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Biphenylene- and Phenyl-End-Capped Oligomeric Polyquinolines Containing Pendent Biphenylenes

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ABSTRACT: A series of oligomeric polyquinolines ($\overline{\mathrm{DP}}$ = 22) containing pendent biphenylenes and capped with either phenyl or biphenylene was prepared. Utilization of the new AB monomer 5-acetyl-2-amino-4′-(biphenylen-2-yloxy)benzophenone allowed the attachment of biphenylene to the oligomer chains through a phenoxy spacer group. The amount of pendent biphenylene was varied so that 6.6, 12.2, and 17.2% of the oligomer units contained pendent biphenylene. Melt processing of the reactive oligomers in the presence of 2.75 wt % of the catalyst bis(triphenylphosphine)dicarbonylnickel(0) for various times gave high-quality films. The films prepared from the various oligomers displayed only slight increases in Young's modulus above the T_g as the cross-link density was increased by increasing biphenylene content. Isothermal aging studies of the cured films and a model compound showed that the cross-link site, tetraphenylene, was not particularly thermooxidatively stable.

Introduction

In an effort to overcome the processability problems inherent in thermally stable, rigid, aromatic polymers, oligomeric polyquinolines ($\overline{\mathrm{DP}}$ = 22 and 11, **1** and **2**, respectively) containing biphenylene end caps were prepared.[1] The oligomers had good melt-flow properties and were easily processed in the presence of a catalytic amount of bis(triphenylphosphine)dicarbonylnickel(0) to give high-quality films. The nickel catalyst lowered the temperature at which the ring-opening reaction of biphenylene occurred so that the oligomers could be melt-processed at 350 °C.[2] Although **2** had a greater biphenylene content and should have afforded a resin with a higher cross-link density than **1**, the Young's moduli (E') of the films prepared from both oligomers were not appreciably different. The major reaction of biphenylene, however, was shown by a model study to proceed by a dimerization reaction to give the tetraphenylene product.[1] A recent study of the reaction product obtained from biphenylene and a number of nickel(0) catalysts has confirmed this dimerization pathway.[3]

Biphenylene also has been shown to react with 2,4-diphenylquinoline to form a biphenyl-substituted polyquinoline.[1] However, the model study and the properties of cross-linked **1** and **2** indicated that this substitution reaction occurred only to a small extent. Since the main reaction of the biphenylene end groups of **1** and **2** was cyclodimerization, chain extension rather than cross-linking was the predominant route through which the oligomers cured.

This paper reports the synthesis of polyquinolines of $\overline{\mathrm{DP}}$ = 22 containing pendent biphenylenes and capped with either phenyl or biphenylene. Attachment of pendent biphenylene units to the oligomer chain allows the functionality of the oligomer to be adjusted so that when the oligomers are cured, various cross-link densities can be obtained. In contrast to oligomers with only biphenylene end caps, oligomers bearing pendent biphenylenes can afford three-dimensional network structures and thus improved mechanical properties.

Results and Discussion

Monomer Synthesis. A synthesis of a biphenylene-containing monomer necessitated the preparation of the substituted acetonitrile **3** (Figure 1). The first step (Figure 1) was an Ullman ether condensation[4] between the potassium salt of methyl 4-hydroxybenzoate and 2-bromobiphenylene (**4**) to yield methyl 4-(biphenylen-2-yloxy)benzoate (**5**) in a 58% yield. An electrophilic bromination of biphenylene with *N*-bromosuccinimide in *N*,*N*-dimethylformamide[5] gave **4** in 79% yield. Conversion of **5** to **3** was effected by a lithium aluminum hydride reduction of **5** (99% yield) followed by the subsequent reaction of benzyl alcohol **6** with thionyl chloride. The intermediate benzyl chloride was treated with potassium cyanide in *N*,*N*-dimethylformamide to produce **3** in 71% yield from **6**.

Modified reaction conditions (basic methanol/tetrahydrofuran, 6.6:1, 55 °C for 20 h) were used for the reaction of 4-(biphenylen-2-yloxy)phenylacetonitrile (**3**) with 2-methyl-2-(4-nitrophenyl)-1,3-dioxolane (**7**) to give benzisoxazole **8** (Figure 1). The product precipitated from solution as the reaction proceeded to give **8** in 40% yield.

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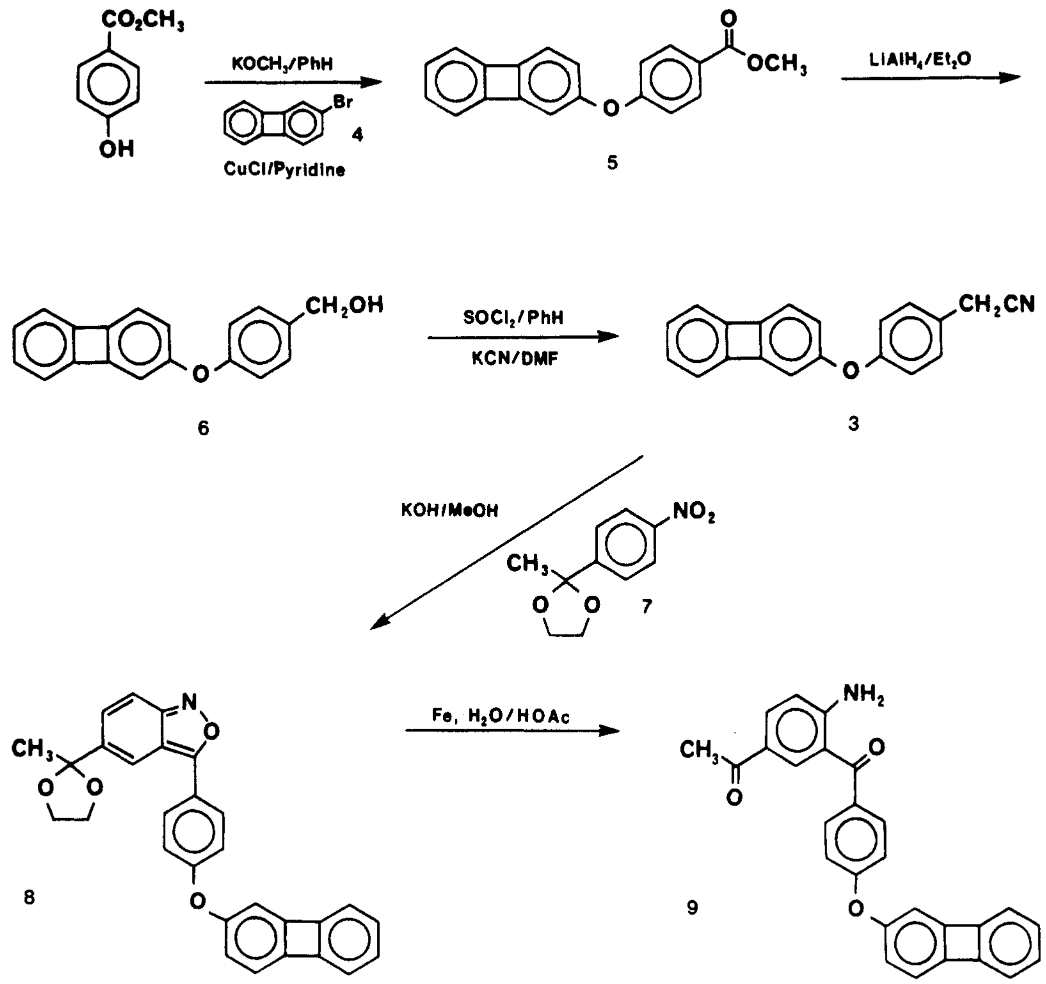

Figure 1. Synthesis of the monomer 5-acetyl-2-amino-4′-(biphenylen-2-yloxy)benzophenone (9).

Table I
Dependence of T_g on the Percent Pendent Biphenylene of Biphenylene- and Phenyl-End-Capped Oligomeric Polyquinolines

	biphenylene end capped			phenyl end capped		
% pendent biphenylene	oligomer	T_g, °C	biphenylene exothermic max, °C	oligomer	T_g, °C	biphenylene exothermic max, °C
6.5	**12a**	228	483	**13a**	228	482
12.2	**12b**	232	482	**13b**	232	482
17.2	**12c**	237	472	**13c**	239	484

The aryl nitro compound **7** was prepared in 74% yield by the ketalization of 4-nitroacetophenone with ethylene glycol.[6]

To complete the monomer synthesis, reduction of the benzisoxazole ring to afford the *o*-amino ketone functionality and removal of the ketal protecting group were necessary. Hydrogenation of biphenylene apparently takes place in the presence of palladium.[7] Consequently, **8** was reduced by treating it with iron and water in glacial acetic acid.[8] Under these reaction conditions, the simultaneous removal of the ketal protecting group was effected to give the new monomer 5-acetyl-2-amino-[4′-(biphenylen-2-yloxy)benzophenone (**9**) in 70% yield.

Oligomer Synthesis and Properties. A series of three reactive oligomeric polyquinolines of $\overline{\mathrm{DP}} = 22$ were prepared by the copolymerization of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**10**), 4,4′-diacetyldiphenyl ether (**11**), and 5-acetyl-2-amino-4′-(biphenylen-2-yloxy)benzophenone (**9**). The proper stoichiometric imbalance of monomer functionalities was maintained through an excess of the bis(amino ketone) monomer. The amount of pendent biphenylene incorporated was such that 6.5, 12.2, and 17.2% of the units contained pendent biphenylene (Figure 2). Each of the three oligomers were end-capped with 2-acetylbiphenylene (oligomers **12a–c**) and acetophenone (oligomers **13a–c**). The synthesis of both biphenylene-end-capped and phenyl-end-capped reactive oligomers allowed the added effect (if any) that the biphenylene end cap might impart to the cured resin to be determined.

Differential scanning calorimetry (DSC) of the oligomers illustrated the effect that the rigid linkage introduced by AB monomer **9** had on the T_g's of the uncured oligomers (Table I). As more units with pendent biphenylene were incorporated in the chain, the T_g of the oligomers increased. Although there was initial concern as to how this would affect the curing process of the oligomers, the T_g's were still low enough so as not to adversely affect their flow properties. The DSC's of the oligomers showed that the exothermic maximum of the ring-opening reaction of the pendent biphenylene occurred at 472–484 °C.

Dilute solution viscosity measurements also showed the effect that increased rigidity had on the oligomers' properties (Table II). Oligomers **12c** and **13c**, which had the highest content of pendent biphenylene and, correspondingly, the highest degree of rigidity, were not completely soluble in chloroform. Both **12c** and **13c** were readily

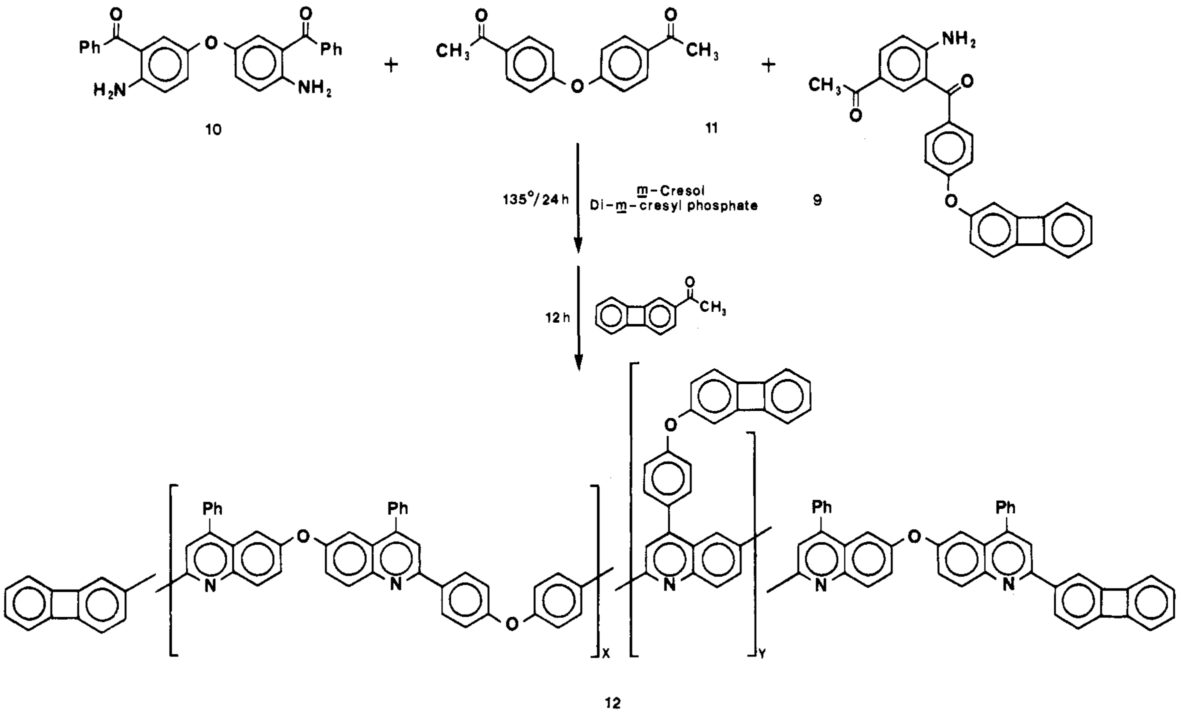

Figure 2. Preparation of biphenylene-end-capped oligomeric polyquinolines with pendent biphenylenes (12).

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

% pendent biphenylene	biphenylene-end-capped oligomer	[η], dL/g	phenyl-end-capped oligomer	[η], dL/g
6.5	**12a**	0.510	**13a**	0.511
12.2	**12b**	0.522	**13b**	0.526
17.2	**12c**	0.536[b]	**13c**	0.538[b]

[a] Viscosity measurements were obtained from chloroform solutions unless otherwise noted. [b] 1,1,2,2-Tetrachloroethane.

soluble in 1,1,2,2-tetrachloroethane.

Oligomer Processing and Cured Properties. Because it was desirable to cure oligomers **12** and **13** under the same conditions used to cure biphenylene-end-capped oligomeric polyquinolines,[1] **12** and **13** were cured at 350 °C under a 5000-lb load for 30 min in the presence of 20 mol % (based on the amount of biphenylene) of the catalyst bis(triphenylphosphine)dicarbonylnickel(0). Tough, chloroform-insoluble films were obtained. However, DSC showed that it was not desirable to cure all of the oligomers with 20 mol % of the nickel catalyst (Table III). When a large amount of catalyst was used (up to 9.86 wt %), the oligomer was plasticized to such a large extent that the T_g's of the cured resin were lower than that of the pristine, uncured oligomer.

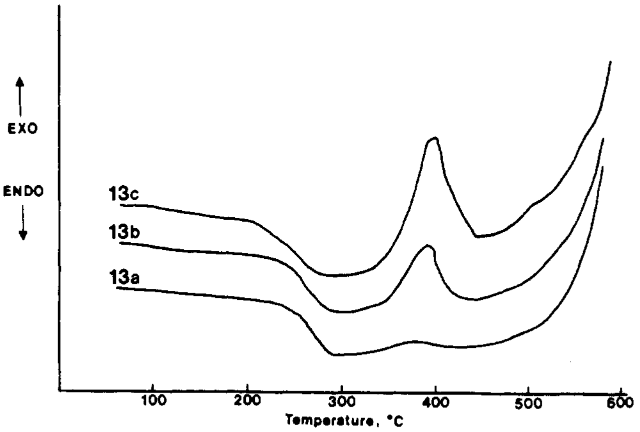

Figure 3. Differential scanning calorimetry of **13** melt-processed in the presence of bis(triphenylphosphine)dicarbonylnickel(0) for 30 min at 350 °C under a 5000-lb load.

The oligomers cured with 20 mol % of the catalyst also showed residual biphenylene by DSC (Table III). The exothermic maximum of the biphenylene ring-opening reaction occurred at a temperature 80–100 °C lower than the uncatalyzed exothermic maximum, demonstrating the effectiveness of bis(triphenylphosphine)dicarbonylnickel(0) as a catalyst for lowering the processing temperature of biphenylene-containing oligomers. Only **13a** showed a complete cure (Figure 3). All of the other cured oligomers

Table III
Properties of Melt-Processed Biphenylene- and Phenyl-End-Capped Oligomeric Polyquinolines[a]

oligomer[b]	wt %[c] of Ni catalyst	T_g, °C		ΔT_g, °C	exothermic max, °C	
		uncured	cured		uncured	cured
12a (B)	5.61	228	236	8	483	390
12b (B)	7.89	232	222	−10	482	403
12c (B)	9.86	237	213	−24	472	387
13a (P)	2.76	228	245	17	482	382
13b (P)	5.12	232	236	4	482	388
13c (P)	7.15	239	220	−19	484	389

[a] Melt processed at 350 °C under a 5000-lb load for 30 min in the presence of 20 mol % $(PPh_3)_2Ni(CO)_2$. [b] Letter in parentheses denotes end cap: B is biphenylene; P is phenyl. [c] Weight percent values correspond to 20 mol % (based on biphenylene) of the nickel catalyst.

Table IV
Properties of Melt-Processed Biphenylene- and Phenyl-End-Capped Oligomeric Polyquinolines[a]

oligomer[b]	cure time, h	T_g, °C uncured	T_g, °C cured	ΔT_g, °C
12a (B)	3	228	245	17
12b (B)	6	232	262	30
12c (B)	8	237	257	20
13a (P)	$^1/_2$	228	245	17
13b (P)	2	232	249	17
13c (P)	6	239	252	13

[a] Melt processed at 350 °C under a 5000-lb load in the presence of 2.75 wt % $(PPh_3)_2Ni(CO)_2$. [b] Letter in parentheses denotes end cap: B is biphenylene; P is phenyl.

Table V
Film Mechanical Properties of Biphenylene- and Phenyl-End-Capped Oligomeric Polyquinolines with Pendent Phenylene[a]

oligomer[b,c]	% pendent biphenylene	total biphenylene content[d]	E' at 25 °C, dyn/cm^2	E' above T_g, dyn/cm^2
1e (B)	0	0.446	2.21×10^{10}	8.26×10^7
13a (P)	6.5	0.446	2.93×10^{10}	9.16×10^8
13b (P)	12.2	0.892	2.89×10^{10}	1.15×10^8
12a (B)	6.5	0.922	2.56×10^{10}	1.26×10^8
13c (P)	17.2	1.338	2.62×10^{10}	1.86×10^8
12b (B)	12.2	1.400	2.75×10^{10}	2.51×10^8
12c (B)	17.2	1.876	2.43×10^{10}	2.06×10^8

[a] Melt-processed at 350 °C under a 5000-lb load in the presence of 2.75 wt % $(PPh_3)_2Ni(CO)_2$ for the times specified in Table IV. [b] Letter in parentheses denotes end cap: B is biphenylene; P is phenyl. [c] Samples tabulated in increasing biphenylene content. [d] Biphenylene content refers to the number of millimoles of biphenylene theoretically incorporated by the samples when prepared on the same scale. [e] Properties of 1 included for comparison.[1]

displayed distinct residual exotherms at 380–400 °C, the magnitude of which increased with the biphenylene content.

Because of the plasticizing effect observed when the oligomers were cured with 20 mol % of the nickel catalyst, alternate cure conditions utilizing a minimal amount of catalyst were used. A 2.75 wt % of catalyst was added since this amount was shown effective for curing **13a** (Table III and Figure 3) and did not give a severe plasticizing effect. In order to effect complete consumption of the biphenylene during the cure process, longer cure times were required.

Empirically determined cure times afforded the desired results (Table IV). Little or no residual biphenylene was observed (DSC) and T_g advancements of 17–30 °C were realized. The films were tough and completely insoluble in chloroform.

Rheovibron analysis of the cured films showed a gradual increase in Young's modulus above T_g as the cross-link density of the resins increased. However, only a moderate increase was realized over the entire range of resins tested (Table V).

Isothermal aging performed in air showed that the cured biphenylene-end-capped oligomers **12a–c** lost significantly less weight after 100 h at 316 °C than did the resins obtained from phenyl-end-capped oligomers **13a–c** (Table VI). No correlation between weight loss and biphenylene content in the oligomers could be made.

Table VI
Thermooxidative Stability of Cured Biphenylene- and Phenyl-End-Capped Oligomers with Pendent Biphenylene When Aged for 100 h at 316 °C[a]

oligomer[b,c]	% pendent biphenylene	total biphenylene content[d]	% wt loss
1e (B)	0	0.446	6.8
13a (P)	6.5	0.446	40.1
13b (P)	12.2	0.892	50.6
12a (B)	6.5	0.922	10.1
13c (P)	17.2	1.338	61.6
12b (B)	12.2	1.400	33.9
12c (B)	17.2	1.876	61.3

[a] Melt processed at 350 °C under a 5000-lb load in the presence of 2.75 wt % $(PPh_3)_2Ni(CO)_2$ for the times specified in Table IV. [b] Letter in parentheses denoted end cap; B is biphenylene; P is phenyl. [c] Samples tabulated in increasing biphenylene content. [d] Biphenylene content refers to the number of millimoles of biphenylene theoretically incorporated by the samples when prepared on the same scale. [e] Properties of 1 included for comparison.[1]

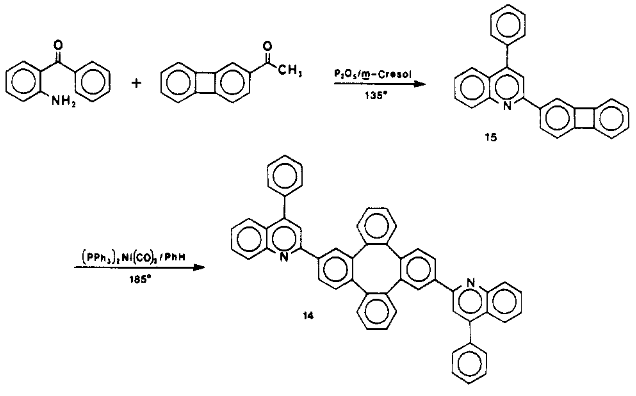

Figure 4. Synthesis of a tetraphenylene model compound (14).

These results suggested either that residual biphenylene was responsible for the degradation or that tetraphenylene, the product of biphenylene dimerization, was not thermooxidatively stable. To determine whether the weight losses observed could be attributed to tetraphenylene decomposition, a model study was carried out. The model compound **14**, which mimics the cross-link site of the resins, was prepared in 38% yield by the nickel(0)-catalyzed dimerization of 2-biphenylen-2-yl-4-phenylquinoline (**15**) in benzene (Figure 4). The balance of the material obtained from the reaction was oligomeric. Although five isomers of the model compound are possible, for clarity the model compound is represented as the least sterically hindered, most symmetrical isomer **14**.

Thermooxidation of **14** (60 h, 316 °C, flowing air atmosphere) produced a 16.8% weight loss. The dark brown, resinous residue, analyzed by thin-layer chromatography, showed the presence of **14** and a wide variety of low-R_f material, presumably oligomeric. The ^{1}H NMR spectrum of the residue was nearly identical with that of **14**, although the splitting pattern was less resolved; infrared analysis showed little difference between **14** and the residue. Analysis of the volatilized material indicated the presence of **14** and other unidentified lower R_f material. Aging **14** at 316 °C in a flowing nitrogen atmosphere for 60 h produced a 12.1% weight loss. Thus, tetraphenylene decomposes under thermal and thermooxidative conditions. The thermal decomposition of tetraphenylene to oligomeric products had been suggested earlier.[9]

Residual biphenylene also contributes to the thermooxidative degradation of resins prepared from biphenylene-end-capped oligomers. A sample of **1** that had been melt-processed in the presence of the nickel(0) catalyst at 300 °C for 2 h under a 5000-lb load showed a 20.8% weight loss when isothermally aged in air at 316 °C for 100 h. The DSC of an unaged sample of **1** showed a considerable amount of residual biphenylene. By contrast, a properly cured sample of **1** (350 °C for 2 h under a

5000-lb load in the presence of the nickel(0) catalyst) showed a 6.8% weight loss. No residual biphenylene was observed by DSC in the unaged sample.

Thus, the attachment of biphenylene through a phenoxy spacer group to oligomeric polyquinoline chains did not afford improved mechanical properties in comparison to biphenylene-end-capped oligomeric polyquinolines. Although cross-linked, three-dimensional network systems were obtained, the cross-link density may not have been high enough to afford the desired results. Results of thermooxidative stability tests on the cured resins prepared in this study and a tetraphenylene model compound indicated that tetraphenylene is not a particularly stable cross-link site. However, biphenylene can be used in combination with acetylenic groups in the oligomers to yield stable cross-link sites, as reported in the following paper.

Experimental Section

Cuprous chloride was purified according to the published procedure[10] and was used immediately in the Ullman ether synthesis reaction. The monomers 4-4′-diamino-3,3′-dibenzoyldiphenyl ether (**10**)[11] and 4,4′-diacetyldiphenyl ether (**11**)[12] were prepared and purified according to the published procedure. Biphenylene was prepared from the *o*-diazocarboxylate[13] and was purified as described.[1]

2-Acetylbiphenylene. To a stirred suspension of 8.0 g (60 mmol) of aluminum trichloride in 60 mL of dry methylene chloride cooled to 0 °C under an atmosphere of nitrogen was added 4.7 g (60 mmol) of acetyl chloride over 5 min. The gray suspension was stirred at 0 °C for 15 min, warmed to room temperature, and cannulated into a pressure-equalizing addition funnel that was fitted to a round-bottom flask. The flask contained a solution of 7.61 g (50.0 mmol) of biphenylene in 65 mL of methylene chloride and was immersed in a cooling bath at −30 °C. Dropwise addition of the preformed complex over 30 min afforded a dark red solution that was stirred at −30 °C for 1.5 h and then at room temperature for 2.5 h. After this time the reaction mixture was poured onto 100 g of ice and 50 mL of concentrated hydrochloric acid. The aqueous layer was extracted with methylene chloride (2 × 50 mL) which was combined with the organic layer, washed with a saturated salt solution (125 mL), and dried over magnesium sulfate. Removal of the solvent under reduced pressure followed by sublimation of the residue (110 °C/(0.05 mmHg)) afforded 8.00 g (82%) of a bright yellow crystalline solid: mp 137.5–139 °C (lit.[7] mp 134–135 °C).

2-Bromobiphenylene (4). A solution of 76.1 g (0.500 mol) of biphenylene and 93.4 g (0.525 mol) of *N*-bromosuccinimide (recrystallized from water) in 500 mL of dry *N*,*N*-dimethylformamide was stirred at room temperature for 24 h. The reaction mixture was poured into 2.5 L of water, and the yellow precipitate was collected by suction filtration and then washed with 250 mL of water. The dry yellow solid was dissolved in a minimal amount of methylene chloride and prepurified by flash chromatography (hexane as the eluent). Sublimation (90 °C (0.05 mmHg)) afforded 99.0 g of a light yellow solid that by GC analysis proved to be a mixture of 7.3 g of biphenylene and 91.7 g (79%) of 2-bromobiphenylene: mp 62.0–64.0 °C. The product was used without any further purification except for an analytical sample that was purified by flash chromatography and then sublimation to afford **4** as a yellow solid: mp 66.5–67.0 °C (lit.[14] mp 64–65 °C).

Methyl 4-(Biphenylen-2-yloxy)benzoate (5). A suspension of 38.0 g (0.250 mol) of methyl 4-hydroxybenzoate and 17.5 g (0.250 mol) of potassium methoxide in 750 mL of dry benzene was heated at the reflux temperature with mechanical stirring for 12 h under an atmosphere of nitrogen. The benzene and methanol were then removed by distillation to give a fine, white solid that was dried at 125 °C under a flow of nitrogen for 4 h and then cooled. The flow of nitrogen was increased and 3.71 g (37.5 mmol) of cuprous chloride was added to the dry salt followed by 250 mL of dry pyridine. The yellow suspension was heated to the reflux temperature, and a solution of 63.6 g (0.275 mol) of 2-bromobiphenylene in 250 mL of pyridine was added over 25 min. After 48 h at the reflux temperature, the dark reaction mixture was cooled and the pyridine was removed under reduced pressure to afford a dark brown oil. Purification by medium-pressure liquid chromatography (hexane/methylene chloride, 1:3) afforded 44.1 g (58%) of **5** as a yellowish-lime solid: mp 95.0–97.0 °C. Sublimation (125 °C (0.05 mmHg)) of an analytical sample gave a yellow solid: mp 99.5–100 °C; IR (KBr) 1725, 1285 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.02–6.99 (q, 4 H), 6.76–6.40 (m, 7 H), 3.89 (s, 3 H). Anal. Calcd for $C_{20}H_{14}O_3$: C, 79.46; H, 4.67. Found: C, 79.54; H, 4.67.

4-(Biphenylen-2-yloxy)benzyl Alcohol (6). A solution of 18.1 g (60.0 mmol) of methyl 4-(biphenylen-2-yloxy)benzoate (**5**) in 240 mL of dry ether was added to a stirred suspension of 1.37 g (36.0 mmol) of lithium aluminum hydride in 60 mL of ether at room temperature over 1 h. When the addition was complete, the reaction mixture was stirred at room temperature for 30 min, and 150 mL of water followed by 25 mL of concentrated hydrochloric acid was carefully added. The layers were separated, and the aqueous layer was extracted with methylene chloride (75 mL). The extracts were combined with the organic layer, washed with water (2 × 150 mL) and saturated salt solution (150 mL), and dried over magnesium sulfate. Removal of the solvent afforded a yellow solid that was dried at 50 °C under reduced pressure (0.05 mmHg) to give 16.3 g (99%) of **6**: mp 109.5–110.5 °C; IR (KBr) 3365, 1275 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.31–6.97 (q, 4 H), 6.74–6.28 (m, 7 H), 4.68–4.66 (d, 2 H), 1.64–1.60 (t, 1 H). (Upon the addition of D_2O to the sample, the doublet at δ 4.68–4.66 collapsed to a singlet at δ 4.66 and the triplet at δ 1.62–1.50 disappeared.) Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.12; H, 5.20.

4-(Biphenylen-2-yloxy)phenylacetonitrile (3). To a stirred suspension of 16.5 g (60.0 mmol) of 4-(biphenylen-2-yloxy)benzyl alcohol (**6**) in 180 mL of dry benzene was added 21.4 g (0.180 mol) of thionyl chloride. The reaction mixture was then suction-filtered through a column of silica and washed through with methylene chloride. Removal of the solvent afforded a yellow solid that was dissolved in 120 mL of dry *N*,*N*-dimethylformamide, and to this solution was added 7.81 g (0.120 mol) of dry potassium cyanide. The suspension was stirred at 50 °C for 22 h, after which time it was poured into 600 mL of water. The yellow solid that was collected by suction filtration was purified by medium-pressure liquid chromatography (hexane/methylene chloride, 1:4) to afford 12.1 g (71%) of **3**: mp 149.5–151.0 °C. An analytical sample was obtained by sublimation (155 °C (0.05 mmHg)): mp 151.5–152.0 °C; IR (KBr) 2235, 1270 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.28–6.99 (q, 4 H), 6.74–6.38 (m, 7 H), 3.70 (s, 1 H). Anal. Calcd for $C_{20}H_{13}NO$: C, 84.78; H, 4.62; N, 4.94. Found: C, 84.62; H, 4.65; N, 4.87.

2-Methyl-2-(4-nitrophenyl)-1,3-dioxolane (7). A solution of 41.3 g (0.250 mol) of 4-nitroacetophenone, 17.1 g (0.275 mol) of ethylene glycol, and 3.24 g (18.8 mmol) of *p*-toluenesulfonic acid monohydrate in 250 mL of benzene was heated at the reflux temperature. Water was removed by means of a Dean–Stark trap. After 24 h the solution was cooled, and the solvent was removed by rotary evaporation. The residue was taken up in 250 mL of methylene chloride, washed with water (2 × 250 mL) and saturated salt solution (250 mL), and dried over sodium sulfate. Removal of the solvent afforded a light yellow solid that was recrystallized from ethanol to give 38.9 g (74%) of **7** as white prisms: mp 76.0–77.0 °C (lit.[6] mp 73–75 °C).

5-(2-Methyl-1,3-dioxolan-2-yl)-3-[4-(biphenylen-2-yloxy)phenyl]-2,1-benzisoxazole (8). To a solution of 40.4 g (0.613 mol, 85% assay) of potassium hydroxide in 85 mL of methanol at 0 °C was added 10.9 g (38.5 mmol) of 4-(biphenylen-2-yloxy)phenylacetonitrile (**3**). The slurry was stirred mechanically at 0 °C for 10 min, after which time a solution of 7.32 g (35.0 mmol) of 2-methyl-2-(4-nitrophenyl)-1,3-dioxolane (**7**) in 55 mL of 2:1 methanol/tetrahydrofuran was added. The mixture was stirred at 0–5 °C for 1.5 h and then heated to 55 °C. At this temperature dissolution of **3** was complete and a reddish-brown color had developed. After 20 h at 55 °C the reaction mixture was cooled to room temperature and then further cooled to 0 °C. Suction filtration afforded a tan solid that was continuously extracted with methanol for 9 h and then dried to give 3.32 g (21%) of **8** as a light yellow solid: mp 185.0–187.0 °C. An additional 3.19 g of **8** was isolated by concentration of the methanolic extracts and purification by flash chromatography (methylene chloride). An analytical sample was obtained by medium-pressure liquid chromatography (methylene chloride): mp 187.0–187.5 °C; IR (KBr) 1505, 1430, 1230 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.02–7.17 (q, 4 H), 7.90–7.89 (d, 1 H), 7.60–7.57 (d, 1 H), 7.45–7.41 (dd, 1 H), 6.79–6.41 (m, 7 H), 4.11–3.81 (m, 4 H), 1.70 (s, 3 H). Anal. Calcd for $C_{29}H_{21}NO_4$: C, 77.84; H, 4.73; N, 3.13. Found: C, 76.54; H, 4.78; N, 3.06.

5-Acetyl-2-amino-4′-(biphenylen-2-yloxy)benzophenone (9). To a suspension of 4.47 g (10.0 mmol) of 5-(2-methyl-1,3-dioxolan-2-yl)-3-[4-biphenylen-2-yloxy)phenyl]-2,1-benzisoxazole (8) in 50 mL of glacial acetic acid heated at 95 °C was added 4.19 g (75.0 mmol) of iron powder and 9.0 mL (0.50 mol) of water in 5 equal portions over 1 h. The dark orange-brown solution was then stirred at 95 °C for 2 h, cooled, and poured into [illegible] mL of water. The yellow precipitate was collected by suction filtration and purified by medium-pressure liquid chromatography (chloroform). Concentration of the fractions containing the product gave an orange oil that was dissolved in methylene chloride. Removal of the solvent under reduced pressure produced a bright yellow honeycombed solid that was dried under reduced pressure (65 °C (0.05 mmHg)) to afford 2.84 g (70%) of monomer-grade 9: mp 148.0–148.5 °C; IR (KBr) 3440, 3320, 1665, 1600, 1230 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.19–8.17 (d, 1 H), 7.93–7.89 (dd, 1 H), 7.69–7.06 (q, 4 H), 6.79–6.42 (m, 10 H), 2.45 (s, 3 H). Anal. Calcd for $C_{27}H_{19}NO_3$: C, 79.98; H, 4.72; N, 3.45. Found: C, 79.88; H, 4.73; N, 3.41.

2-(Biphenylen-2-yl)-4-phenylquinoline (15). Under a static atmosphere of nitrogen, a mixture of 17.0 g of phosphorus pentoxide and 40 mL of *m*-cresol was mechanically stirred for 30 min at 135 °C to afford a light straw-colored solution. The solution was allowed to cool to room temperature, and then 3.94 g (20.0 mmol) of 2-aminobenzophenone (recrystallized from ethanol) and 3.88 g (20.0 mmol) of 2-acetylbiphenylene were added. After the system was purged with nitrogen, the dark red-orange solution was heated with stirring at 135 °C for 24 h, after which time it was poured into a rapidly stirred solution of 95 mL of concentrated ammonium hydroxide in 375 mL of water. The yellow precipitate that formed was collected by suction filtration, washed with water, and then continuously extracted with methanol for 3.5 days. The extracts were cooled to 0 °C and suction-filtered to afford 6.61 g (93%) of **15** as a bright yellow, microcrystalline solid: mp 151.0–151.5 °C; IR (KBr) 1590, 1550, 1480, 1415, 1340, 1205, 1155 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.20–8.17 (d, 1 H), 7.88–7.85 (d, 1 H), 7.74–7.41 (m, 10 H), 6.81–6.68 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 156.5, 152.5, 151.9, 150.8, 150.7, 149.0, 148.7, 139.9, 138.4, 130.0, 129.5, 128.7, 128.54, 128.48, 128.4, 126.2, 125.8, 125.6, 118.8, 117.8, 117.7, 117.3, 116.5. Anal. Calcd for $C_{27}H_{17}N$: C, 91.24; H, 4.82; N, 3.94. Found: C, 90.93; H, 5.01; N, 3.87.

Bis(4-phenylquinolin-2-yl)tetraphenylene (14). In a 200-mL-capacity, oven-dried pressure bottle were placed 1.07 g (3.00 mmol) of 2-(biphenylen-2-yl)-4-phenylquinoline (15), 0.192 g (0.300 mmol) of bis(triphenylphosphine)dicarbonylnickel(0), and 6 mL of dry benzene. The bottle was flushed with argon, sealed, and immersed in a silicone oil bath heated at 195 °C. The yellow solution in the bottle was heated with stirring for 30 min, during which time the solution's color changed to orange and finally black. After cooling to room temperature, the bottle was placed in a freezer at −25 °C for 15 min before opening. To the black mass was added 10 mL of methylene chloride. Filtration through Celite afforded a clear, yellow solution. The solvent was removed under reduced pressure, and the yellow residue was purified by medium-pressure liquid chromatography (hexane/methylene chloride, 1:9). Isolated was 0.406 g (38%) of **14** as a cream-colored solid: mp (DSC) 465 °C; IR (KBr) 1590, 1545, 1490, 1415, 1360, 770, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.16–7.23 (m); ^{13}C NMR ($CDCl_3$) δ 156.4, 149.1, 148.8, 142.6, 141.9, 141.4, 141.3, 138.7, 138.4, 130.1, 129.9, 128.8, 128.5, 126.2, 125.8, 125.6, 119.4; mass spectrum, *m/e* (relative intensity) 711.6 (52.1), 710.7 (M$^+$, calcd 710.9, 100), 355.7 (30.5), 355.2 (48.2). Anal. Calcd for $C_{54}H_{34}N_2$: C, 91.24; H, 4.82; N, 3.94. Found: C, 91.04; H, 4.92; N, 3.86.

Biphenylene-End-Capped Polyquinoline 12a. Into the bottom of a resin kettle were weighed 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (10), 0.7590 g (2.985 mmol) of 4,4′-diacetyldiphenyl ether (11), and 0.1808 g (0.4460 mmol) of 5-acetyl-2-amino-4′-(biphenylen-2-yloxy)benzophenone (9) followed by 23.0 g (82.6 mmol) of di-*m*-cresyl phosphate and 7.4 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 2.06 g (98%) of **12a** as a light yellow powder: [η] = 0.51 dL/g (25.0 °C, chloroform). Anal. Calcd C, 85.90; H, 4.41; N, 4.61. Found: C, 84.35; H, 4.48; N, 4.45.

Biphenylene-End-Capped Polyquinoline 12b. The above procedure was followed except 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (10), 0.7550 g (2.969 mmol) of 4,4′-diacetyldiphenyl ether (11), and 0.3617 g (0.8920 mmol) of 5-acetyl-2-amino-4′-(biphenylen-2-yloxy)benzophenone (9) were used as the monomer reagents together with 24.5 g (88.0 mmol) of di-*m*-cresyl phosphate and 7.9 g of *m*-cresol. The monomers were polymerized, end-capped with 0.1733 g (0.8920 mmol) of 2-acetylbiphenylene, and precipitated and purified as above to afford 2.22 g (98%) of **12b** as a light yellow powder: [η] = 0.52 dL/g (25.0 °C, chloroform). Anal. Calcd: C, 86.04; H, 4.39; N, 4.56. Found: C, 84.10; H, 4.49; N, 4.45.

Biphenylene-End-Capped Polyquinoline 12c. The above procedure was followed except 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (10), 0.7512 g (2.954 mmol) of 4,4′-diacetyldiphenyl ether (11), and 0.5425 g (1.338 mmol) of 5-acetyl-2-amino-4′-(biphenylen-2-yloxy)benzophenone (9) were used as the monomer reagents together with 26.0 g (93.3 mmol) of di-*m*-cresyl phosphate and 8.3 g of *m*-cresol. The monomers were polymerized, end-capped with 0.1733 g (0.8920 mmol) of 2-acetylbiphenylene, and precipitated and purified as above to afford 2.38 g (98%) of **12c** as a light yellow powder: [η] = 0.54 dL/g (25.0 °C, 1,1,2,2-tetrachloroethane). Anal. Calcd: C, 86.15; H, 4.37; N, 4.51. Found: C, 84.81; H, 4.45; 4.35.

Phenyl-End-Capped Polyquinoline 13a. Into the bottom of a resin kettle were weighed 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (10), 0.7590 g (2.985 mmol) of 4,4′-diacetyldiphenyl ether (11), and 0.1808 g (0.4460 mmol) of 5-acetyl-2-amino-4′-(biphenylen-2-yloxy)benzophenone (9) followed by 23.0 g (82.6 mmol) of di-*m*-cresyl phosphate and 7.4 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 0.1072 g (0.8920 mmol, 104 μL) 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 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 2.00 g (97%) of **13a** as a cream-colored powder: [η] = 0.51 dL/g (25.0 °C, chloroform).

Phenyl-End-Capped Polyquinoline 13b. The above procedure was followed except 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (10), 0.7550 g (2.969 mmol) of 4,4′-diacetyldiphenyl ether (11), and 0.3617 g (0.8920 mmol) of 5-acetyl-2-amino-4′-(biphenylen-2-yloxy)benzophenone (9) were used as the monomer reagents together with 24.5 g (88.0 mmol) of di-*m*-cresyl phosphate and 7.9 g of *m*-cresol. The monomers were polymerized, end-capped with 0.1072 g (0.8920 mmol, 104 μL) of acetophenone, and precipitated and purified as above to afford 2.17 g (97%) of **13b** as a light yellowish cream-colored powder: [η] = 0.50 dL/g (25.0 °C, chloroform).

Phenyl-End-Capped Polyquinoline 13c. The above procedure was followed except 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (10), 0.7512 g (2.954 mmol) of 4,4′-diacetyldiphenyl ether (11), and 0.5425 g (1.338 mmol) of 5-acetyl-2-amino-4′-(biphenylen-2-yloxy)benzophenone (9) were used as the monomer reagents together with 26.0 g (93.3 mmol) of di-*m*-cresyl phosphate and 8.3 g of *m*-cresol. The monomers were polymerized, end-capped with 0.1072 g (0.8920 mmol, 104 μL) of acetophenone, and precipitated and purified as above to afford 2.33 g (97%) of **13c** as a pale yellowish-white powder: [η] = 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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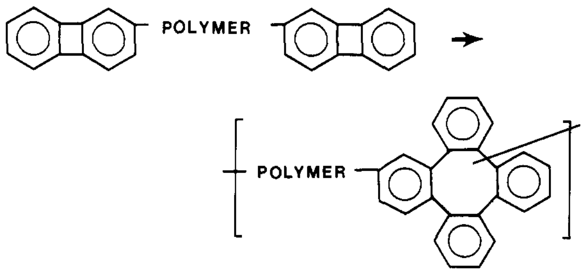
ABSTRACT: A series of oligomeric polyquinolines ($\overline{\mathrm{DP}}$ = 22) containing acetylene linkages and capped by biphenylene or phenyl groups was prepared. The monomer, 4,4′-diacetyldiphenylacetylene, was used to incorporate the acetylene linkages. Oligomers with 0, 12.5, 25, 50, and 100% 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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