afford 2.33 g (97%) of **13c** as a pale yellowish-white powder: $[\eta] = 0.54$ dL/g (25.0 °C, 1,1,2,2-tetrachloroethane).

**Sample Preparation for Melt Processing.** To 50 mL of stirred hexane (distilled prior to use) was added the appropriate amount of bis(triphenylphosphine)dicarbonylnickel(0) dissolved in a minimal amount of benzene (generally 7.5 mg of catalyst was dissolved in 0.5 mL of benzene). The catalyst was not soluble in hexane unless it was introduced in this manner. Next, 250 mg of the polymer sample was added. The suspension was stirred for 15 min, after which time the solvent was removed under reduced pressure to afford the polymer sample as a powder that was dried at 80 °C (15 mmHg) for 12 h. The recovered yield of the polymer sample was 75–95%.

**Neat Resin Film Melt Processing.** A Wabash hydraulic press (Model 12 10) that had been fitted with Carver heat platens (no. 2102) was used for the melt processing of neat resin films. The platens were heated to 350 °C while the polymer sample was prepared. A 200-mg powder sample of the polymer (with or without catalyst) was placed in an elliptical pile between two 3 in. × 3 in. pieces of copper foil (0.005 in. thick, Baker no. 1-1714). Two strips of 0.005-in. copper foil (0.25 in. × 3 in.) were used as spacers. The assembly was then placed between the preheated platens in the hydraulic press and melt-processed at 350 °C under a 5000-lb load for the desired amount of time. The platens were then cooled to 200 °C without releasing the pressure before the sample was taken out of the press and plunged into cold water. The copper foil was carefully peeled away from the film. If necessary, removal of the foil was facilitated by soaking the film adhering to the copper foil in concentrated ammonium hydroxide for 30 min. All films were thoroughly washed with water and air-dried prior to testing.

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# Biphenylene- and Phenyl-End-Capped Oligomeric Polyquinolines Containing Acetylene Linkages: Preparation, Processing, and Composite Application

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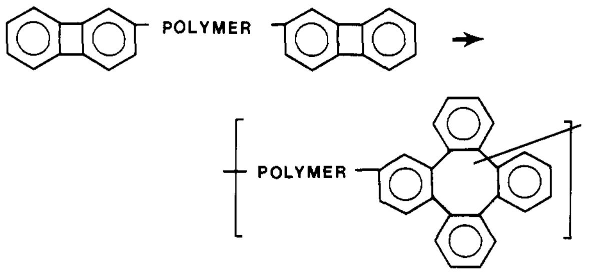
ABSTRACT: A series of oligomeric polyquinolines ($\overline{\mathrm{DP}} = 22$) containing acetylene linkages and capped by biphenylene or phenyl groups was prepared. The monomer, 4,4′-diacetyldiphenylacetylene, was used to incorporate the acetylene linkages. Oligomers with 0, 12.5, 25, 50, and 100% acetylene content per recurring unit were prepared by adjusting the amounts of the monomers in the polymerization reaction. Melt processing the oligomers at 350 °C under a 5000-lb load for 2 h with and without the catalyst bis(triphenylphosphine)dicarbonylnickel(0) gave high-quality films except for the oligomers with 100% acetylene content, which did not exhibit sufficient melt flow. Young's modulus above the $T_g$ of the cured resins increased with the amount of acetylene content for both the biphenylene- and phenyl-end-capped oligomers. The resins prepared from the oligomers with 25 and 50% acetylene content showed good to excellent retention of their mechanical properties above $T_g$. Graphite-cloth-reinforced composites were prepared by utilizing biphenylene-end-capped oligomeric polyquinolines containing acetylene linkages ($\overline{\mathrm{DP}} = 11$) as the matrix resin. The composites demonstrated excellent initial properties and low weight loss after oxidative aging at 316 °C. Useful mechanical properties were retained up to 400 h of isothermal aging at 316 °C.

## Introduction

Although a number of oligomeric, high-temperature polymers containing biphenylene end caps and/or biphenylene pendent groups have been investigated, the thermooxidative stability of the cured oligomers, particularly under isothermal aging conditions, has been quite poor.[1,2] This lack of thermooxidative stability of the cured resins has been attributed to the instability of the biphenylene reaction product, tetraphenylene (eq 1).[2]



(1)

In order to utilize this versatile, reactive group for cross-linking oligomeric aromatic polymers, it was clear that an alternate reaction that did not generate the tetraphenylene unit was desirable. In addition, this reaction should be capable of taking place under the appropriate

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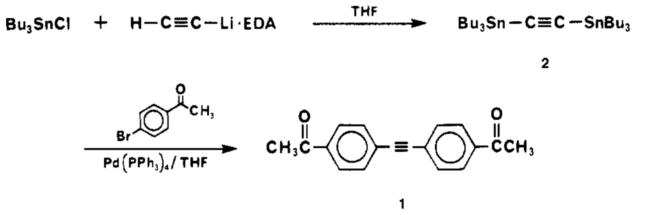
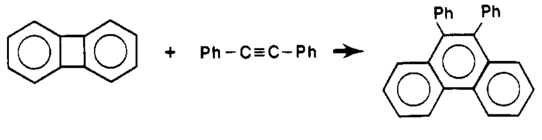
**Scheme I**



reaction conditions (temperature) without generating volatile byproducts and at the same time yield a thermally stable link.

Biphenylene is known to react with diphenylacetylene under thermal[3] and nickel-catalyzed[4] conditions to yield 9,10-diphenylphenanthrene (eq 2). The use of this reaction as a mode of cross-linking in curing a resin appeared to meet all the requirements. Thus the synthesis and reactions of an oligomeric polyquinoline matrix resin containing biphenylene end caps and diarylacetylenic units in the main chain were undertaken. The resulting cross-linking unit could be expected to show the desired thermal stability.[5]



(2)

## Results and Discussion

**Monomer Synthesis.** A polyquinoline synthesis utilizing the bis(ketomethylene) monomer 4,4′-diacetyldiphenylacetylene (1) would allow the incorporation of acetylene linkages in the backbone of biphenylene-end-capped oligomeric polyquinolines. The synthesis of 1 involved a palladium-catalyzed coupling of bis(tributylstannyl)acetylene (2) with 2 equiv of 4-bromoacetophenone (Scheme I). Bis(tributylstannyl)acetylene (2) was prepared in 82% yield by allowing tributyltin chloride to react with an excess of lithium acetylide in refluxing tetrahydrofuran. The intermediate (tributylstannyl)acetylene was deprotonated by the excess lithium acetylide, and subsequent reaction of the anion with tributyltin chloride afforded 2. The palladium-catalyzed cross-coupling of 2 with 2 equiv of 4-bromoacetophenone gave 1, which crystallized from the reaction mixture in 66% yield.

**Oligomer Synthesis and Properties.** A series of five reactive oligomeric polyquinolines of $\overline{DP}$ = 22 was prepared by the copolymerization of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**3**), 4,4′-diacetyldiphenyl ether (**4**), and 4,4′-diacetyldiphenylacetylene (**1**). The proper imbalance of monomer functionalities was maintained through an excess of the *o*-amino ketone functionality. The amount of diphenylacetylene incorporated was such that 0, 12.5, 25, 50, and 100% (designated **a**–**e**) of the repeat units contained diphenylacetylene (Scheme II). Each of the five oligomers was end-capped with 2-acetylbiphenylene (oligomers **5a**–**e**) and acetophenone (oligomers **6a**–**e**). The effectiveness of the internal acetylene linkage as a cross-linking reagent by itself could be determined by making both biphenylene-end-capped and phenyl-end-capped oligomers. The phenyl-end-capped oligomers also served as a control by providing information as to what added effect the biphenylene end cap would impart to the cured oligomers.

In order to verify that the internal acetylene linkage would survive the polymerization conditions, model compound 8 was prepared (Scheme III). Analysis of the product by $^1$H NMR showed no aliphatic protons; the product was wholly aromatic. A $^{13}$C NMR spectrum of the isolated product indicated the presence of an acetylenic carbon (91.0 ppm). Differential scanning calorimetry (DSC) of 8 showed an exotherm with a maximum at 430 °C, which was due to reaction of the acetylenic bond.

The increased rigidity of the oligomers as more acetylene linkages were incorporated in the chain was reflected by an increase in the $T_g$'s (Table I). How the increased rigidity would affect their flow properties and ultimately the curing of the oligomers was not known. However, **5e** and **6e**, which are the most rigid oligomers, containing 100% incorporation of acetylene linkages in the repeat unit, showed $T_g$'s of only 248 °C, which was thought to be still low enough so as not to adversely affect their flow properties.

**Scheme II**

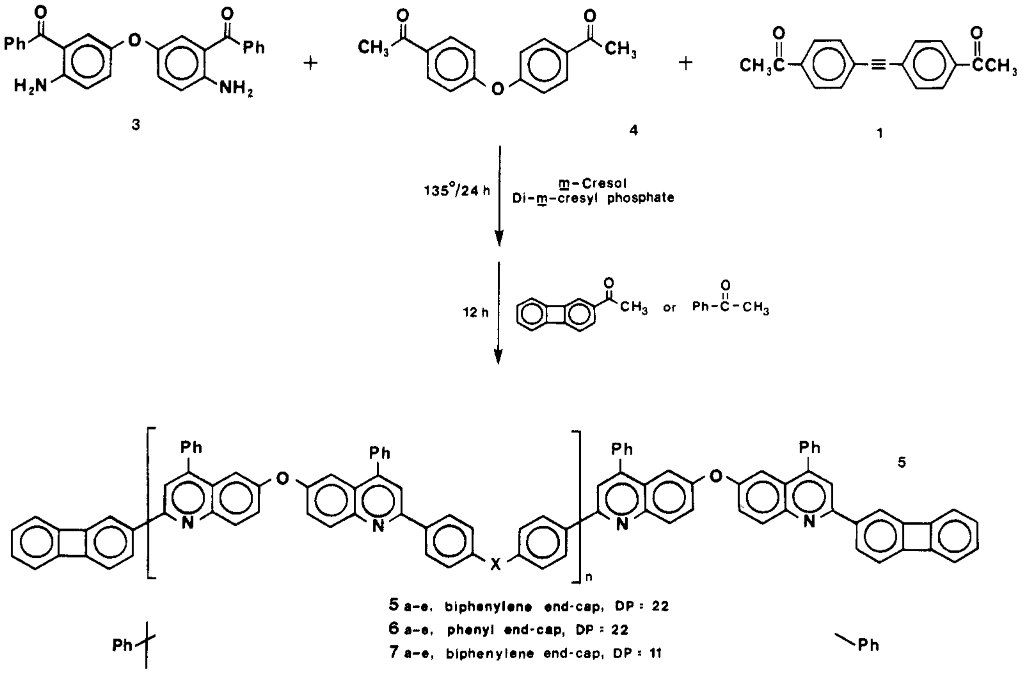
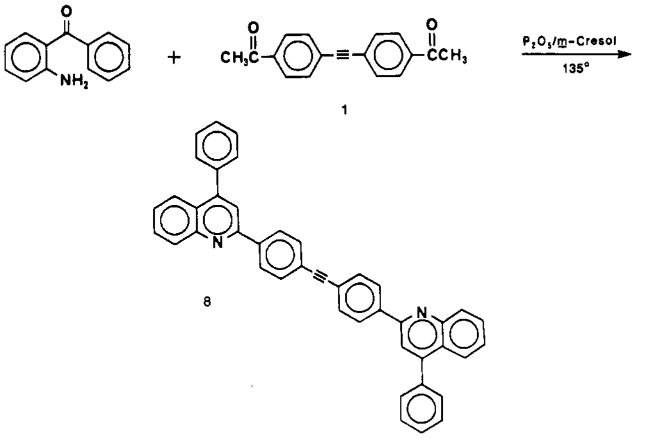


Table I
Dependence of $T_g$ and Exothermic Maximum on the Percent Acetylene Content of Biphenylene- and Phenyl-End-Capped Oligomeric Polyquinolines

| | biphenylene end cap | | | | phenyl end cap | | |
|---|---|---|---|---|---|---|---|
| % acetylene[a] | oligomer | $T_g$, °C | acetylene exo max, °C | biphenylene exo max, °C | oligomer | $T_g$, °C | acetylene exo max, °C |
| 0 | **5a** | 223 | c | 497 | **6a** | 224 | c |
| 12.5 | **5b** | 225 | 440 | b | **6b** | 227 | 442 |
| 25 | **5c** | 231 | 431 | b | **6c** | 230 | 433 |
| 50 | **5d** | 236 | 419 | b | **6d** | 238 | 423 |
| 100 | **5e** | 244 | 404 | b | **6e** | 248 | 407 |

[a] Per repeat unit. [b] Not observed. [c] Not determined.

Scheme III



The exothermic maximum (DSC) for the reaction of the acetylene linkages with the biphenylene unit ranged from 404 to 442 °C, increasing as the amount of diphenylacetylene decreased (Table I). Only in the DSC of **5a**, which had no acetylene linkages, was an exotherm for the exclusive ring-opening reaction of biphenylene observed, in agreement with the idea that the exotherm for **5b–e** probably was due to a reaction of the biphenylene end caps with the acetylene. It also is possible that the biphenylene exotherm, which is usually only a moderately intense transition, could have been buried under the downslope of the strong exothermic transition for the reaction of the acetylene linkages and/or under the exotherm due to the onset of decomposition. However, a closer inspection of the area on the DSC traces of **5b–e** where the biphenylene exotherm should have occurred indicated that if biphenylene was present after reaction with the acetylenic link, it would have been observed.

All of the oligomers prepared were soluble in chloroform. The increased chain rigidity—as the acetylene content increased—resulted in an increase in the dilute solution viscosity (Table II). A plot of ln [η] vs. the percent acetylene content of **5a–e** showed a linear increase from 0 to 100% (Figure 1).

Biphenylene-end-capped oligomeric polyquinoline **5a** underwent a complete cure when melt-processed for 15 min at 350 °C under a 5000-lb load in the presence of 20 mol % (based on the amount of biphenylene) of the catalyst bis(triphenylphosphine)dicarbonylnickel(0).[6] When oligomers **5b–e** were cured under the same conditions, the DSC showed a strong exotherm due to residual acetylene in all of the cured resins. In order to determine the conditions that would provide a complete cure of the acetylene linkages, a DSC cure study was performed.

Four samples of oligomer **6e**, which had the highest acetylene content, were cured in the DSC at 350 °C for 30 min, 1 h, 2 h, and 4 h. All of the cured resins showed residual acetylene when analyzed by DSC. A more complete cure was realized after 2 h in comparison to the 30-min and 1-h cures. The 4-h-cured sample showed no improvement in the extent of the cure over the 2-h sample. When **6e** was cured for 2 h in the DSC at 375 °C, no exotherm due to residual acetylene was observed. Thus, the appropriate cure conditions for oligomers **5** and **6** were 375 °C, 2 h, and 5000 lb. Due to equipment limitations, the oligomers were melt-processed at 350 °C instead.

Table II
Dependence of [η] on the Percent Acetylene Content of Biphenylene- and Phenyl-End-Capped Oligomeric Polyquinolines

| % acetylene | biphenylene-end-capped oligomer | [η], dL/g | phenyl-end-capped oligomer | [η], dL/g |
|---|---|---|---|---|
| 0 | **5a** | 0.47 | **6a** | 0.49 |
| 12.5 | **5b** | 0.51 | **6b** | 0.50 |
| 25 | **5c** | 0.56 | **6c** | 0.55 |
| 50 | **5d** | 0.70 | **6d** | 0.70 |
| 100 | **5e** | 1.02 | **6e** | 0.99 |

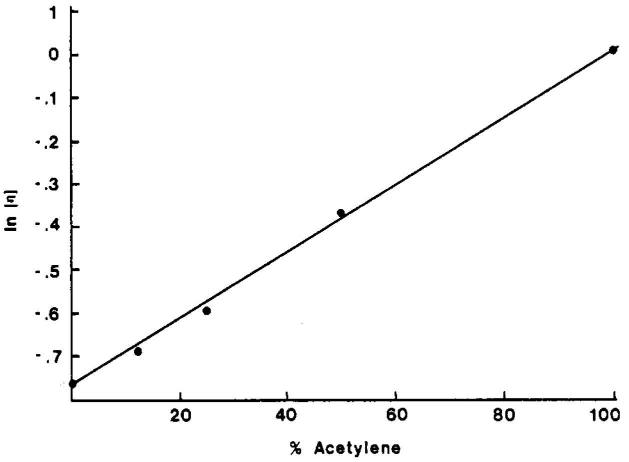


**Figure 1.** ln [η] vs. percent acetylene per recurring unit for biphenylene-end-capped oligomers **5**.

Each sample was processed with and without 20 mol % (based on the amount of biphenylene or phenyl end cap) bis(triphenylphosphine)dicarbonylnickel(0). High-quality films were obtained when **5b–d** and **6b–d** were melt-processed at 350 °C, 2 h, and 5000 lb, both with and without catalyst. The films were tough, transparent, and completely insoluble in chloroform. The magnitude of the slightly advanced glass transitions of catalytically and thermally cured **5d** and **6d** was minimal, whereas **5b**, **5c**, **6b**, and **6c** displayed strong glass transitions (Tables III and IV).

Of the oligomers with no acetylene linkages (**5a** and **6a**), only **5a**, when cured with catalyst, was completely insoluble. When **5a** was cured thermally, an exotherm (490 °C) in the cured sample was evident as a result of residual biphenylene and the cured resin was totally soluble in

Table III
Properties of Melt-Processed Biphenylene-End-Capped Oligomers[a]

| | | catalytically cured[b] | | | | thermally cured | | | |
|---|---|---|---|---|---|---|---|---|---|
| oligomer | % acetylene | uncured $T_g$, °C | cured $T_g$, °C | $\Delta T_g$, °C | exo max, °C | uncured $T_g$, °C | cured $T_g$, °C | $\Delta T_g$, °C | exo max, °C |
| **5a** | 0 | 223 | 245 | 22 | *d* | 223 | 238 | 15 | 490 |
| **5b** | 12.5 | 225 | 253 | 28 | 419 | 225 | 252 | 27 | 458 |
| **5c** | 25 | 231 | 252 | 21 | 443 | 231 | 257 | 26 | 480 |
| **5d** | 50 | 236 | 249 | 13 | 455 | 236 | 248 | 12 | 485 |
| **5e** | 100 | 244 | *c* | *d* | 482 | 244 | *b* | *d* | >500 |

[a] Melt-processed at 350 °C under a 5000-lb load for 2 h. [b] Cured in the presence of 20 mol % $(PPh_3)_2Ni(CO)_2$. [c] No $T_g$ was observed. [d] Not determined.

Table IV
Properties of Melt-Processed Phenyl-End-Capped Oligomers[a]

| | | catalytically cured[b] | | | | thermally cured | | | |
|---|---|---|---|---|---|---|---|---|---|
| oligomer | % acetylene | uncured $T_g$, °C | cured $T_g$, °C | $\Delta T_g$, °C | exo max, °C | uncured $T_g$, °C | cured $T_g$, °C | $\Delta T_g$, °C | exo max, °C |
| **6a** | 0 | 224 | 224 | 0 | *d* | 224 | 232 | 8 | *d* |
| **6b** | 12.5 | 227 | 240 | 13 | 436 | 227 | 241 | 14 | 461 |
| **6c** | 25 | 231 | 247 | 17 | 445 | 230 | 242 | 22 | 461 |
| **6d** | 50 | 238 | 249 | 11 | 458 | 238 | 243 | 5 | 469 |
| **6e** | 100 | 240 | *c* | *d* | >500 | 248 | *b* | *d* | >500 |

[a] Melt-processed at 350 °C under a 5000-lb load for 2 h. [b] Cured in the presence of 20 mol % $(PPh_3)_2Ni(CO)_2$. [c] No $T_g$ was observed. [d] Not determined.

Table V
Film Mechanical Properties of Melt-Processed Biphenylene-End-Capped Oligomeric Polyquinolines[a]

| | | catalyzed cure[b] | | thermal cure | |
|---|---|---|---|---|---|
| oligomer | % acetylene | $E'$ at 25 °C, dyn/cm$^2$ | $E'$ above $T_g$,[c] dyn/cm$^2$ | $E'$ at 25 °C, dyn/cm$^2$ | $E'$ above $T_g$,[c] dyn/cm$^2$ |
| **5a** | 0 | $2.28 \times 10^{10}$ | $8.97 \times 10^7$ (303) | | |
| **5b** | 12.5 | $3.00 \times 10^{10}$ | $3.34 \times 10^8$ (304) | $3.06 \times 10^{10}$ | $1.81 \times 10^8$ (303) |
| **5c** | 25 | $2.70 \times 10^{10}$ | $1.50 \times 10^9$ (295) | $2.84 \times 10^{10}$ | $6.69 \times 10^8$ (300) |
| **5d** | 50 | $2.92 \times 10^{10}$ | $8.40 \times 10^9$ (292) | $2.14 \times 10^{10}$ | $7.29 \times 10^9$ (290) |

[a] Melt-processed at 350 °C under a 5000-lb load for 2 h. [b] Cured in the presence of 20 mol % $(PPh_3)_2Ni(CO)_2$. [c] Temperature at which the storage modulus ($E'$) was observed is given in °C.

Table VI
Film Mechanical Properties of Melt-Processed Phenyl-End-Capped Oligomeric Polyquinolines[a]

| | | catalyzed cure[b] | | thermal cure | |
|---|---|---|---|---|---|
| oligomer | % acetylene | $E'$ at 25 °C, dyn/cm$^2$ | $E'$ above $T_g$,[c] dyn/cm$^2$ | $E'$ at 25 °C, dyn/cm$^2$ | $E'$ above $T_g$,[c] dyn/cm$^2$ |
| **6b** | 12.5 | $3.07 \times 10^{10}$ | $1.13 \times 10^8$ (295) | $1.74 \times 10^{10}$ | $6.12 \times 10^7$ (294) |
| **6c** | 25 | $2.79 \times 10^{10}$ | $3.80 \times 10^8$ (301) | $2.92 \times 10^{10}$ | $3.29 \times 10^8$ (294) |
| **6d** | 50 | $2.99 \times 10^{10}$ | $3.90 \times 10^9$ (300) | $2.97 \times 10^{10}$ | $5.51 \times 10^9$ (296) |

[a] Melt-processed at 350 °C under a 5000-lb load for 2 h. [b] Cured in the presence of 20 mol % $(PPh_3)_2Ni(CO)_2$. [c] Temperature at which the storage modulus was observed is given in °C.

Table VII
Thermooxidative Stability of Cured Biphenylene- and Phenyl-End-Capped Oligomers with Acetylene Linkages When Aged for 100 h at 316 °C

| | % wt loss, biphenylene end capped | | | % wt loss, phenyl end capped | | |
|---|---|---|---|---|---|---|
| % acetylene | oligomer | catalyzed cure | thermal cure | oligomer | catalyzed cure | thermal cure |
| 0 | **5a** | 6.8 | *a* | **6a** | *a* | *a* |
| 12.5 | **5b** | 43.0 | 68.6 | **6b** | 45.2 | 81.6 |
| 25 | **5c** | 38.2 | 77.3 | **6c** | 54.7 | 88.3 |
| 50 | **5d** | 43.7 | 67.2 | **6d** | 47.1 | 81.5 |
| 100 | **5e** | 47.3 | 45.9 | **6e** | 44.4 | 66.8 |

[a] Samples had weight losses greater than 75% at 25 h.

chloroform. This clearly demonstrated the need for a catalyst to effect the ring-opening reaction of biphenylene at the lower processing temperature. Oligomers **5e** and **6e** afforded poor-quality, brittle, opaque films when melt-processed with or without catalyst, but cross-linking did occur since the films were completely insoluble in chloroform.

The effect of temperature on the storage modulus (Rheovibron) showed that as the amount of acetylene incorporated in an oligomer was increased, a greater retention of the mechanical properties above $T_g$ was realized (Tables V and VI). For catalytically cured biphenylene-end-capped **5**, Young's modulus above $T_g$ increased by about half an order of magnitude for each increase in the

**Table VIII**

**Solution and Thermal Properties of Biphenylene-End-Capped Oligomeric Polyquinolines with Acetylene Linkages ($\overline{DP}$ = 11)**

| oligomer | % acetylene | acetylene/ biphenylene ratio | $[\eta]$,[a] dL/g | $T_g$, °C | acetylene exo max, °C | biphenylene exo max, °C |
|---|---|---|---|---|---|---|
| **8a** | 25.6 | 0.72 | 0.289 | 212 | 425 | 498 |
| **8b** | 35.6 | 1.00 | 0.315 | 213 | 426 | 491 |
| **8c** | 45.6 | 1.28 | 0.344 | 215 | 418 | 491 |

[a] Viscosity measurements were obtained from chloroform solutions.

acetylene content (**5a–d**). Thus, an overall improvement by 2 orders of magnitude was realized. Oligomer **5d** suffered only half an order of magnitude loss in Young's modulus from its room-temperature value to a temperature above its $T_g$, a significant improvement in the 2 orders of magnitude loss suffered by **5a** (Figure 2). Internal acetylenes apparently are effective cross-linking reagents, since biphenylene-end-capped oligomers **5b–d** displayed only slightly improved mechanical properties over those of the phenyl-end-capped oligomers **6b–d**.

Isothermal aging of the cured films in air (Table VII) showed that samples cured in the presence of the nickel catalyst afforded resins that displayed better weight retention. (The weight losses of **5e** and **6e** should be interpreted with caution because, due to their brittleness, aging samples of uniform dimensions were not obtained.) Although little difference was observed in the mechanical properties of thermally and catalytically cured films (Tables V and VI), a catalyzed cure may have been more efficient than a thermal cure and resulted in a more complete consumption of the reactive functionalities. Thus, fewer initiation sites for thermooxidative degradation would have been left in catalytically cured films, imparting greater thermal resistance and better weight retention properties. In general, weight loss increased with decreasing acetylene content. When complete cures were obtained (**5d** and **6d**, Tables III and IV), the better stability of catalytically cured films over thermally cured films is quite apparent.

**Preparation of Graphite-Fiber Composites Utilizing Biphenylene-End-Capped Oligomeric Polyquinolines with Acetylene Linkages as Matrix Resins.** A primary interest in melt-processable reactive oligomers is in their use as matrix resins for fiber-reinforced composites. Graphite-fiber- and graphite-cloth-reinforced composites that utilized **5a** as a laminating resin have been shown to display good initial mechanical properties.[1] However, when postcured in air for 50–100 h, the composites displayed severely diminished mechanical properties, although weight loss during aging was only 1–2.5%. The aged composites also failed to give a metallic-like ring when dropped on a hard surface. These observations suggested that the cured biphenylene-end-capped matrix resins were not particularly thermooxidatively stable.[1] The instability was attributed to either residual biphenylene or the product of the cross-linking reaction, tetraphenylene, both of which could be a source of high-energy radicals that initiate a degradative process by reacting with oxygen.

More recent results[2] also indicate that both biphenylene and tetraphenylene are thermooxidatively unstable. Biphenylene appeared to be significantly less stable than tetraphenylene since a resin with residual biphenylene, which was obtained under inappropriate cure conditions, showed a greater weight loss than a resin with no residual biphenylene. Thus, biphenylene-end-capped oligomeric polyquinolines with acetylene linkages were good candidates for use as matrix resins in fiber-reinforced composites, provided that complete consumption of the acetylenic linkages and biphenylene could be effected.

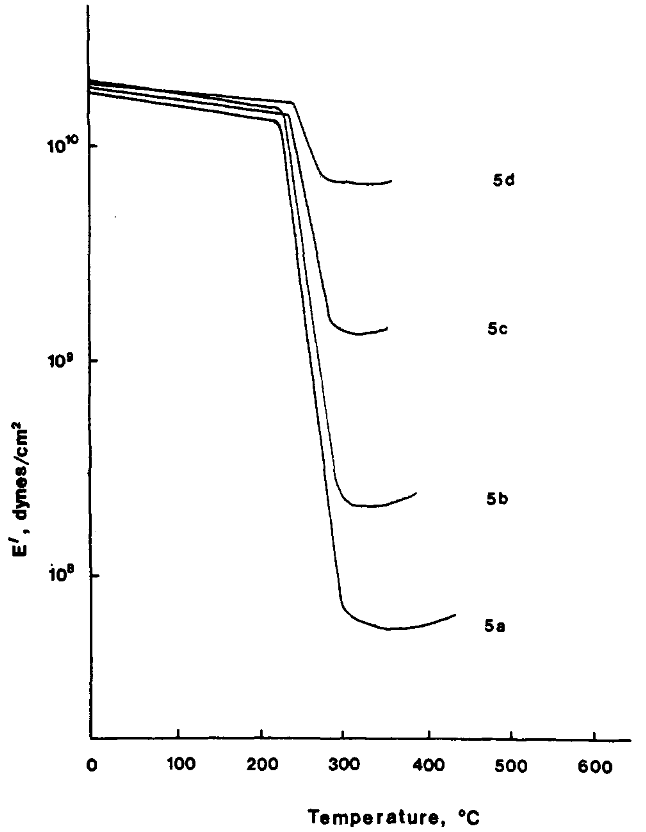


**Figure 2.** Comparison of Young's modulus as a function of temperature for biphenylene-end-capped oligomers 5.

**Oligomer Synthesis and Properties.** Because of the inherent problems associated with prepreg preparation utilizing unidirectional graphite fiber and biphenylene-end-capped oligomeric polyquinoline **5a** of $\overline{DP}$ = 22,[1] the oligomers prepared for this study had a $\overline{DP}$ = 11 (**7a–c**). It was anticipated that chloroform solutions of **7** would have better wetting characteristics by virtue of their lower viscosity.

Biphenylene-end-capped oligomers **7a–c** were prepared in the same way as **5a–e** except a stoichiometric imbalance of monomers was used in order to give oligomers with a calculated $\overline{DP}$ of 11. The amount of diphenylacetylene incorporated was such that 25.6, 35.6, and 45.6% of the repeat units contained acetylene linkages, corresponding to acetylene/biphenylene ratios for **7a–c** of 0.720, 1.00, and 1.28, respectively. Due to the higher concentration of biphenylene in the oligomers with $\overline{DP}$ = 11, the exothermic maxima of biphenylene were distinctly observable (Table VIII).

**Neat Resin Processing.** To determine the appropriate cure and postcure conditions to be used for the preparation of graphite-fiber- and/or -cloth-reinforced composites, neat resin disks, 0.786-in. diameter, of **7a–c** were made. This technique allowed the utilization of a minimum amount of sample (e.g., 200–600 mg) to obtain the cure information. Melt processing at 2000 psi gave tough, homogeneous disks,

Table IX
**Comparison of the $T_g$ Advancement of Catalytically and Thermally Cured Neat Resin Samples during a Postcure Cycle**

| | | postcure conditions | | | | |
|---|---|---|---|---|---|---|
| oligomer | cure[a] | none | 12 h/316 °C | 35 h/316 °C | 75 h/316 °C | 12 h/316 °C + 6 h/344 °C |
| **8a** | catalytic | 234 | 273 | 304 | 336 | 291 |
| **8b** | catalytic | 241 | 288 | 329 | 349 | 354 |
| **8c** | catalytic | 271 | 323 | 334 | 350 | 362 |
| **8a** | thermal | 281 | 294 | 328 | 350 | 334 |
| **8b** | thermal | 291 | 315 | 338 | 354 | 360 |
| **8c** | thermal | 312 | 327 | 347 | 351 | *b* |

[a] Thermal cure conditions: 375 °C under 2000 psi for 2 h. Catalytic cure conditions: 330 °C under 2000 psi for 2 h in the presence of 2.5 wt % $(PPh_3)_2Ni(CO)_2$. [b] No $T_g$ observed.

while 500 psi afforded disks filled with voids. Each oligomer was processed with and without catalyst. After their preparation, the resin disks were cut into small pieces and postcured. Thermomechanical analysis (TMA) was used to follow the $T_g$ advancement of the samples during the postcure study and served to determine the effectiveness of a postcure condition.

The $T_g$'s (TMA) of the catalytically cured oligomers were initially 40–50 °C lower than those of their thermally cured analogues (Table IX). The 375 °C cure temperature is well above the onset of the acetylenic linkage exotherm, whereas 330 °C is below the onset of the exotherm. Although bis(triphenylphosphine)dicarbonylnickel(0) lowered the temperature of the ring-opening reaction of biphenylene and also lowered the reaction temperature of acetylenes somewhat, the extent of cross-linking with the catalyst at the lower temperature is obviously not as great as the higher 375 °C thermal cure. However, after a postcure at 316 °C for 75 h, the $T_g$ values were comparable, and regardless of the percent acetylene content, the $T_g$ reached a maximum value of about 350 °C. Short postcure times at higher temperatures (Table IX) afforded results similar to long postcure times at lower temperatures, with the exception of catalytically cured **7a**.

Analysis of the neat resin samples with no postcure by DSC showed that only the thermally cured samples achieved a complete cure. No residual acetylene or biphenylene was observed. In contrast, the catalytically cured samples showed considerable amounts of residual acetylene and biphenylene because of the lower cure temperature used. The results of the TMA and DSC studies indicated that a high-temperature thermal cure was more effective than a lower temperature, catalyzed cure.

**Composites.** The original intent of this work was to prepare unidirectional graphite-fiber-reinforced composites. However, when a chloroform solution of **7a** ($\overline{DP}$ = 11) was brush-coated onto the fiber, a boardy prepreg that shrunk to half its original size was obtained. Additionally, the solution did not entirely impregnate the fiber. No polymer was observed on the backside of the prepreg. These same problems were experienced when graphite fiber was impregnated with a solution of $\overline{DP}$ = 22 biphenylene-end-capped oligomer **5a**.[1]

To improve the quality of the prepreg, graphite cloth was used as the fiber reinforcement for the composites. A chloroform solution of each oligomer was brush-coated onto both sides of a piece of graphite cloth that was restrained on all four edges. After the solvent had evaporated, a boardy, but good-quality prepreg was obtained. The prepreg was cut into 0.9 × 2.5 in. pieces that were melt-processed as 6-ply layups at 370 °C (725 °F) under 1500 psi for 2 h. A test composite that was melt-processed under 2000 psi at the same temperature had excessive flash (resin that oozed out of the composite during processing). To minimize the loss of resin due to flash, the processing pressure was reduced to 1500 psi. All of the composites were prepared with 30% resin content, had a good ap-

Table X
**Room-Temperature Flex Strength ($10^3$ psi) of Composites Prepared from Biphenylene-End-Capped Oligomeric Polyquinolines with Acetylene Linkages and Celion-3000 Graphite Cloth**

| oligomer (% acetylene) | postcure conditions | | isotherm. aged at 316 °C in air | | | |
|---|---|---|---|---|---|---|
| | none | 8 h/343 °C | 100 h | 200 h | 300 h | 400 h |
| **8a** (25.6) | 88.2 | 83.0 | *a* | 37.1 | *a* | 18.6 |
| **8b** (35.6) | 94.9 | 113 | 106 | 82.9 | 74.4 | 47.5 |
| **8c** (45.6) | 102 | 95.0 | 100 | 66.6 | 47.0 | 35.1 |

[a] Not determined.

Table XI
**Room-Temperature Flex Modulus ($10^6$ psi) of Composites Prepared from Biphenylene-End-Capped Oligomeric Polyquinolines with Acetylene Linkages and Celion-3000 Graphite Cloth**

| oligomer (% acetylene) | postcure conditions | | isotherm. aged at 316 °C in air | | | |
|---|---|---|---|---|---|---|
| | none | 8 h/343 °C | 100 h | 200 h | 300 h | 400 h |
| **8a** (25.6) | 11.2 | 10.2 | *a* | 10.7 | *a* | 1.43 |
| **8b** (35.6) | 11.2 | 9.38 | 10.4 | 9.35 | 7.19 | 4.71 |
| **8c** (45.6) | 11.2 | 9.99 | 11.6 | 8.72 | 7.46 | 4.30 |

[a] Not determined.

Table XII
**Flex Strength ($10^3$ psi) at 316 °C (600 °F) of Composites Prepared from Biphenylene-End-Capped Oligomeric Polyquinolines with Acetylene Linkages and Celion-3000 Graphite Cloth**

| oligomer (% acetylene) | postcure conditions | | isotherm. aged at 316 °C in air | | | |
|---|---|---|---|---|---|---|
| | none | 8 h/343 °C | 100 h | 200 h | 300 h | 400 h |
| **8a** (25.6) | *a* | 31.1 | *a* | 33.3 | *a* | 9.56 |
| **8b** (35.6) | 71.1 | 43.1 | 58.9 | 47.0 | 43.9 | 42.3 |
| **8c** (45.6) | 85.0 | 52.4 | 60.8 | 42.4 | 30.3 | 16.7 |

[a] Not determined.

Table XIII
**Flex Modulus ($10^6$ psi) at 316 °C (600 °F) of Composites Prepared from Biphenylene-End-Capped Oligomeric Polyquinolines with Acetylene Linkages and Celion-3000 Graphite Cloth**

| oligomer (% acetylene) | postcure conditions | | isotherm. aged at 316 °C in air | | | |
|---|---|---|---|---|---|---|
| | none | 8 h/343 °C | 100 h | 200 h | 300 h | 400 h |
| **8a** (25.6) | 8.72 | 6.36 | *a* | 8.39 | *a* | 2.06 |
| **8b** (35.6) | 10.1 | 7.52 | 8.09 | 8.15 | 7.13 | 5.59 |
| **8c** (45.6) | 9.90 | 8.74 | 9.43 | 8.14 | 7.42 | 5.07 |

[a] Not determined.

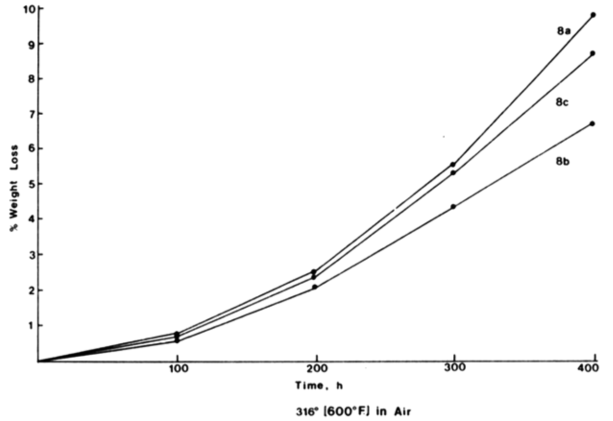


**Figure 3.** Comparison of the weight loss of composites prepared from oligomers **7a–c**.

pearance, and gave a metallic-like ring when dropped on a hard surface.

All of the composites that had not yet been postcured had reasonable flex properties (Tables X–XIII) but only modest interlaminar shear strengths (Tables XIV–XVI). The properties after postcuring were comparable. Overall, the initial properties of composites prepared from **7a–c** were comparable, though slightly improved over those of **5a**.[1]

The effect that the incorporation of acetylene linkages into biphenylene-end-capped oligomers had on their properties was made evident in thermooxidative aging experiments of the composites. The samples were aged at 316 °C (600 °F) in air. At 100-h intervals samples were taken out of the oven, and their weight loss and mechanical properties were determined.

The composites retained useful mechanical properties for 200–300 h (Tables X–XVI). In contrast, the use life of composites prepared from **5a** was only 50 h.[1] At 400 h some of the composites displayed mechanical properties superior to those of **5a** at 50 h. Additionally, although some loose surface fibers were observed at 400 h, the quality of the composites was much better than that of composites of **5a** at 50 h. At 400 h, the composites prepared in this study still displayed a metallic-like ring.

The most striking feature of this study is that composites of **8b** containing equivalent amounts of biphenylene and acetylene units displayed the greatest retention of mechanical properties under thermooxidative conditions (Tables X–XVI). Accordingly, the composites of **7b** also showed the greatest weight retention (Figure 3). Composites prepared from **7a** that had an acetylene/biphenylene ratio of 0.720 displayed the least retention of mechanical properties and weight, while composites of **7c** were between those of **7a** and **7b** in property retention.

**Table XIV**
**Room-Temperature Interlaminar Shear Strength ($10^3$ psi) of Composites Prepared from Biphenylene-End-Capped Oligomeric Polyquinolines with Acetylene Linkages and Celion-3000 Graphite Cloth**

| oligomer (% | postcure conditions | | isotherm. aged at 316 °C in air | | | |
|---|---|---|---|---|---|---|
| acetylene) | none | 8 h/343 °C | 100 h | 200 h | 300 h | 400 h |
| **8a** (25.6) | 5.67 | 6.53 | *a* | 3.63 | *a* | 1.34 |
| **8b** (35.6) | 7.33 | 6.72 | 5.50 | 4.92 | 4.86 | 4.36 |
| **8c** (45.6) | 6.67 | 5.99 | 5.57 | 5.14 | *a* | 3.82 |

[a] Not determined.

**Table XV**
**Interlaminar Shear Strength ($10^3$ psi) at 260 °C (500 °F) of Composites Prepared from Biphenylene-End-Capped Oligomeric Polyquinolines with Acetylene Linkages and Celion-3000 Graphite Cloth**

| oligomer (% | postcure conditions | | isotherm. aged at 316 °C in air | | | |
|---|---|---|---|---|---|---|
| acetylene) | none | 8 h/343 °C | 100 h | 200 h | 300 h | 400 h |
| **8a** (25.6) | 3.66 | 5.51 | *a* | 3.35 | *a* | 1.27 |
| **8b** (35.6) | 6.20 | 6.19 | 6.13 | 5.43 | 4.70 | 4.28 |
| **8c** (45.6) | 6.29 | 6.47 | 5.55 | 4.15 | 2.45 | 2.05 |

[a] Not determined.

**Table XVI**
**Interlaminar Shear Strength ($10^3$ psi) at 316 °C (600 °F) of Composites Prepared from Biphenylene-End-Capped Oligomeric Polyquinolines with Acetylene Linkages and Celion-3000 Graphite Cloth**

| oligomer (% | postcure conditions | | isotherm. aged at 316 °C in air | | | |
|---|---|---|---|---|---|---|
| acetylene) | none | 8 h/343 °C | 100 h | 200 h | 300 h | 400 h |
| **8a** (25.6) | *a* | 4.36 | *a* | 3.21 | *a* | 1.63 |
| **8b** (35.6) | 3.97 | 4.91 | 4.41 | 4.33 | 4.77 | 3.00 |
| **8c** (45.6) | 4.71 | 4.86 | 4.61 | 3.16 | 3.01 | 2.57 |

[a] Not determined.

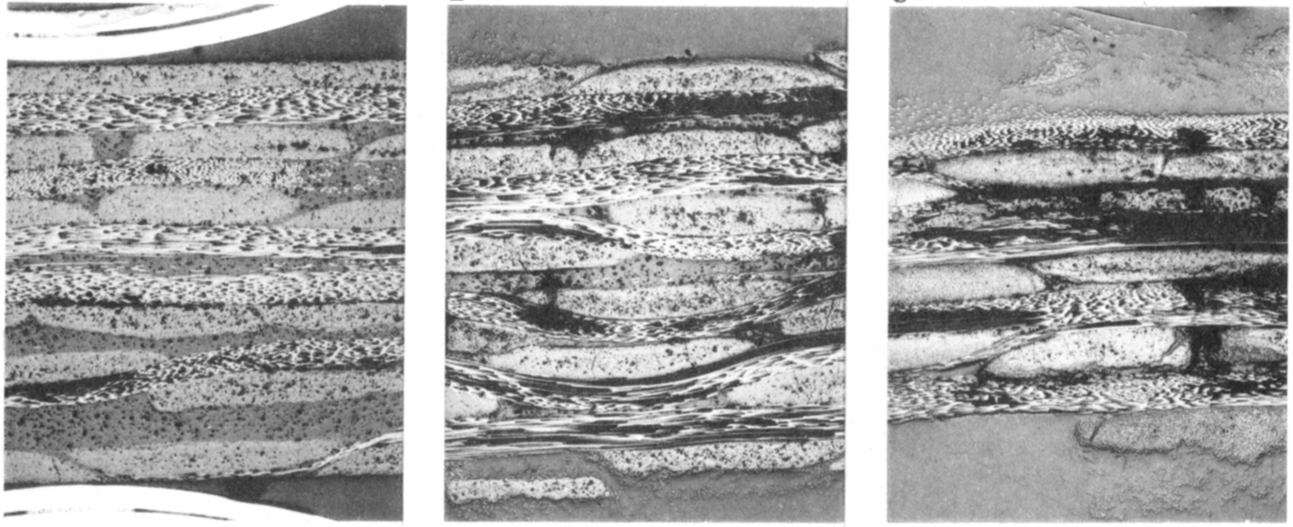


**Figure 4.** Photomicrographs of composites prepared from biphenylene-end-capped oligomer **7a**: (A) no postcure; (B) aged at 316 °C (600 °F) for 200 h; (C) aged for 400 h. Light gray areas are fiber, darker gray areas are resin, and very dark areas are voids.

Therefore, excessive biphenylene is more detrimental than excessive acetylene (compare properties of **8a** with those of **8c**).

Photomicrographs of the aged composites showed the presence of voids, indicating degradation of the matrix resin (Figure 4). Voids also were observed in photomicrographs of the cured, nonaged composites, although they were fewer and smaller in size. Apparently, decreasing the cure pressure to 1500 psi from 2000 psi in order to minimize the loss of resin through flash formation also significantly affected the consolidation of the laminate.

In summary, the incorporation of acetylene linkages into the backbone of biphenylene-end-capped oligomeric polyquinolines did afford improved mechanical properties in the cured resins. The improved properties were obtained by the formation of a three-dimensional network system when the oligomers were cured, cross-linking taking place through the reaction of a biphenylene end cap with an acetylene linkage. The fact that internal acetylene linkages by themselves also are effective cross-linking reagents was shown by the properties of cured phenyl-end-capped oligomeric polyquinolines containing acetylene linkages. Although the mechanical properties of catalytically cured oligomers were only slightly improved compared to those of the thermally cured oligomers, the use of a catalyst apparently afforded at 370–375 °C a more efficient cure than a thermal cure since the weight losses of catalytically cured oligomers were less than those of thermally cured oligomers. At 375 °C complete cures were obtained (DSC), whereas at 350 and 330 °C, with or without catalyst, the cures were incomplete, residual acetylene and biphenylene both being observed.

Utilization of the biphenylene-end-capped oligomers as matrix resins for graphite-cloth-reinforced composites gave materials that displayed initial properties similar to those of biphenylene-end-capped oligomers containing no acetylene linkages. The advantage of the incorporated acetylene linkages was made evident in the retention of the mechanical properties after isothermal aging. Composites prepared from **7** had useful lifetimes up to 400 h at 316 °C, whereas composites prepared from **5a** had a useful lifetime of less than 100 h.

## Experimental Section

**Instrumentation.** Infrared spectra were recorded on a Beckman 4240 spectrophotometer, and absorbances are reported in wavenumbers ($cm^{-1}$). An IBM WP-270SY (270 MHz for $^1H$ and 69 MHz for $^{13}C$) spectrometer was used to obtain all nuclear magnetic resonance spectra. Chemical shifts are reported in parts per million (ppm), with tetramethylsilane ($Me_4Si$) as the defined internal reference for proton spectra and chloroform for carbon spectra. The carbon-13 magnetic resonance spectra were decoupled. A V. G. Micromass 16F mass spectrometer was used to obtain mass spectra.

The reported intrinsic viscosity values, $[\eta]$, were determined by dilute solution viscosity measurements of polymer solutions obtained with Cannon-Ubbelohde microdilution viscometers Nos. 50 (chloroform) and 75 (1,1,2,2-tetrachloroethane). Measurements were taken on polymer solutions with concentrations of 0.500, 0.400, 0.333, and 0.250 g/dL.

A Du Pont 990 differential scanning calorimeter (DSC) cell base was used to perform thermal analyses on uncured and neat, cured polymer samples (films and resin disks). Thermal analyses of resin disks and composite samples were performed with Du Pont 942 and 943 thermomechanical analyzers (TMA) interfaced with an Omnitherm data reduction system. Dynamic thermomechanical analyses of film samples were obtained on a Rheovibron DDV-II-C dynamic viscoelastometer. Interlaminar shear strengths, flex strengths, and flex moduli of composites were determined with an Instron equipped with a high-temperature oven. A Du Pont 951 thermogravimetric analyzer (TGA) was used for thermooxidative stability tests. Oxidative isothermal aging of cured polymer samples was performed in circulating-air ovens.

**Bis(tri-*n*-butylstannyl)acetylene (2).** A mixture of 48.8 g (0.150 mol) of tributyltin chloride and 20.7 g (0.225 mol) of lithium acetylide ethylenediamine in 300 mL of dry tetrahydrofuran was heated at the reflux temperature for 24 h, cooled, and treated with 50 mL of water. After the solvent was removed under reduced pressure, the residue was taken up in 150 mL of ether and then suction-filtered through Celite with a 150-mL ether wash to afford a clarified solution that was washed with water (2 × 100 mL) and saturated salt solution (100 mL) and dried over magnesium sulfate. Removal of the solvent followed by distillation under reduced pressure gave 37.2 g (82%) of **2** as a colorless liquid: bp 160–166 °C (0.3 mmHg) (lit.[7] bp 158–159 °C (0.08 mmHg)).

**4,4′-Diacetyldiphenylacetylene (1).** A mixture of 23.9 g (0.120 mol) of 4-bromoacetophenone and 2.89 g (2.50 mmol) of tetrakis(triphenylphosphine)palladium(0) under an atmosphere of nitrogen was dissolved in 150 mL of dry tetrahydrofuran. A solution of 30.2 g (50.0 mmol) of bis(tri-*n*-butylstannyl)acetylene (**2**)[7] in 50 mL of tetrahydrofuran was transferred by a cannula into the reaction flask, and then the reaction mixture was heated at its reflux temperature for 60 h. The solution was then allowed to cool to room temperature, during which time crystal growth occurred. The reaction mixture was further cooled to 0 °C and then suction-filtered. Sublimation (200 °C (0.05 mmHg)) of the crystals gave 8.60 g (66%) of a white solid that was recrystallized from benzene/methanol (2:1, 40 mL/g) to afford monomer-grade **1** as colorless plates: mp 202.0–202.5 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 7.97–7.61 (q, 8 H), 2.62 (s, 6 H); IR (KBr) 1680, 1605, 1400, 1355, 1285, 1270 $cm^{-1}$. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.50; H, 5.43.

**4,4′-(4-Phenylquinolin-2-yl)diphenylacetylene (8).** To a mechanically stirred solution of 17.0 g (120 mmol) of phosphorus pentoxide in 40 mL of *m*-cresol (prepared by heating the mixture at 135 °C for 0.5 h) under an atmosphere of nitrogen were added 3.94 g (20.0 mmol) of 2-aminobenzophenone (recrystallized from ethanol) and 2.62 g (10.0 mmol) of 4,4′-diacetyldiphenylacetylene (**1**). The amber-orange solution was heated for 24 h with stirring and then poured into a rapidly stirred solution of 95 mL of concentrated ammonium hydroxide in 375 mL of water. Suction filtration followed by continuous extraction with methanol for 6 h afforded 5.33 g (91%) of **8** as a pale, yellowish-white solid: mp 279.5–280.5 °C; IR (KBr) 1590, 1540, 1490, 1415, 1310, 770, 695 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.26–7.72 (q, 8 H), 7.94–7.47 (m, 18 H), 7.85 (s, 2 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 155.9, 149.2, 149.1, 139.5, 138.6, 132.2, 130.3, 129.6, 128.6, 128.5, 127.5, 126.5, 126.1, 125.7, 124.4, 119.1, 91.0. Anal. Calcd for $C_{44}H_{28}N_2$: C, 90.38; H, 4.83; N, 4.79. Found: C, 90.20; H, 4.88; N, 4.72.

**Biphenylene-End-Capped Polyquinoline 5e.** Into the bottom of a resin kettle were weighed 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**3**) and 0.7869 g (3.000 mmol) of 4,4′-diacetyldiphenylacetylene (**1**) followed by 21.5 g (77.3 mmol) of di-*m*-cresyl phosphate and 6.9 g of *m*-cresol. The resin kettle was assembled, fitted with a mechanical stirrer, and flushed with nitrogen for 10 min. The amber-orange solution was heated with stirring at 136–138 °C for 24 h under a static atmosphere of nitrogen and then cooled slightly before 0.1733 g (0.8920 mmol) of 2-acetylbiphenylene was added. Heating at 136–138 °C was continued for 12 h. After this time the hot, dark red solution was poured into a rapidly stirred mixture of 360 mL of ethanol and 30 mL of triethylamine to precipitate the polymer, which was then ground in a Waring blender set at high speed for 3 min. The polymer was isolated by suction filtration, continuously extracted with a mixture of 300 mL of ethanol and 25 mL of triethylamine for 24 h, and dried at 110 °C (0.05 mmHg) for 24 h to afford 1.86 g (95%) of **5e** as a light yellow powder: $[\eta]$ = 1.02 dL/g (25.0 °C, chloroform). Anal. Calcd: C, 88.37; H, 4.38; N, 4.61. Found: C, 88.19; H, 4.43; N, 4.61.

**Biphenylene-End-Capped Polyquinoline 5d.** The above procedure was followed except 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**3**), 0.3814 g (1.500 mmol) of 4,4′-diacetyldiphenyl ether (**4**), and 0.3935 g (1.500 mmol) of 4,4′-diacetyldiphenylacetylene (**1**) were used as the monomer reagents. The monomers were polymerized and end-capped with 0.1733 g (0.8920 mmol) of 2-acetylbiphenylene, and then the polymer was precipitated and purified as above to afford 1.89 g (97%) of **5d** as a light yellow powder: $[\eta]$ = 0.70 dL/g (25.0 °C, chloroform). Anal. Calcd: C, 87.07; H, 4.41; N, 4.64. Found: C, 87.17; H, 4.38; N, 4.61.

**Biphenylene-End-Capped Polyquinoline 5c.** The above procedure was followed except 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**3**), 0.5721 g (2.250 mmol) of 4,4′-diacetyldiphenyl ether (**4**), and 0.1967 g (0.7500 mmol) of 4,4′-diacetyldiphenylacetylene (**1**) were used as the monomer reagents. The monomers were polymerized and end-capped with 0.1733 g (0.8920 mmol) of 2-acetylbiphenylene, and then the polymer was precipitated and purified as above to afford 1.93 g (99%) of **5c** as a light yellow powder: [$\eta$] = 0.56 dL/g (25.0 °C, chloroform). Anal. Calcd: C, 86.41; H, 4.42; N, 4.66. Found: C, 86.75; H, 4.38; N, 4.51.

**Biphenylene-End-Capped Polyquinoline 5b.** The above procedure was followed except 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**3**), 0.6675 g (2.625 mmol) of 4,4′-diacetyldiphenyl ether (**4**), and 0.0984 g (0.3750 mmol) of 4,4′-diacetyldiphenylacetylene (**1**) were used as the monomer reagents. The monomers were polymerized and end-capped with 0.1733 g (0.8920 mmol) of 2-acetylbiphenylene, and then the polymer was precipitated and purified as above to afford 1.93 g (99%) of **5b** as a light yellow powder: [$\eta$] = 0.51 dL/g (25.0 °C, chloroform). Anal. Calcd: C, 86.08; H, 4.43; N, 4.66. Found: C, 86.68; H, 4.42; N, 4.47.

**Biphenylene-End-Capped Polyquinoline 5a.** The above procedure was followed except 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**3**) and 0.7629 g (3.000 mmol) of 4,4′-diacetyldiphenyl ether (**4**) were used as the monomer reagents. The monomers were polymerized and end-capped with 0.1733 g (0.8920 mmol) of 2-acetylbiphenylene, and then the polymer was precipitated and purified as above to afford 1.92 g (99%) of **5a** as a light yellow powder: [$\eta$] = 0.47 dL/g (25.0 °C, chloroform). Anal. Calcd: C, 85.75; H, 4.44; N, 4.67. Found: C, 86.10; H, 4.40; N, 4.49.

**Phenyl-End-Capped Polyquinoline 6e.** Into the bottom of a resin kettle were weighed 1.3165 g (3.223 mmol) of (4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**3**) and 0.7869 g (3.000 mmol) of 4,4′-diacetyldiphenylacetylene (**1**) followed by 21.5 g (77.3 mmol) of di-*m*-cresyl phosphate and 6.9 g of *m*-cresol. The resin kettle was assembled, fitted with a mechanical stirrer, and flushed with nitrogen for 10 min. The amber-orange solution was heated at 136–138 °C for 24 h under a static atmosphere of nitrogen and then cooled slightly before 0.1072 g (0.8920 mmol, 104 $\mu$L) of acetophenone was added. Heating at 136–138 °C was continued for 12 h. After this time the hot, amber-orange solution was poured into a rapidly stirred mixture of 360 mL of ethanol and 30 mL of triethylamine to precipitate the polymer, which was then ground in a Waring blender set at a high speed for 3 min. The polymer was isolated by suction filtration, continously extracted with a mixture of 300 mL of ethanol and 25 mL of triethylamine for 24 h, and dried at 110 °C (0.05 mmHg) for 24 h to afford 1.79 g (94%) of **6e** as a cream-colored powder: [$\eta$] = 0.99 dL/g (25.0 °C, chloroform).

**Phenyl-End-Capped Polyquinoline 6d.** The above procedure was followed except 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**3**), 0.3814 g (1.500 mmol) of 4,4′-diacetyldiphenyl ether (**4**), and 0.3935 g (1.500 mmol) of 4,4′-diacetyldiphenylacetylene (**1**) were used as the monomer reagents. The monomers were polymerized and end-capped with 0.1072 g (0.8920 mmol, 104 $\mu$L) of acetophenone, and then the polymer was precipitated and purified as above to afford 1.90 g (99%) of **6d** as a light yellow powder: [$\eta$] = 0.69 dL/g (25.0 °C, chloroform).

**Phenyl-End-Capped Polyquinoline 6c.** The above procedure was followed except 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**3**), 0.5721 g (2.250 mmol) of 4,4′-diacetyldiphenyl ether (**4**), and 0.1967 g (0.7500 mmol) of 4,4′-diacetyldiphenylacetylene (**1**) were used as the monomer reagents. The monomers were polymerized and end-capped with 0.1072 g (0.8920 mmol, 104 $\mu$L) of acetophenone, and then the polymer was precipitated and purified as above to afford 1.86 g (98%) of **6c** as a light yellow powder: [$\eta$] = 0.55 dL/g (25.0 °C, chloroform).

**Phenyl-End-Capped Polyquinoline 6b.** The above procedure was followed except 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**3**), 0.6675 g (2.265 mmol) of 4,4′-diacetyldiphenyl ether (**4**), and 0.0984 g (0.3750 mmol) of 4,4′-diacetyldiphenylacetylene (**1**) were used as the monomer reagents. The monomers were polymerized and end-capped with 0.1072 g (0.8920 mmol, 104 $\mu$L) of acetophenone, and then the polymer was precipitated and purified as above to afford 1.88 g (99%) of **6b** as a light yellow powder: [$\eta$] = 0.50 dL/g (25.0 °C, chloroform).

**Phenyl-End-Capped Polyquinoline 6a.** The above procedure was followed except 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**3**) and 0.7629 g (3.000 mmol) of 4,4′-diacetyldiphenyl ether (**4**) were used as the monomer reagents. The monomers were polymerized and end-capped with 0.1072 g (0.8920 mmol, 104 $\mu$L) of acetophenone, and then the polymer was precipitated and purified as above to afford 1.78 g (96%) of **6a** as a light yellow powder: [$\eta$] = 0.49 dL/g (25.0 °C, chloroform).

**Biphenylene-End-Capped Polyquinoline 7a.** In a 250-mL, three-neck, round-bottom flask were placed 6.7363 g (16.492 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**3**), 2.6486 g (10.416 mmol) of 4,4′-diacetyldiphenyl ether (**4**), and 0.9401 g (3.584 mmol) of 4,4′-diacetyldiphenylacetylene (**1**) followed by 110.2 g (0.396 mol) of di-*m*-cresyl phosphate and 35.4 g of *m*-cresol. The flask was fitted with a mechanical stirrer and then flushed with nitrogen for 10 min. The amber-orange solution was heated with stirring at 136–138 °C for 24 h under a static atmosphere of nitrogen and then cooled slightly before 1.4521 g (7.476 mmol) of 2-acetylbiphenylene was added. Heating at 136–138 °C was continued for 12 h. After this time the hot, dark red solution was poured into a rapidly stirred mixture of 1850 mL of ethanol and 155 mL of triethylamine to precipitate the polymer, which was then ground in a Waring blender set at high speed for 3 min. The polymer was isolated by suction filtration, continuously extracted with a mixture of 1240 mL of ethanol and 105 mL of triethylamine for 24 h, and dried at 110 °C (0.05 mmHg) for 24 h to afford 9.94 g (98%) of **7a** as a fine, light yellow powder: [$\eta$] = 0.29 dL/g (25.0 °C, chloroform). Anal. Calcd: C, 86.74; H, 4.43; N, 4.57. Found: C, 85.37; H, 4.17; N, 4.21.

**Biphenylene-End-Capped Polyquinoline 7b.** The above procedure was followed except 6.7363 g (16.492 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**3**), 2.2926 g (9.016 mmol) of 4,4′-diacetyldiphenyl ether (**4**), and 1.3073 g (4.984 mmol) of 4,4′-diacetyldiphenylacetylene (**1**) were used as the monomer reagents. The monomers were polymerized and end-capped with 1.4521 g (7.476 mmol) of 2-acetylbiphenylene, and then the polymer was precipitated and purified as above to afford 9.98 g (99%) of **7b** as a fine, light yellow powder: [$\eta$] = 0.32 dL/g (25.0 °C, chloroform). Anal. Calcd: C, 86.98; H, 4.42; N, 4.57. Found: C, 86.21; H, 4.23; N, 4.28.

**Biphenylene-End-Capped Polyquinoline 7c.** The above procedure was followed except 6.7363 g (16.492 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**3**), 1.9366 g (7.616 mmol) of 4,4′-diacetyldiphenyl ether (**4**), and 1.6746 g (6.384 mmol) of 4,4′-diacetyldiphenylacetylene (**1**) were used as the monomer reagents. The monomers were polymerized and end-capped with 1.4521 g (7.476 mmol) of 2-acetylbiphenylene, and then the polymer was precipitated and purified as above to afford 9.98 g (99%) of **7c** as a fine, light yellow solid: [$\eta$] = 0.34 dL/g. Anal. Calcd: C, 87.21; H, 4.42; N, 4.56. Found: C, 86.41; H, 4.32; N, 4.41.

**Sample Preparation for Melt Processing.** To 50 mL of stirred hexane (distilled prior to use) was added the appropriate amount of bis(triphenylphosphine)dicarbonylnickel(0) dissolved in a minimal amount of benzene (generally 7.5 mg of catalyst was dissolved in 0.5 mL of benzene). The catalyst was not soluble in hexane unless it was introduced in this manner. Next, 250 mg of the polymer sample was added. The suspension was stirred for 15 min, after which time the solvent was removed under reduced pressure to afford the polymer sample as a powder that was dried at 80 °C (15 mmHg) for 12 h. The recovered yield of the polymer sample was 75–95%.

**Neat Resin Film Melt Processing.** A Wabash hydraulic press (Model 1210) that had been fitted with Carver heat platens (No. 2102) was used for the melt processing of neat resin films. A 200-mg powder sample of the polymer (with or without catalyst) was placed in an elliptical pile between two 3 in. × 3 in. pieces of copper foil (0.005 in. thick, Baker no. 1-1714). Two strips of 0.005-in. copper foil (0.25 in. × 3 in.) were used as spacers. The assembly was then placed between the platens preheated to 350 °C in the hydraulic press and melt-processed at 350 °C under a 5000-lb load for the desired amount of time. The platens were then cooled to 200 °C without releasing the pressure before the sample was taken out of the press and plunged into cold water. The copper foil was carefully peeled away from the film. If necessary, removal of the foil was facilitated by soaking the film adhering to the copper foil in concentrated ammonium hydroxide for 30 min. All films were thoroughly washed with water and air-dried prior to testing.

**Neat Resin Disk Melt Processing.** A steel die with brass punches of a diameter of 0.790 in. was used to make the neat resin disks. A 200-mg powder sample of the polymer (with or without catalyst) was placed in the die and then melt-processed in a hydraulic press at 2000 psi for 2 h between two platens heated at 330 °C (625 °F) for catalyzed cures or at 375 °C (707 °F) for uncatalyzed/thermal cures. The die was cooled to <200 °C (392 °F) under pressure before it was taken out of the press and disassembled to obtain the neat resin disk.

**Prepreg Preparation.** Chloroform solutions of **7a–c** were brush-coated onto both sides of a piece of Celion-3000 graphite cloth of specific dimension/weight such that the prepreg would result in a 30% resin content. The cloth was solidly restrained on all four edges to prevent shrinkage. After it had air-dried overnight, the prepreg was cut into pieces with dimensions of 0.99 in. × 2.70 in.

**Composite Preparation.** The prepreg was staged as a 6-ply layup in a ~1 in. × 27 in. steel mold for 1 h at 121 °C (250 °F) and then melt-processed at 375 °C (707 °F) under 1500 psi for 2 h. The steel mold was cooled to <200 °C (392 °F) under pressure before it was taken out of the press and then disassembled to obtain the graphite-cloth-reinforced composite.

**Interlaminar Shear Strength (ILSS).** The interlaminar (or short beam) shear strength was determined as per ASTM D2344-76 by applying a load to a short (span/depth = 5/1) composite specimen supported lengthwise in a variable-span vise. The specimen was pushed against a pin until failure. The pressure at failure was measured by an Instron and used to calculate the ILLL. (Because the specimen is short, failure occurs between plies. Thus, the ILSS affords a measure of the resin's ability to transfer the load from one ply to the next in a composite.)

**Flex Strength and Flex Modulus.** An analysis similar to the above was performed except longer (2 in.) specimens were used and tested as per ASTM D790-1. (Because the specimen is considerably longer, failure occurs perpendicular to the longest axis of the specimen and requires breakage of the fibers. As a result, flex strength and flex modulus are fiber-dependent properties and quantify the extent to which the composite retains the high strength imparted by the fiber reinforcement. Flex strength is an indication of the composite's ultimate strength, while flex modulus is an indication of the composite's initial stiffness.)

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# Metal Poly(benzodithiolenes)

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ABSTRACT: The title polymers were prepared by several different approaches employing benzene-1,2,4,5-tetrathiol and transition-metal salts. The two best-characterized solids were an iron and a cobalt salt, the subjects of this publication. Preliminary results on pressed-pellet conductivities (on the order $0.2–10^{-5}$ S/cm), magnetic susceptibility, and Mössbauer spectroscopy are presented.

## Introduction

The metal dithiolenes are a unique and large family of transition- and main-group-metal complexes.[1] They have been of interest because they are easily formed (particularly the maleonitrilodithiolato (mnt) complexes), they are room temperature and atmosphere stable, and they exhibit a number of stable oxidation states containing open-shell molecular orbitals. It is this last property that has been the main reason for interest in these coordination complexes by solid-state scientists. Open-shell molecules are essential for achieving highly conducting systems, and they offer the potential of achieving organic and organometallic ferromagnets. As early as 1972, attempts were made to develop organic metals based on dithiolenes.[2] The most recent success has been with hydrated lithium dithiolene salts.[3] There has also been a report on polymers containing metal dithiolenes.[4]

The metal dithiolenes of the nickel triad (Ni, Pd, Pt) as well as those of Co, Cu, Zn, and Cd are square planar. Presumably, in solution, the apical coordination sites are solvated in coordinating solvents and open in noncoordinating solvents. In most cases in the solid state, the axial coordination sites are occupied by sulfur atoms of neighboring molecules. One important exception is the structure of the conducting mixed-valent mnt salts of Underhill,[3] where flat metal complexes form a zigzag stack reminiscent of the structure of most organic superconductors.[5]

In this paper we describe the preparation of new polymers that use the ligand benzene-1,2,4,5-tetrathiol[6] (1) in conjunction with divalent transition metals as backbone (see Scheme I). The rationale for the development of these polymers rests on several principles:

(a) The possibility of mixed valence (through doping) and electron delocalization will produce conducting polymers.

(b) A high density of unpaired spins (up to one per each metal atom) will be possible, leading to the formation of paramagnetic polymers. Ferromagnetic and/or antifer-

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