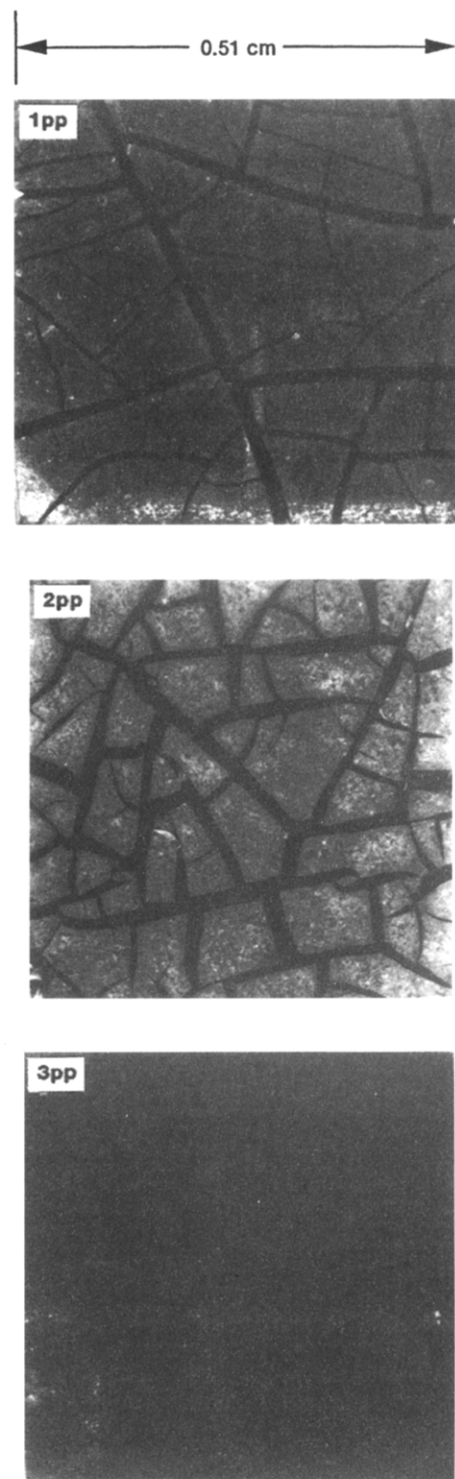
Dynamic mechanical analysis (DMA) measurements on polymers 1p–3p and neat resins 1pp–3pp showed the temperature dependence of the shear storage modulus *G'* (Table 4). Note that 1p, 1pp, and 2p have similar *G'*'s, at 23 °C, ~1.5 GPa, which corresponds to a Young's modulus of 4.2 GPa. These results are in good agreement with earlier studies conducted in our lab. The flexural moduli *E'* of biphenyl- and naphthalene-substituted polyesters<sup>5</sup> at 23 °C were 4.5 and 4.8 GPa, respectively. Although *G'* for 2pp is lower than that of the unpostcured 2p (Table 4), this does not mean that postcuring 2p yields a resin with lower *G'*. These samples were processed using different molds and heating presses. Polymer 2p processed very well and had a dark brown, shiny surface that indicates good

Figure 6. DMA thermograms of **2p**, **3p**, and **3pp**.Table 5. IGA in Air at 288 °C; % Weight Loss for Postcured Polymers **1pp**–**3pp**

polymer	postcure	weight loss (%) after			500 h (standard deviation <sup>a</sup> (%))
		24 h	265 h		
<b>1pp</b>	0.6	0.7	8.3		18.5 (1.2)
<b>2pp</b>	1.1	1.3	14.9		40.6 (0.7)
<b>3pp</b>	0.5	0.6	2.7		3.0 (0.4)

<sup>a</sup> Five samples each.Figure 7. IGA thermograms of **1pp**–**3pp** (aged at 290 °C in air).

consolidation; **2pp**, however, had a light brown, dull surface that implied scattering of light due to voids in the polymer sheet (poor consolidation). We found that **2pp** had 9% voids in some sections; these were responsible for its inferior thermomechanical properties.<sup>7</sup> Conversely, both **3p** and **3pp** have a similar  $G'$  at 23 °C,  $\sim 0.8$  GPa. These low values are due to 6% voids in some sections of the resin plaque.<sup>7</sup> Processing conditions were not optimized for all monomers; however, **1p** and **2p** were processed under well-defined conditions. In previous SEM studies<sup>5</sup> of biphenyl- and naphthalene-substituted polyesters, we showed that we were able to make cohesive, void-free, high modulus polymer sheet by solid state polymerization of and moderate pressure on rigid rod monomers. Only after the appropriate processing conditions are found will the maximum properties for **2pp**, **3p**, and **3pp** be determined. We did find that postcuring for 2 h in  $N_2$  at 315 °C improved the thermomechanical properties of these polymers. For example,  $G'$  of **1p** at 200 °C dropped to one-half that of  $G'$  at 20 °C, where  $G'$  of **1pp** at 200 °C remained the same as  $G'$  at 20 °C (Table 4). Note in Table 4 how the  $G'$  values of all the postcured resins constitute a larger

Figure 8. Optical micrographs for postcured polymers **1pp**–**3pp** after isothermal aging for 500 h at 290 °C in air.

fraction of their  $G'$  value at 20 °C than do those of the unpostcured polymers. Such results indicate that postcuring in  $N_2$  improved the thermomechanical properties of these polymers.

By using DMA, the  $T_g$ 's of the polymers were determined from the combination of their  $G'$  and  $\tan \delta$  data. The  $\tan \delta$ 's for **2p**, **3p**, and **3pp** (Figure 5) did not show distinct transitions (peaks) because of the small change in  $G'$ . The **2p**  $\tan \delta$  (Figure 5) showed a broad maximum centered at 420 °C. Its storage modulus (Figure 6) dropped by a factor of 5 from 300 °C (0.8 GPa) to 380 °C (0.16 GPa) and then rose to 0.4 GPa at 420 °C. The rise in  $G'$  between 380 and 420 °C was

attributed to chemical reactions that changed the chemical structure of the polymer. Thus, the values of  $G'$  above 380 °C reflect the properties of a degraded and reconstructed material much different from **2p**. That is why the midpoint in the log  $G'$  drop at 360 °C in Figure 6 was considered as the  $T_g$  of **2p**. The tan  $\delta$ 's of **3p** and **3pp** showed very broad shallow peaks centered between 390 and 490 °C (Figure 5), which might be the  $T_g$ . Because **3p** and **3pp** are heavily cross-linked, the changes in the properties at the transitions are very small and the results are equivocal. A similar  $T_g$  value for **3p** was found by using another type of DMA measurements<sup>7</sup> in our laboratory.

Isothermal thermogravimetric analysis (IGA) was used to evaluate the thermooxidative stability of **1pp**–**3pp**. Before isothermal aging, **1p**–**3p** were postcured to complete cross-linking and to increase their  $T_g$ 's. Earlier studies<sup>6,8</sup> reported that thermal polymerization and postcuring of acetylene-terminated resins in air rather than in  $N_2$  afforded resins better thermooxidative stability. Separate samples of **1p** and **2p** were postcured for 2 h at 315 °C in air and  $N_2$ . Subsequently, the samples were isothermally aged at 288 °C for 250 h in an air-circulating oven. After aging, the resins postcured in  $N_2$  lost only 5–6% of their weight, but the resins postcured in air lost 30–35% of their weight. Clearly, postcuring resins **1p** and **2p** in  $N_2$  at 315 °C increased their high-temperature oxidative stability. Presumably, the oxidation that took place during the air postcure caused accelerated weight loss of these polymers. After establishing that nitrogen postcuring produced lower weight losses for **1pp** and **2pp**, we did a second weight loss study that included all three polymers, **1pp**–**3pp**. For this study, samples were postcured for 2 h at 315 °C in  $N_2$ , and subsequently aged for 500 h at 288 °C in an air-circulating oven. The results from this study (Table 5) and the IGA thermograms of **1pp**–**3pp** (Figure 7) show that **3pp** is the most oxidatively stable polymer. It lost only 3% of its postcured weight after aging for 500 h at 288 °C. Only 0.3% of that loss occurred in the last 250 h. Of the two ETP's with ester linking groups, **1pp** had much higher thermooxidative stability than did **2pp**. The biphenyl-substituted **1pp** lost 18.5% by weight, whereas the naphthyl-substituted **2pp** lost 40.5%. Optical microphotographs of **1pp**–**3pp** taken after aging for 500 h at 288 °C in air are shown in Figure 8. Both **1pp** and **2pp** were cracked, the latter more severely, but **3pp** had no cracks at all. During periodic weighing, we noted that the cracks in **2pp** appeared after 200 h, whereas the cracks in **1pp** appeared only after 350 h. The qualitative evidence of cracking is in agreement with the quantitative weight loss data in Table 5.

## Summary and Conclusions

*p*-Ethynyl-substituted rigid rod monomers, 4,4'-bis-[[[(4-ethynylphenyl)carbonyl]oxy]biphenyl, designated **1**,

1,5-bis[[[(4-ethynylphenyl)carbonyl]oxy]naphthalene, designated **2**, and bis(4-ethynylphenyl)pyromellitimide, designated **3**, were polymerized in  $N_2$  and in air. Their  $\Delta H$ 's of polymerization in air were twice those in  $N_2$ . The main decomposition product for the three polymers (**1p**–**3p**) at high temperatures (over 450 °C) in air was  $CO_2$  that was evolved at a maximum rate between 500 and 600 °C.

Void-free neat resin moldings were made by compression molding and heating even though the monomers polymerized without melting. The polymers had  $T_g$ 's that were much higher than their processing (polymerization) temperatures; for example, **1p** had a  $T_g$  of 420 °C, which is 130 °C higher than its polymerization temperature. The linear thermal expansion for both **1p** and **3p** in air was 1% between 23 and 422 °C. When the three postcured polymers were heated from 23 to 450 °C, their shear storage moduli decreased only slightly, because of the extensive cross-linking through the ethynyl group. And when they were postcured in  $N_2$  rather than in air, their thermooxidative stabilities improved. In addition, **3p** lost only 3% of its initial weight, while maintaining structural integrity, after it was heated for 500 h at 288 °C in air.

We have demonstrated that void-free, completely polymerized resins can be made by solid state polymerization under moderate pressure. Furthermore, our results show that monomers **1** and **3** yield matrices with very high  $T_g$ 's and moduli; therefore, they may be good candidates for matrices in high-temperature composites. In addition, because they show zero polymerization shrinkage and have a linear thermal expansion of about 1% between 23 and 420 °C, the interfacial stress in the matrix–fiber bond should be minimized and, thus, their composites may exhibit good mechanical properties.

## References and Notes

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