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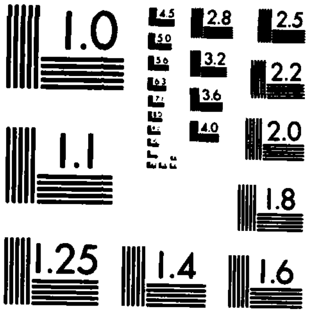

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CROSS-LINKING REACTIONS OF THERMALLY STABLE HIGH PERFORMANCE POLYMERS

Final Report

J. K. Stille

January 1980-December 1982

U.S. Army Research Office

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The relationships between the structures and the morphology, solution properties and mechanical properties of polyquinolines depend upon the manner in which the quinoline units are linked together. A wide variety of structures account for polyquinolines that either are amorphous, soluble in common organic solvents and have moderately high glass transition temperatures (~250 °C) or are crystalline, are soluble only in acidic solvents, forming anisotropic solutions, and have high crystalline transition temperatures (>500 °C). The conduct-

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ing properties of certain doped polyquinolines containing either total conjugation or sulfur linkages between quinoline units are described.

Biphenylene end-capped polyquinoline pre-polymers of DP=3, 11 and 22 were prepared by adjusting the stoichiometry of the bis(aminoketone)monomer, 4,4'-diamino-3,3'-dibenzoyldiphenyl ether, the bisketomethylene monomer, 4,4'-diacetyldiphenyl ether and the ketomethylene end cap, 2-acetylbiphenylene. Melt processing of the pre-polymers in the presence of bis(triphenylphosphine)dicarbonylnickel(0) was carried out at 325-340°C under 500 psi to give quality transparent films. Very short cure times (15 min) were realized in the presence of the nickel(0) catalyst, and the resulting films were 75-100 percent insoluble, had increased Tg's and showed improved mechanical properties both above and below the Tg as compared with the uncured resins. On the basis of model reactions and the observation that the degree of crosslinking in the cured resins was essentially independent of the DP of the pre-polymer, chain extension by conversion of biphenylene end-caps to tetrabenzocyclooctatetraene linkages was proposed to be the major reaction of the biphenylene end-groups with crosslinking occurring to a lesser extent after the chain length increased and the concentration of biphenylene ends decreased.

Biphenylene end-capped polyimide, poly(ether-keto-sulfone), and polyphenylquinoxaline prepolymers were synthesized. The polyimide pre-polymer of DP 3 obtained from 3,3'-4,4'-benzophenonetetracarboxylic dianhydride, 4,4'-diaminodiphenyl ether and 2-aminobiphenylene, was melt processed at 325°C under 500 psi in the presence of a Ni(0) catalyst for 15 min to give films that showed good mechanical properties and a Tg of 261°C. The polymerization to give a biphenylene end-capped poly(ether-keto-sulfone) could not be controlled under conventional conditions (aluminum chloride in methylene chloride) by utilizing a monomer imbalance to yield the desired molecular weight pre-polymer. Polyphenylquinoxaline pre-polymers prepared by the reaction of 4,4'-oxydibenzil, 3,3'-diaminobenzidine and 2-(phenylglyoxalyl)biphenylene were melt processed at 340°C under 500 psi in the presence of a Ni(0) catalyst for 15 min gave insoluble film with a Tg of 291°C and improved mechanical properties above Tg.

Graphite reinforced composites were prepared from biphenylene end-capped polyquinoline and polyimide pre-polymers. The composites demonstrated excellent initial properties and low weight loss after oxidative aging at 316°C. However, the mechanical properties were severely diminished after aging for 50-100 h at 316°C in air and photomicrographs of the composites after aging showed the presence of voids.

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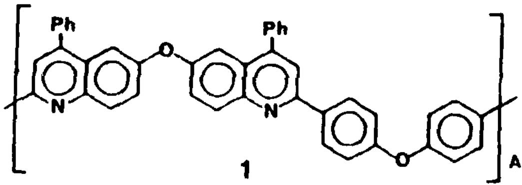
INTRODUCTION

Polyquinolines have been synthesized by a polymerization reaction that allows the introduction of a wide range of structural features. As a result, the linearity and rigidity of the polymer can be adjusted to provide materials that are amorphous and have good solubility in common organic solvents and lower glass transition temperatures (250°C) or materials that are highly crystalline, insoluble in the common solvents, and have crystalline transition temperatures greater than 550°C. In addition, inert or reactive groups can be incorporated into the main chain of the polymer, appended from the main chain or placed at the chain ends. The synthesis and properties of such polymers are discussed herein. Specifically, the structure-property realtionships of semirigid and rigid-rod polyquinolines, the effect of large pendent groups on the solubility of such polymers and the electrical properties of certain polyquinolines are considered. Finally, the crosslinking reaction of thermally stable polymers, particularly polyquinolines that contain biphenylene groups, and the use of such materials as matrix resins in composites are described.

LINEAR POLYQUINOLINES

As a result of the availability of a wide variety of aminoketone and ketomethylene monomers that could be synthesized, and the ability of the Friedlander reaction to generate high molecular weight polymers under relatively mild conditions, a series of polyquinolines containing a variety of structural differences could be obtained. The chain stiffness could be altered from a semirigid main chain to a linear, rigid-rod main chain. A review of the synthesis, structures and properties of these polyquinolines has appeared.[1,2] The monomers were designed to yield only thermally stable materials, such that the resulting polymers had excellent thermal stability, with the initial weight loss occurring between 500 and 600°C in air (TGA), the exception being that polyquinolines having perfluoromethylenes in the main chain started oxidative degradation at somewhat lower temperatures (~400°C).[3] Isothermal ageing studies of certain polyquinolines showed them to be among the most thermally stable organic polymers known.[4]

High molecular weight polyquinolines ($\overline{Mn}$=325,000) containing flexible oxygen linkages between the aromatic units, for example structure 1, are largely amorphous and are soluble in common organic solvents.[1,2] Clear, transparent films can be cast from chloroform or tetrachloroethane, and although the materials are largely amorphous, crystalline transitions can be detected. The semirigid polymers have glass transitions in the 255-300°C range. None of these semirigid polyquinolines were crystalline enough such that they maintained good mechanical properties above the glass transition temperature.



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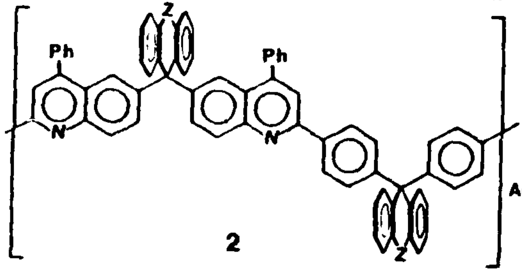

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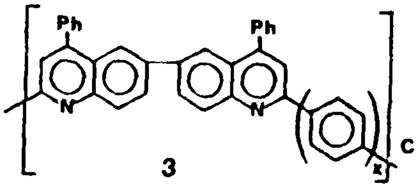


3

			Tg (°C)	Tm
1	Amorphous		266	448
2	Amorphous	Z=nil	390	
		Z=CO	390	
3	x = 2 Crystalline		360	>500

Because the use temperature of the amorphous semirigid polyquinolines is limited to their glass transition temperatures, an effort was made to increase the glass transition temperature by synthesizing a more rigid chain, but still maintaining the amorphous nature to enable solution processability. Polyquinolines containing pendent loops attached to the polymer main chain (eg. 2) give the polymer enhanced rigidity.[5-7] These loops are perpendicular to the main chain, and have the effect of raising the glass transition temperature, while maintaining the good solubility in common organic solvents that is characteristic of the amorphous polyquinolines. Replacing the oxygen linkages in the semirigid polyquinoline (1) by pendent loops (2) has the effect of raising the glass transition temperature by about 120°C, raising its use temperature nearly to 400°C.

Polyquinolines having directly bonded quinoline units in the 6-positions and connected in the 2-positions by p-phenylene units (eg. 3) are rigid rods that are highly crystalline, having crystalline transition temperatures at 500°C or above.[8] These polymers are soluble only in the polymerization medium -- m-cresol/di-(m-cresyl phosphate) -- or strong acids (eg. trifluoromethanesulfonic acid), in which they form anisotropic solutions at about 9 wt %. Even solutions of very low concentrations ($\sim$1%) will give anisotropic solutions on shearing. These dilute solutions become isotropic on heating, but form anisotropic solutions again at ambient temperatures on shearing.

The rigid-rod polyquinolines are characterized by high glass transition temperatures, but not any higher than the polyquinolines containing the pendent loops. In some cases the Tg was not apparent due to the relatively high degree of crystallinity, and in some cases the crystalline transition temperatures could not be observed because they were apparently above the decomposition temperature. Thus, for these rigid-rod polyquinolines, the decomposition temperature and the crystalline transition temperature nearly coincide. The comparison of the mechanical properties of the semirigid and rigid-rod polyquinolines is exemplified by a comparison of the dynamic storage moduli of the two types, 1 and 3 (x=1) (Figure 1).

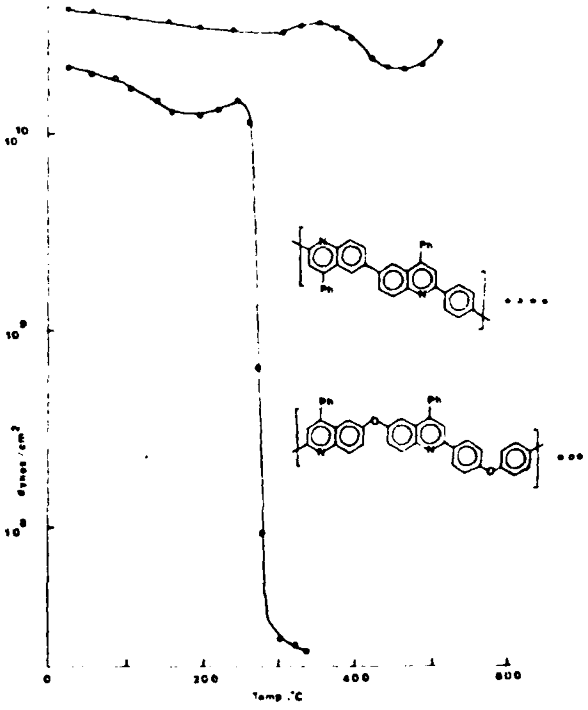
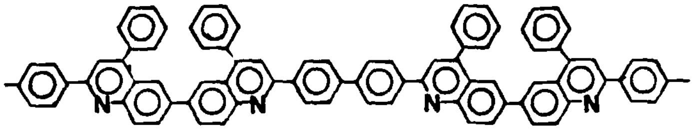
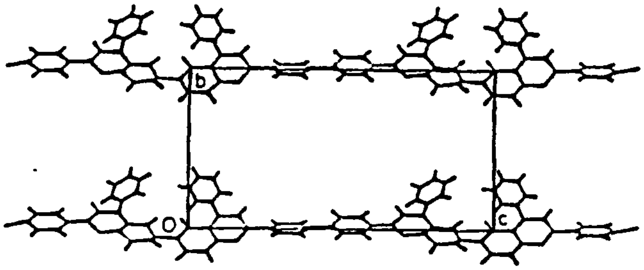


Figure 1 Thermomechanical properties of polyquinolines.

Rigid-rod polyquinolines could be wet spun in some preliminary trials (8-18.5 wt % solids) from the polymerization dope to give fibers with good tensile strengths (9 gpd) and high moduli. The x-ray structure of a fiber of poly[2,2'-(<u>p</u>,<u>p</u>-biphenyl)-6,6'-bis(4-phenylquinoline)], (3, x=2 idealized) shows that the parallel chains oriented along the direction of the fiber axis tend to stack in nearly coplanar sheets.[9]



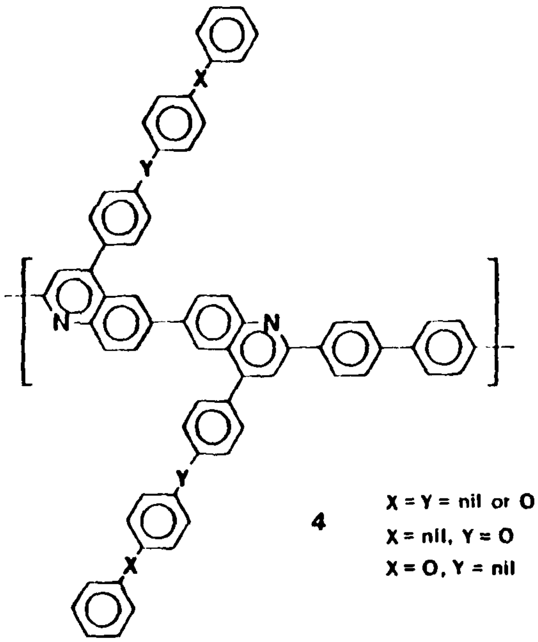


POLYQUINOLINES WITH IMPROVED SOLUBILITY

Part of the difficulty in studying the solution properties of s rigid-rod polymers is that the solubility is limited to strongly acidic media. In a number of cases, the solubility of polyaromatics has been improved by the attachment of phenyl groups on the main chain. Polyquinoline 3 (x=2) already has two pendent groups per recurring unit, but does not have the desired solubility in the more usual organic solvents.

In order to disrupt the crystal structure and improve solubility, longer pendent arms were placed in the 4-positions of the quinoline units. With an arm at least two phenylene units long, the crystal packing observed for 3 (x=2) could not be achieved, and a third phenyl group would necessitate rotation of the quinoline units out of the plane. In addition, it was hoped that the aromatic arms would keep adjacent chains at a distance that would tend not to allow a dense packing.

The synthesis of such polyquinolines has been carried out to give structures of the type **4**. Thus far, polyquinolines with improved solubility have not been achieved, at least from the polymer (**4**) containing X=O, Y=nil.



4

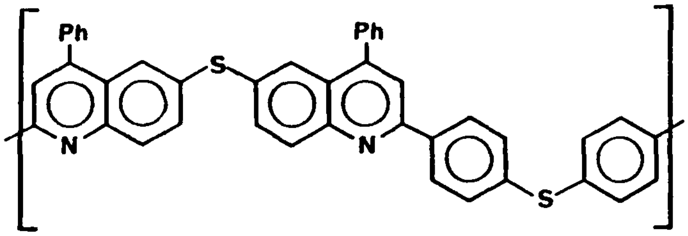
X = Y = nil or O
X = nil, Y = O
X = O, Y = nil

ELECTRICAL PROPERTIES OF POLYQUINOLINES

The wide range of structural features that can be incorporated into polyquinolines, plus the fact that these materials are readily processably and possess good mechanical properties, made certain polyquinolines prime candidates for semiconducting and conducting materials. Although polyquinoline 1 is an excellent high temperature insulating material, certain other polyquiolines should possess conducting properties on doping. Two types of polyquinolines were utilized for this purpose, those containing conjugated stacked planar structures (eg. 3, x=2) and those which are non-planar, but contain sulfur linkages in the main chain (5,6).

TCNQ forms charge-transfer complexes and simple complex salts with quinoline that have high conductivity.[10] The structure of 3 (x=2), having stacked coplanar aromatic sheets, resembles, in some respect, the structure of graphite, for which very high conductivity is observed for the arsenic pentafluoride intercalate.[11,12] Preliminary conductivity measurements on oriented fibers of **3** (x=2) doped with arsenic pentafluoride (400 torr) show that the conductivity rises rapidly from $\sigma=10^{-11}$ to 10^{-8}.

Although poly(p-phenylene sulfide) contains phenyl rings nearly at right angles to each other, the doped polymer yields a material that exhibits conductivity.[12] Films of polyquinolines containing sulfur connecting groups as exemplified by **5** and **6** are insulators. Preliminary experiments show that doping raises the conductivity from 10^{-12} to 10^{-5}.



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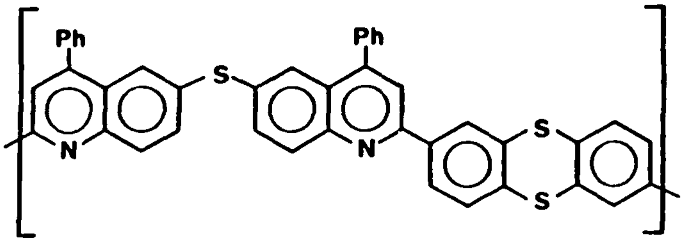

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CROSSLINKING AND CHAIN EXTENSION REACTIONS OF POLYAROMATICS CONTAINING BIPHENYLENE END GROUPS

Introduction

Polymers of the highest thermal stability are those constructed of aromatic carbocyclic and heterocyclic units linked to yield a conjugated chain. In addition to outstanding thermooxidative stability, these polymers show excellent retention of mechanical properties at high temperatures as a result of rigid backbones, high degrees of crystallinity and high crystalline transition temperatures. However, the processability of these polymers is problematic, due to their poor solubility and infusibility. The inclusion of flexible linkages into an all-aromatic polymer chain generally improves the processability, but lowers the use temperature as a consequence of lower phase transition temperatures.

One approach to the processability problem inherent in thermally stable polymers is to crosslink a processable polymer after or during fabrication to give a material with improved properties. Any chemical reaction intended for this purpose must fulfill the following requirements: 1) the reaction must proceed without the evolution of volatile by-products in order to prevent the formation of voids which decrease the strength of fabricated components, 2) the temprature necessary for the reaction should be above the Tg but below the decomposition temperature of the polymer, 3) the products of the reaction should show thermal stability comparable to that of the unaltered polymer, and 4) the rate of the reaction must be consonant with the processing method.

The crosslinking site may be introduced to the polymers in a number of ways: 1) in the polymer backbone, 2) as a pendent group, 3) as an additive, and 4) as an end-cap for low molecular weight oligomers. The last approach has received the most attention because it is particularly amenable to the melt processing of thermally stable polymers due to the improved melt flow characteristics of oligomers compared to high molecular weight polymers.

A variety of crosslinking sites have been used to improve the properties of readily processable thermally stable polymers. For example, acetylene[13] and nadic (bicyclo[2.2.1]hept-4-ene-2,3-dicarboxylic acid anhydride)[14-18] end-groups are currently being used in commercially available imide pre-polymers. While these pre-polymers give crosslinked resins that show impressive performance at high temperatures, the retention of mechanical properties for extended times at high temperatures is less for these materials than those of high molecular weight, all-aromatic polyimides.[19,20] Thus, a reactive end-group which would yield wholly aromatic crosslink or chain extension structures, was particularly desirable since the all-aromatic character of the polymer would be maintained in the cured resin.

The thermolysis of biphenylene has been shown,[21-23] depending on the reaction conditions, to afford primarily tetrabenzocyclooctatetraene, aromatic polymer, or stable adducts with aromatic compounds. This "inner ring chemistry" of biphenylene was the basis for the use of biphenylene as a crosslinking site for thermally stable polymers, because it was expected that any structures formed as a result of biphenylene inner ring chemistry would be aromatic and would show stability comparable to that of the parent polymer. Furthermore, volatile products would not be generated during crosslinking, thereby allowing void-free processing.

The first application of biphenylene as a crosslinking site was the incorporation of biphenylene into the main chain of various high molecular weight polyquinolines.[24,25] After curing, the polymers were insoluble, showed higher Tg's, and demonstrated improved mechanical properties both above and below the Tg compared to the uncured polymers. Similar results were observed with aromatic polyamides, polyquinoxalines, and a polybenzimidazole containing biphenylene units in the main chain.[26] The viability of biphenylene as a crosslinking site for thermally stable polymers was further demonstrated by the preparation of bisbiphenylene compounds as crosslinking additives in which the group linking the biphenylenes was a structural unit similar to that contained in the polymer to be crosslinked.[27] Solutions of polymer and crosslinking additive were cast into films which were thermally cured to give insoluble polymers.

Biphenylene End-Capped Polyquinoline Pre-Polymers

Ether-linked polyquinolines (1) showed the most desirable processing characteristics when compared to other polyquinolines.[1] High quality films cast from solutions of the polymer in common organic solvents showed no weight loss after oxidative isothermal aging for 100 hours at 300°C.[28] The ability of ether-linked polyquinolines to undergo melt processing also has been demonstrated; wire has been extruded from the melt by passage through a 1 mm bore at 430°C.[29] This combination of high thermal stability and good processability indicated that 1 was particularly well suited for the preparation of biphenylene end-capped polyquinoline pre-polymers.

A preliminary investigation of the flow characteristics of 1 showed that a $\overline{DP} \leq 22$ was necessary in order to achieve good melt processing. A series of biphenylene end-capped polyquinoline pre-polymers (11) with DP = 3, 11 and 22 were prepared by overbalancing with an appropriate amount of 7 relative to 8 ($\overline{DP} = \frac{1 + r}{1 + r - 2\,rp}$) to give pre-polymers with the desired DP (Figure 2). To effect end-capping, 2-acetylbiphenylene--prepared in 70 percent yield from acetic anhydride and biphenylene under Friedel-Crafts conditions--was added after 24 h to the polymerization medium containing the pre-formed polymers. The completeness of the end-capping reaction was verified by the lack of an appreciable ketone absorption in the infrared spectra of the pre-polymers. Furthermore, the ^{13}C NMR spectrum of

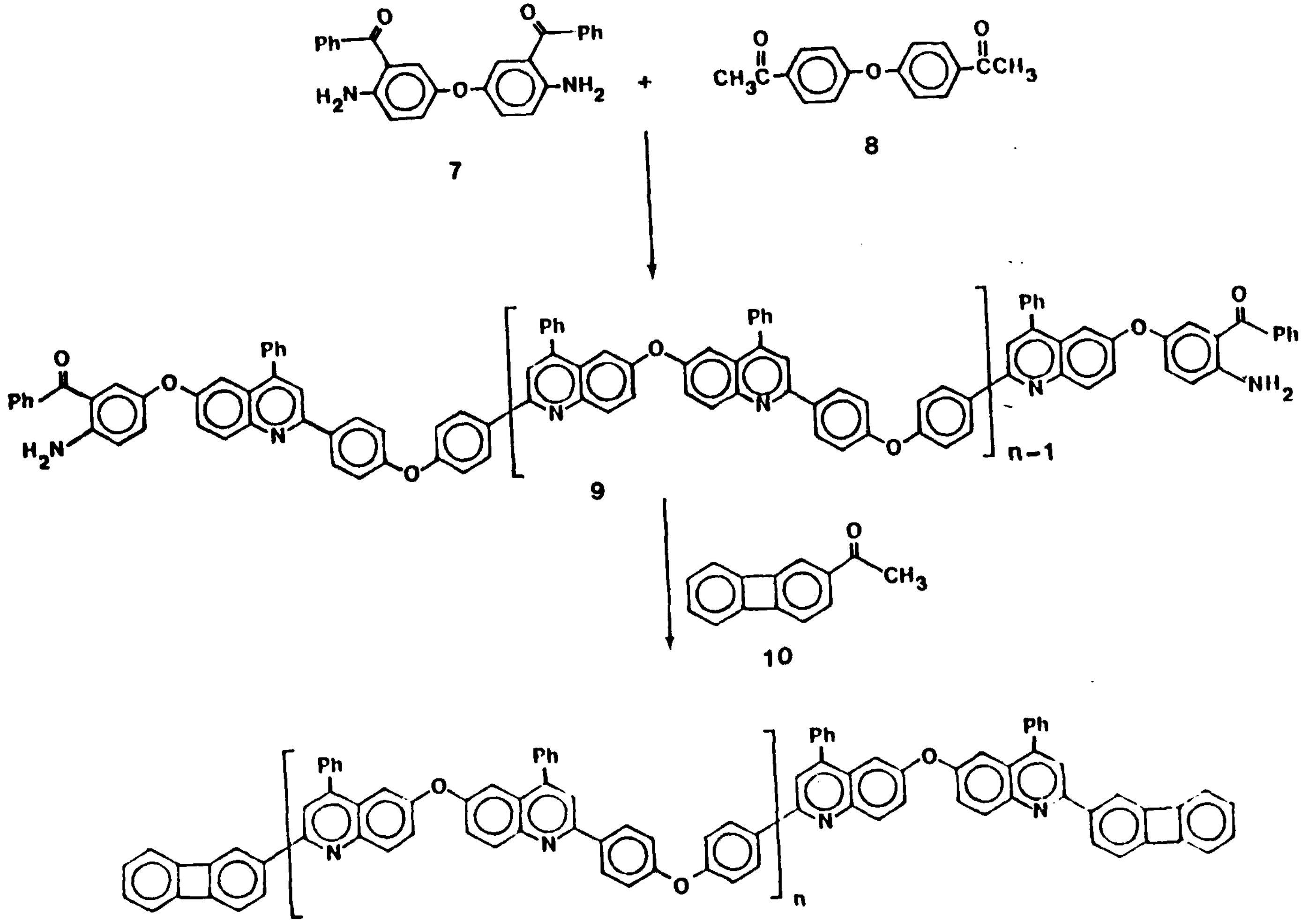


Figure 2. Synthesis of Biphenylene End-capped Pre-polymers

11 (DP = 3) was consistent with the calculated chemical shifts and the ^{13}C NMR spectra of polyquinolines containing biphenylene units in the main chain,[24] and did not show the presence of a carbonyl carbon.

Excellent agreement between the $\overline{DP}$ calculated on the basis of monomer imbalance and the DP obtained from molecular weight determination was realized (Table 1). Biphenylene end-capped polyquinoline 11 prepared via a calculated imbalance of the monomers to give $\overline{DP}$ = 22 had an intrinsic viscosity of 0.47 dL/g which corresponded to a $\overline{DP}$ of 22 obtained from the Mark-Houwink equations.[28]

The molecular weight distributions of the biphenylene end-capped polyquinoline pre-polymers were determined by gel permeation chromatography (GPC). Even though absolute values of the average molecular weights ($\overline{Mn}$), ($\overline{Mw}$), and (Mz) were expected to be unimportant since the analysis was relative to polystyrene standards, excellent agreement between the molecular weight from viscosity and the molecular weight from GPC was observed (Table 1).

Table 1

Comparison of Calculated and Observed Degrees of Polymerization for Biphenylene End-capped Polyquinoline Pre-polymers 11

Calculated		Observed			
$\overline{DP}^{a}$	$\overline{Mn}^{b}$	$[\eta]$	$\overline{DP}^{c}$	$\overline{Mn}^{c}$	$\overline{Mn}^{d}$
3	1800	0.09	2	1100	600
11	6500	0.25	8	5000	6500
22	13,000	0.47	22	13,000	12,000

a. $\overline{DP} = 1 + r/1 + r - 2rp$

b. $\overline{Mn} = \overline{DP} \times 590$.

c. $[\eta] = K\overline{Mn}^{a}$; $\overline{DP} = \overline{Mn}/590$; $K = 9.0 \times 10^{-4}$ and $a = 0.66$ (ref. 28)

d. GPC

The Tg of the pre-polymers as determined by differential scanning calorimetry (DSC) was a function of the molecular weight (Table 2).

Table 2

Dependence of the Tg on the $\overline{Mn}$ of Biphenylene End-capped Polyquinoline Pre-polymers

Polymer	$\overline{Mn}^a$	Tg, °C (DSC)	Tm, °C (DSC)	Tg, °C (calcd)[b]
11 ($\overline{DP}$=3)	1100	153	230[c]	157
11 ($\overline{DP}$=11)	5000	212	d	215
11 ($\overline{DP}$=22)	13,000	232	d	234
1[d]	40,000	266	448[c]	-
1[d]	100,000	266	448[c]	-

a. From viscosity.

b. Not observed after annealing at 300°C.

c. Not observed.

d. No end-cap.

Pre-polymer Processing and Properties of Cured Polymer. The polymer melt temperature of pre-polymer **11** ($\overline{DP}$ = 22) was approximately 300°C, which indicated that melt processing of the pre-polymers could be performed at moderate temperatures (300-325°C). However, the ring opening of biphenylene occurs at much higher temperatures, as demonstrated by differential scanning calorimetry (DSC) of **11** which showed an exotherm with maximum at 445°C. As a result, a catalyst was used to effect the ring opening of biphenylene at lower temperatures and thus allow lower processing temperatures.[24,25,30]

In addition of 20 mole percent (based on biphenylene) of bis(triphenylphosphine)(dicarbonyl)nickel(I) to polymers containing bisbiphenylene additives has been shown to effectively catalyze the crosslinking reaction.[27] Thus, pre-polymer **11** was melt-processed in the presence of 20 mole percent (based on biphenylene) of the Ni(0) catalyst. The resultant transparent, high quality films were completely insoluble and showed increased Tg's as well as improved mechanical properties both above and below the Tg (Table 3). Most striking was the observation that curing for only 15 min in the presence of the Ni(0) catalyst gave a film with nearly identical properties to those cured for much longer times. Differential scanning calorimetry of the film cured for 15 min showed no exotherm attributable to residual biphenylene, indicating that the reaction had gone to completion. This was clearly demonstrated by the DSC of films prepared by melt processing **11** ($\overline{DP}$ = 11) under the same conditions in the presence of the Ni(0) catalyst for 5 min, 7.5 min, and 15 min. In this case, the decrease of the ring opening exotherm was observed (DSC) as a function of time and shown to be essentially absent after 15 min (Figure 3). Thus, curing biphenylene end-capped polyquinoline pre-polymers in the presence of the Ni(0) catalyst afforded high quality, crosslinked films in very short cure times.

Although cured polymer **11**, $\overline{DP}$ = 11, contained a higher concentration of biphenylene end-groups than polymer **11** of $\overline{DP}$ = 22, the resulting films had nearly identical Young's modulus above Tg, indicating an equal crosslink density for the two films. This suggested that the major reaction of the biphenylene end-group was a dimerization reaction to give tetrabenzocyclooctatetraene linkages, providing primarily a chain extended polymer. Crosslinking occurred only when the biphenylene ends became inaccessible to one another. Since this would be expected to occur at the

Table 3

Film Properties of 11 Melt Processed at 340°C under 500 psi

Weight % $(PPh_3)_2Ni(CO)_2$	Processing time (min)	Tg°C (DSC)	Solubility[a]	$E'_{25°C}$ (dyn/cm^2)	$E'_{above\ Tg}/T$ (dyn/cm^2/°C)[b]
-	120	236	>95	2.2×10^{10}	c
2.5	15	243	0	2.8×10^{10}	1.0×10^8/291° - 330°
2.5	120	243	0	2.7×10^{10}	1.0×10^8/290° - 334°

a. Percent soluble after 24 h in chloroform.

b. $E'_{above\ Tg}$ is the lowest value of the storage modulus obtained above Tg. The temperature at which the modulus was observed is also given.

c. Not measurable even at the highest sensitivity of the instrument.

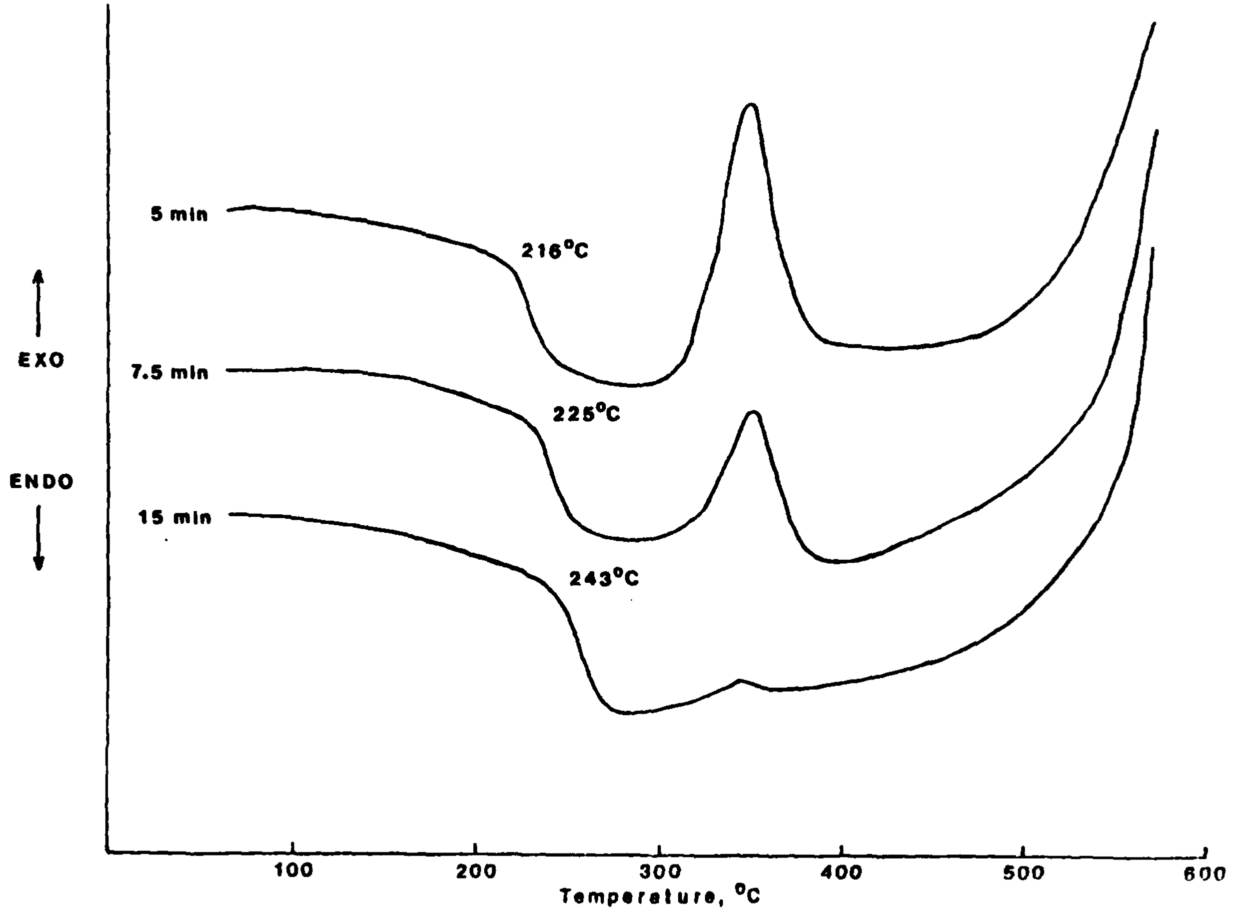


Figure 3. Differential Scanning Calorimetry of 11 Melt Processed in the Presence of Bis(triphenylphosphine)(dicarbonyl)nickel(0) for Various Times at 340°C under 500 psi

same $\overline{DP}$ the same crosslink density was observed in both films. Pre-polymer 11 of $\overline{DP}$ = 3, containing the greatest concentration of biphenylene end-groups, gave a brittle film after processing in the presence of the Ni(0) catalyst. While the pre-polymer clearly underwent crosslinking/chain extension during processing, as indicated by the increase in Tg and the considerable insolubility of the cured polymer (Table 4), the film quality was only fair. Apparently, the processing "window" in the case of 11 ($\overline{DP}$ = 3) was very narrow in the presence of the Ni(0) catalyst and the polymer set-up before adequate flow had been realized.

The melt processing of pre-polymers 11 ($\overline{DP}$ = 3 and $\overline{DP}$ = 11), at 340°C in the absence of added catlayst, did not afford coherent films and the resultant polymers remained completely soluble. At this melt processing temperature, in the absence of catalyst, biphenylene rections do not take place and these polymers are not high enough molecular weight to give coherent films. The involvement of biphenylene end-groups in crosslinking/chain extension was unambigously demonstrated by the melt processing of phenyl end-capped polyquinoline pre-polymer ($\overline{DP}$ = 22) containing the Ni(0) catalyst. The resultant film was completely soluble and showed no increase in the glass transition temperature after processing.

Oxidative isothermal aging of polyquinoline films was conducted at 300°C (Table 5). Melt processed films prepared from biphenylene end-capped pre-

Table 4

Comparison of Film Properties of **11** Melt Processed at 340°C under 500 psi

Pre-Polymer **11**, $\overline{DP}$	Weight % biphenylene	Weight % $(PPh_3)_2Ni(CO)_2$	Tg, °C (DSC) after processing	ΔTg, °C[a]	Solubility[b]	E'$_{25°C}$ (dyn/cm^2)	E'$_{above\ Tg}$/T (dyn/cm^2/°C)[c]
3	23	7.0	217	+64	-	d	d
3^d	23	7.0	235	+82	26%	d	d
11	7.5	4.2	243	+31	0%	$2.8x10^{10}$	$1.4x10^8$/ 285°-335°
22	3.5	2.5	243	+11	0%	$2.8x10^{10}$	$1.0x10^8$/ 291°-330°

a. ΔTg is the difference in Tg between the cured and uncured resins (see Table XXII).

b. Percent soluble after 24 hours in chloroform.

c. E'$_{above\ Tg}$ is the lowest value of the storage modulus obtained above Tg. The temperature at which the modulus was observed is also given.

d. Film quality not sufficient for modulus measurement.

e. Melt processed for 45 min. All others melt processed for 15 min.

Table 5

Oxidative Isothermal Aging of Polyquinolines for 100 h at 300°C in Air

Polymer	% Weight loss
Phenyl end-capped $(\overline{DP}=22)^a$	8.2
11 $(\overline{DP} = 22)^a$	1.9
11 $(\overline{DP} = 22)^b$	2.6
11 $(\overline{DP} = 11)^b$	3.4
1^c	1.5
1^d	0.3

a. Melt processed without added catalyst.

b. Melt processed in the presence of 20 mole % (based on biphenylene) bis(triphenylphosphine)(dicarbonyl)nickel(0).

c. Cast film of 1 $(\overline{Mn} = 45{,}000)$.

d. Powder samples of very high molecular weight 1 $(\overline{Mn} = 220{,}000)$.

polymers showed improved thermooxidative stability compared to a phenyl end-capped polyquinoline pre-polymer $(\overline{DP} = 22)$ but showed higher weight loss than a cast film of 1 $([\eta] = 1.06, \overline{Mn} = 45{,}000)$ and a powder sample of very high molecular weight 1 $([\eta] = 3.0, \overline{Mn} = 220{,}000)$. The weight loss of pre-polymers 11 (DP = 11 and 22) melt processed in the presence of the bis(triphenylphosphine)(dicarbonyl)nickel(0) catalyst cannot be compared directly to 11 $(\overline{DP} = 22)$ melt processed without added catalyst, since the latter did not undergo crosslinking/chain extension under the melt processing conditions (340°C, 500 psi). While the weight loss of cured polymers prepared from the biphenylene end-capped pre-polymers was somewhat greater than the weight loss of the high molecular weight parent polyquinoline, a prolonged useful lifetime at 300°C still was expected since the weight loss was not severe.

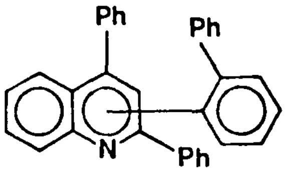
Mechanisms of Crosslinking/Chain Extension of Biphenylene Ends

The dimerization of biphenylene end-groups to tetrabenzocyclooctatetraene linkages would afford only chain extension and not crosslinking. Since the properties of cured biphenylene end-capped pre-polymers clearly showed moderate degrees of crosslinking, the biphenylene end-group must be able to react with aromatic units in adjacent polymer chains to form crosslink structures. However, the only reported addition of biphenylene to an aromatic compound via the ring opening reaction was the formation of small amounts of terphenyl and triphenylene when biphenylene and benzene were subjected to vapor phase pyrolysis at 700°C.[21,23] These conditions are quite different than those encountered in the condensed phase (300-400°C) curing reaction.

Biphenylene was allowed to react with suitable model compounds under both catalytic and thermal conditions. All reactions were performed in glass tubes sealed under reduced pressure. The bis(triphenylphosphine)(dicarbonyl) nickel(0) catalyzed reaction (10 mole percent based on biphenylene) were conducted at 200°C for 1.5 h while the uncatalyzed thermal reactions were run at 400°C for 1 h. Product mixtures were analyzed by GCMS and, in some cases, by direct insertion probe mass spectroscopy (DIPMS).

The reaction of biphenylene with 10 equivalents of benzene-d_6 was limited to catalytic conditions, since the temperature for the thermal reaction was much higher than the critical temperature of benzene. The product mixture from the catalytic reaction was composed primarily of tetrabenzocyclooctatetraene (12) fluorenone (13), and biphenyl. Deuterated products and residual biphenylene were not detected. Furthermore, an addition product of biphenylene to benzene-d_6 was not observed. (The lack of deuterium incorporation into the biphenyl is not readily explained since the source of hydrogen is not known).

Since the mechanism of crosslinking of polyquinolines with biphenylene was of particular interest, two model compounds based on ether-linked polyquinoline 1 were chosen: 2,4-diphenylquinoline and diphenyl ether. The catalyzed reaction of biphenylene with 5 equivalents of 2,4-diphenyl quinoline afforded the same major products in essentially the same distribution as the catalyzed reaction with benzene-d_6 (GCMS). However, when the product mixture was analyzed by DIPMS with the probe heated to 300°C, a small amount of product with m/e 432 was observed. This has been ascribed to the high boiling product **14** of the addition of biphenylene to 2,4-diphenylquinoline.



14

The thermal reaction of biphenylene with 2,4-diphenylquinoline without catalyst gave primarily recovered biphenylene and some biphenyl (GCMS). However, DIPMS of the product mixture again demonstrated the presence of **14** and the total ion intensity of **14** in the product mixture from the thermal reaction was greater than the total ion intensity of **14** in the product mixture from the Ni(0) catalyzed reaction. The lack of tetrabenzocyclooctatetrane (12) formation in the thermal reaction can be attributed to a concentration effect in which the 5-fold excess of 2,4-diphenylquinoline resulted in a decreased collision frequency for the intermediate biradicals with one another. This quenching effect also was observed when biphenylene was pyrolyzed with three or more equivalents of anthracene.[22]

The Ni(0) catalyzed reaction of biphenylene with 10 equivalents of diphenyl ether gave recovered biphenylene, fluorenone (13) and biphenyl (GCMS). Only a trace of tetrabenzocyclootatetraene was detected (12), in contrast to the Ni(0) catalyzed reactions of biphenylene with benzene-d_6 and 2,4-diphenylquinoline, in which (12) was the major product. This observation was not readily explained, since the thermal reaction of biphenylene with 10 equivalents of diphenyl ether afforded primarily 12, residual biphenylene, and biphenyl. Quenching was not observed in this reaction even though 10 equivalents of diphenyl ether was present. No addition product of biphenylene to the diphenyl ether was detected.

The conclusions from this model study are: 1) the dimerization of biphenylene to tetrabenzocyclooctatetraene (12) occurs under both Ni(0) catalyzed and uncatalyzed conditions. However, in agreement with previous reports,[21-23] the formation of 12 is quite dependent on the reaction conditions. 2) Biphenylene does react with 2,4-diphenylquinoline to give 14 as a minor product under both Ni(0) catalyzed and uncatlayzed conditions, but apparently does not react with benzene or diphenyl ether under the same conditions. 3) The crosslinking of polyquinoline probably occurs via the reaction of biphenylene with quinoline groups in the polymer chain. 4) The presence of fluorenone (13) in the product mixtures from the catalyzed reactions confirms that Ni(0) inserts into the biphenylene inner ring via an oxidative-addition (Figure 4). While the thermal reactions of biphenylene have been postulated to involve a biradical intermediate[21-23] a free biradical is unlikely in the catalyzed ring opening and tetraphenylene most probably arises from addition of a second molecule of biphenylene to the nickel metallocycle.

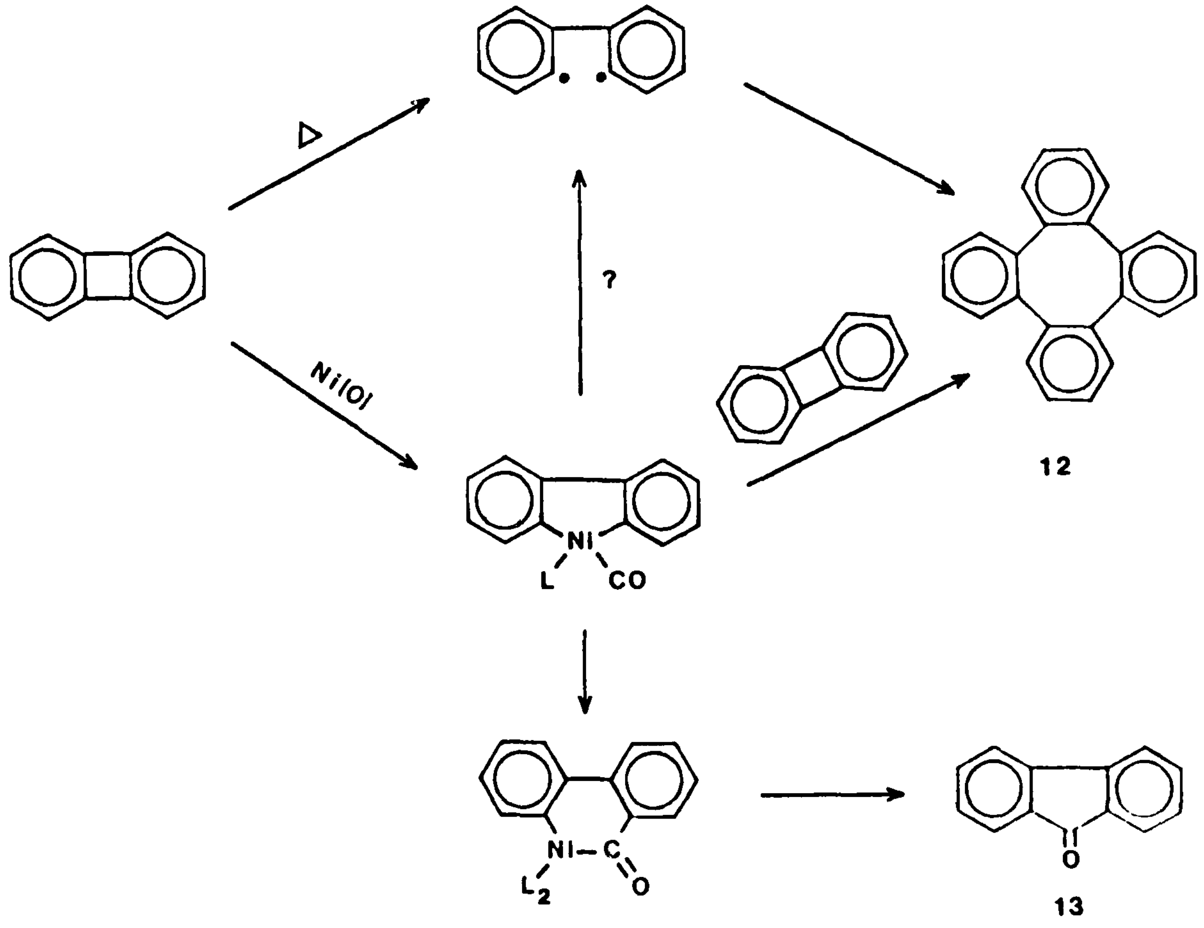
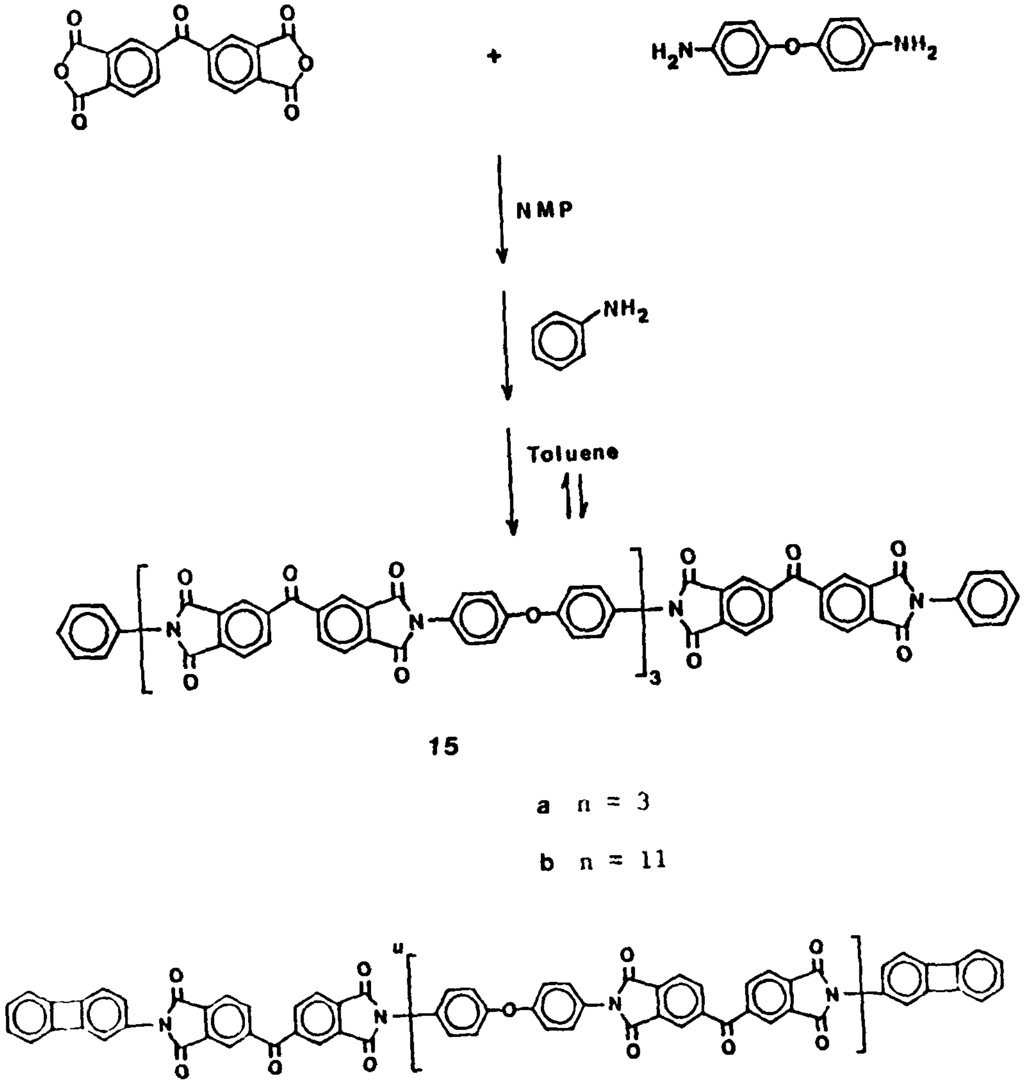


Figure 4 Mechanisms for the Formation of Tetraphenylene from Biphenylene

The results of the model study are consistent with the results observed with the biphenylene end-capped pre-polymers. Since tetrabenzocyclooctatetraene (**12**) formation is a major reaction of biphenylene, chain extension via the formation of **12** would be expected to be an important reaction of the biphenylene end-group. Crosslinking would be expected to be the primary reaction only when the biphenylene end-groups become inaccessible to one another. This offers a plausible explanation for the independence of the degree of crosslinking on the degree of polymerization of the pre-polymers. Pre-polymers of low DP would chain extend via the formation of **12** to give pre-polymers with increased $\overline{DP}$'s. At some $\overline{DP}$, the collision frequency of the end-groups would be severely diminished and biphenylene reaction with aromatic nuclei would the prevail and result in the formation of crosslink structures. Thus, decreasing the $\overline{DP}$ (ergo, increasing the concentration of biphenylene end-groups) only facilitates the chain extension reaction and similar crosslink densities are observed for the cured polymer irrespective of the $\overline{DP}$ of the biphenylene end-capped pre-polymer.

BIPHENYLENE END-CAPPED POLYIMIDE, POLY(ETHER-KETO-SULFONE) AND POLYQUINOLINE

The poor flow of high molecular weight polyimides necessitated the determination of a DP suitable for melt processability. Thus, phenyl end-capped polyimide pre-polymers of calculated $\overline{DP}$ of 3 and 11, were prepared from 3,3'-4,4'-benzophenonetetracarboxylic dianhydride (in the appropriate excess) and 4,4'-diaminodiphenyl ether with aniline as the end-cap (Figure 5). Pre-polymers **15a** ($\overline{DP}$ = 3) showed for superior flow properties compared to **15b** ($\overline{DP}$ = 11) when melt processed at 325°C and 500 psi. (Neither pre-polymer afforded a good film under the melt processing conditions due to



15

a n = 3

b n = 11

16

Figure 5. End-Capped Polyimides

the low molecular weight of the pre-polymers). Thus, biphenylene end-capped polyimide pre-polymer (**16**), with a calculated $\overline{DP}$ = 3, was prepared similarly using 2-aminobiphenylene[27] as the end-cap. The infrared spectra of both **15a** and **16** indicated complete imidization as evidenced by thee absence of an -OH absorption after refluxing the intermediate amide-acid in toluene. The characteristic imide C=O stretch (1770, 1710 cm^{-1}) also was observed. The poor solubility of **16** in common organic solvents hindered a molecular weight approximation by GPC.

Differential scanning calorimetry (DSC) of uncured phenyl end-capped **15a** showed a glass transition at 175°C. Biphenylene end-capped **16** melt processed at 325°c under 500 psi for 15 min in the presence of 10 mole percent (based on biphenylene) bis(triphenylphosphine)(dicarbonyl)nickel(0), gave a film which showed a clearly resolved Tg at 261°C (Tg = +86°C, DSC). Young's modulus measured as a function of temperature showed that the cured film maintained mechanical properties above the Tg.

While the resultant film from **16** ($\overline{DP}$ = 3) was suitable for the determination of its mechanical properties, the film quality indicated that there was some restricted flow during the melt processing of **16** in the presence of the Ni(0) catalyst.

Poly(ether-keto-sulfone)s were prepared from isophthaloyl dichloride and 4,4'-diphenoxyphenyl sulfone using calculated stoichiometric imbalances of the monomers (sulfone in excess) in an attempt to give $\overline{DP}$'s of 11 and 22 (**17**, Figure 6). The polymerizations were performed under Friedel-Crafts conditions (aluminum chloride in methylene chloride) and in both polymerizations, polymer precipitated early in the reaction due to aluminum chloride-complexation. This complicated end-capping of the pre-polymers via the addition of a monofunctionalized monomer late in the polymerization

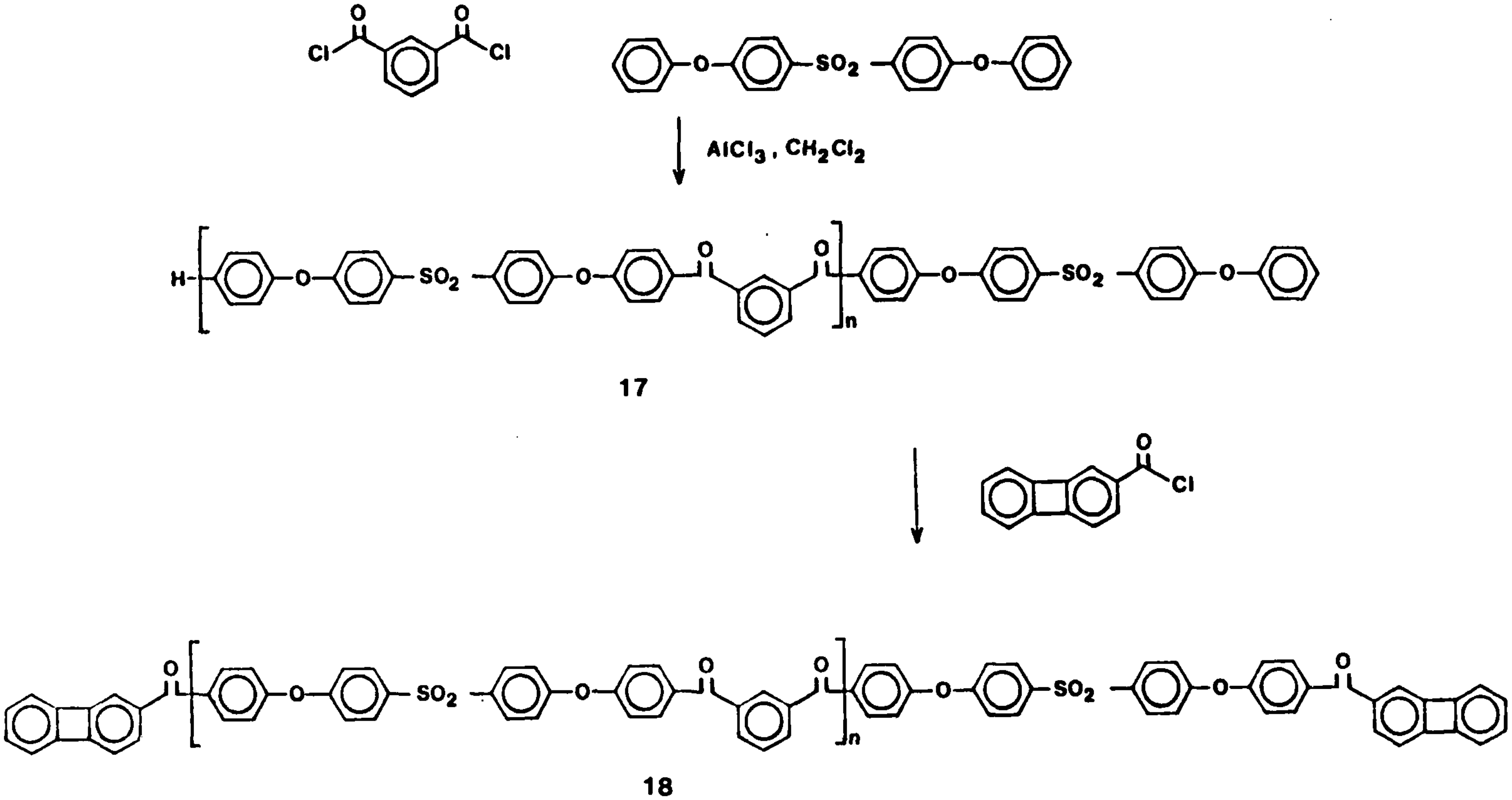
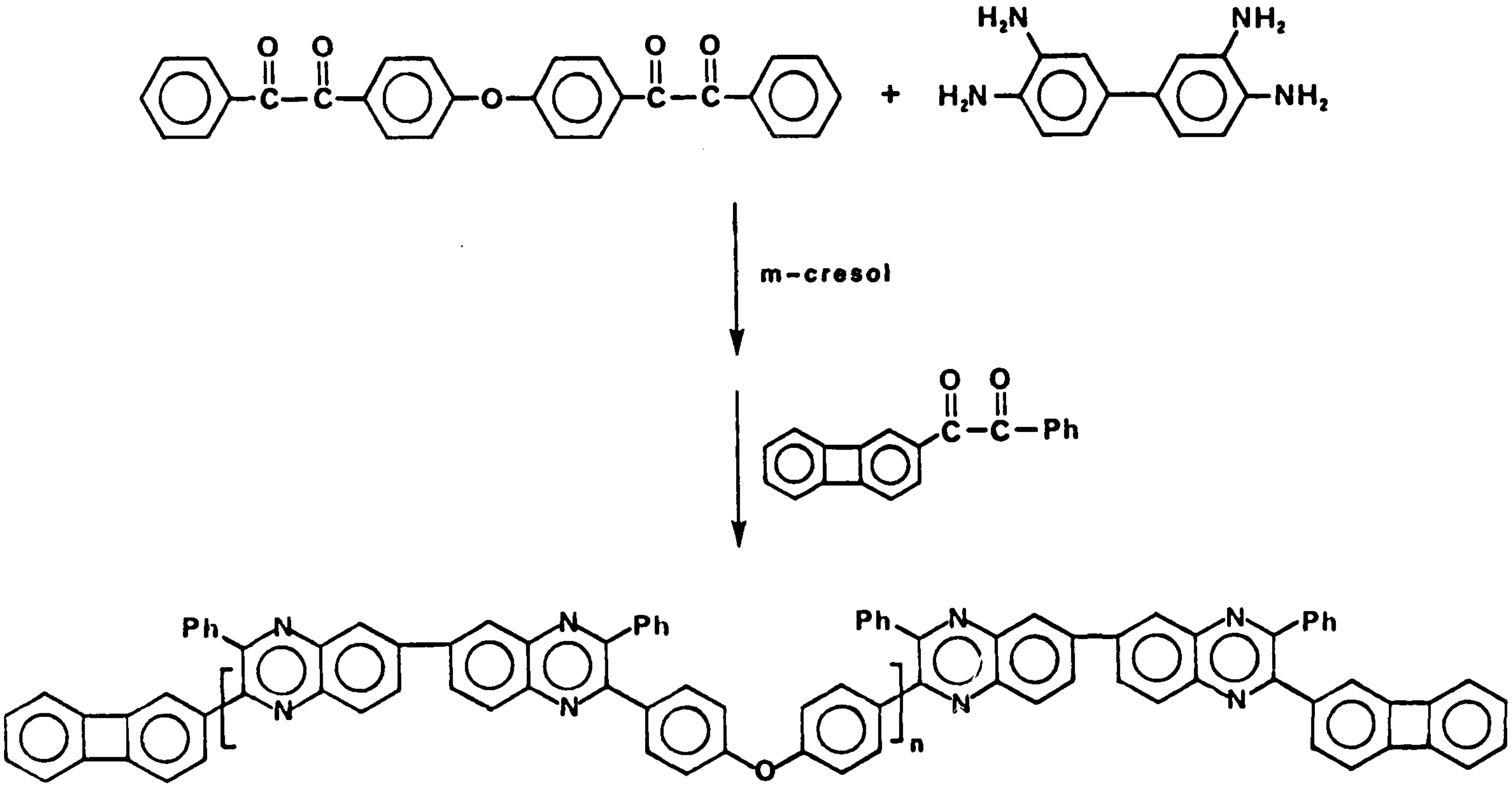


Figure 6. Synthesis of Biphenylene End-capped Poly(ether-keto-sulfone) Pre-polymers

reaction. To circumvent this difficulty, a solution of the isolated pre-polymer and biphenylene-2-carboxylic acid chloride[27] in methylene chloride was added to a mixture of aluminum chloride in methylene chloride with the expectation that the end-capping reaction would occur prior to polymer precipitation. The resulting pre-polymers, **18**, (calculated $\overline{DP}$ = 11, 22) were melt processed in the presence of the Ni(0) catalyst at 300°C under 1000 psi. In both cases, the resulting films showed little improvement in properties compared to **3** melt processed in the absence of catalyst. Subsequent gel permeation chromatography showed that **17a,b** (calculated $\overline{DP}$ = 11, 22) were actually high polymers of approximately the same molecular weight rather than pre-polymers with different DP's. As a result, a low incorporation of biphenylene end-groups was realized due to the limited number of chain ends, and this explained the poor crosslinking results. Apparently, under the polymerization conditions, the reaction was relatively insensitive to monomer stoichiometry.

A biphenylene end-capped polyphenylquinoxaline pre-polymer (**19**) was prepared (Figure 7) using a stoichiometric imbalance reported[31] to give $[\eta]_{inh}$ = 0.5 dL/g. Pre-polymer **19** had an inherent viscosity of 0.44 dL/g (0.5 percent solution (w/w), sulfuric acid). Differential scanning calorimetry of **19** showed Tg = 267°C and an uncatalyzed ring opening exothermic maximum for the biphenylene end-group at 480°C.

Melt processing **19** in the presence of bis(triphenylphosphine)(dicarbonyl)nickel(0) at 340°C under 500 psi for 15 min gave an insoluble film that showed an increased Tg relative to uncured **6** (Tg = 299°C and 267°C, respectively, DSC). However, the film quality clearly demonstrated that restricted flow was present during processing. A higher quality film was obtained by employing a step-wise processing approach. Pre-polymer **6**



19

Figure 7. Synthesis of Biphenylene End-capped Polyphenylquinoxaline Pre-polymer

containing the Ni(0) catalyst was introduced into a 225°C press, 500 psi was applied, the temperature was increased over 15 min to 370°C, and maintained at 370°C for 15 min. The resulting film was suitable for dynamic mechanical testing (Rheovibron) which demonstrated a light to moderate crosslink density [$E'_{25°C} = 2.5 \times 10^{10}$ dyn/cm^2, E'_{above} Tg = 7.2×10^7 dyn/cm^2 (measured at 365°C), E''_{max} (Tg) = 268°C]. The degree of crosslinking was about the same as that observed in cured polymers prepared from the biphenylene end-capped polyquinoline and polyimide pre-polymers.

BIPHENYLENE END-CAPPED POLYQUINOLINE AND POLYIMIDE PRE-POLYMERS AS MATRIX RESINS FOR COMPOSITES

In order to evaluate the biphenylene approach to fiber reinforced composites, the preparation of laminates of biphenylene end-capped polyquinolines and polyimides were undertaken. Polyquinolines were selected because of their excellent processing characteristics, and polyimides were included since 2-aminobiphenylene was compatible with the polyimide processing technology exhibited by the state-of-the-art nadic end-capped polyimide, PMR-15.[32] The polyimide resin, PMR-15, contains not only a benzylic carbon (diphenylmethane-type unit) in the main chain, but aliphatic units resulting from the norbornene imide end groups. Thus, the thermooxidative stability and long-term high temperature properties of PMR-15[32,33] would be expected to be less than those of high molecular weight polyimide resins void of aliphatic groups.[20,34,35] Modified PMR polyimide resins containing flexible perfluoroisopropylidene units in the main chain in place of methylene units have better thermooxidative stability and comparable high temperature mechanical properties as compared with PMR-15[36,37] but still have the potential to undergo degradation at the site of crosslinking due to the aliphatic crosslinker. Polyimide resins containing a higher content of nadic crosslinking groups have improved processability but, in fact, also exhibit lower thermooxidative stability.[17,18,38] The initial weight loss in the thermooxidative degradation of PMR-15, has been shown to be attributable primarily to the methylene unit but ultimately the nadic crosslinking unit becomes a significant contributor to overall resin weight loss.[39] Thus, biphenylene end-capped pre-polymers--such as a polyquinoline or a polyimide containing no aliphatic in-chain units--held promise as a superior matrix resin, since the biphenylene end groups would undergo chain extension to yield the all aromatic tetrabenzocyclooctatetraene unit, or react with the polymer main chain to yield an aromatic crosslink.

In the preparation of laminates, large quantities (~500 g) of pre-polymers usually are necessary for reasonable composite evaluation, due to the necessity of determining optimum processing and post-cure cycles. Since there was a limited amount of biphenylene end-capped polyquinoline available, an alternative approach to the preparation of test specimens was used. Small molds (1 x 2.7 in) which required a minimum amount of resin per composite (1.5 g) were utilized. Each 1 x 2.7 in composite afforded three flexural speciments and five interlaminar shear speciments.

Unidirectional graphite fiber-reinforced composites were prepared from biphenylene end-capped polyquinoline pre-polymer **11** ($\overline{DP}$ = 22) containing 20 mole percent (based on biphenylene) bis(triphenylphosphine)(dicarbonyl)-nickel(0). The pre-preg was prepared by brush coating a chloroform solution of the pre-polymer and catalyst onto the graphite fiber reinforcement. Application from only one side did not afford suitable fiber wetting and resin had to be applied to both sides of the fiber. The resultant pre-preg was boardy and of only fair quality due to shrinkage of the fiber bundle as a result of the inability to restrict the unidirectional reinforcement from all sides during application of the resin.

The pre-preg was assembled in 7- or 8-ply stacks and melt processed in a 1. x 2.7 in mold at 330°C (625°F) under 1500 psi for 2 hours. The cured composites gave a metallic-like ring when dropped on a hard surface exhibited good room temperature flex properties but only modest interlaminar shear strength (Table 6). Thermoplastic breaks were observed in all cases, which suggested a low crosslink density. Post-curing increased the Tg and resulted in improved mechanical properties at 316°C (600°F) due to the higher Tg. However, after post-curing, the laminate failed to ring when dropped on a hard surface suggesting that the mechanical properties severely diminished during post-curing.

In an effort to improve the pre-pregging of pre-polymer 11, graphite cloth was employed in place of unidirectional graphite fiber. Brush coating of a chloroform solution of pre-polymer 11 onto the fiber reinforcement restrained on all four edges gave a boardy but good quality pre-preg which showed minimum shrinkage upon solvent removal. The Ni(J) catalyst was not used in the preparation of the cloth composites in order to determine if the catalyst had a deleterious effect on the composite properties. Since the uncatalyzed ring opening of biphenylene occurs at ~440°C (maximum exotherm), a higher cure temperature was required. The melt processing of 6-ply layups was conducted at 388°C (730°F) under 2000 psi for 3 h and gave composites which showed good flow as indicated by the presence of flash. The composites had good ring and appearannce. Again, post-curing resulted in severely decreased mechanical properties (Table 7) and thermoplastic breaks were observed in all samples. The thermoplastic (nonbrittle) breaks were attributable to a low crosslink density and a flexible polymer backbone.

Table 6

Properties of Polyquinoline Composites Prepared in the Presence of Bis(triphenylphosphine)(dicarbonyl)nickel(0)
Unidirectional Celion-6000® Graphite Fiber[a]

Post-Cure Conditions[b] (h/temperature)	Tg,°C(TMA)[c]	RT ILSS, psi[d]	Flex Strength, psi[d]		Flex Modulus, psi[d]	
			RT	316°C(600°F)	RT	316°C(600°F)
-	222 (432°F)	9000	228,000	36,000[e]	16,200,000	3,400,000
100h/316°C(600°F)	261 (502°F)	6800	182,000	59,000	14,800,000	7,900,000
51h/343°C(650°F)	-	2200	145,000	52,000	15,200,000	4,500,000

a. 36% resin content by weight.

b. In circulating air.

c. Thermal mechanical analysis.

d. Thermoplastic (nonbrittle) breaks observed in all cases.

e. Tested at 260°C (500°F) due to low Tg.

Table 7

Properties of Polyquinoline Composites Prepared without Added Catalyst
Celion-3000 Graphite Cloth[a]

Post-cure Conditions[a] (h/temperature)	Tg, °C (TMA)[c]	ILSS, psi[d] RT	ILSS, psi[d] 316°C(600°F)	RT Flex Strength, psi[d]	RT Flex Modulus, psi[d]
-	219 (426°F)	5000	-	88,000	10,500,000
100h/316°C(600°F)	242 (468°F)[e]	3900	1300	-	-

a. 30% resin content by weight.

b. In circulating air.

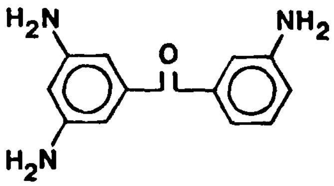
c. Thermal mechanical analysis.

d. Thermoplastic (nonbrittle) breaks observed in all cases.

e. After 48 h at 316°C (600°F).

The PMR (polymerization of monomer reactants)[32] approach was employed in the preparation of biphenylene end-capped polyimide graphite fiber-reinforced composites. A methanolic solution of 4,4'-diaminodiphenylether, 2-aminobiphenylene and the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic dianhydride was brush coated onto unidirectional Celion-6000^R graphite fiber (Figure 8). The resultant pre-preg showed desirable tack and drape. (The Ni(0) catalyst was not used due to poor solubility in the binder solution and the previous observation that low DP pre-polymers showed restricted flow when melt processed in the presence of the Ni(0) catalyst). Staging of 9-ply layups at 204°C (400°F) permitted loss of volatiles prior to molding. Composites were prepared by processing the ply-stack at 391°C (735°F) under 1500 psi for 3 hours. The resultant composites showed excellent properties; however, testing at 316°C (600°F) indicated thermoplastic breaks even after post-curing (Table 8) which suggested that only a moderate degree of crosslinking had been realized. As a control, a phenyl end-capped polyimide was prepared similarly, except aniline was used in place of 2-aminobiphenylene. The composite made from phenyl end-capped polyimide clearly showed inferior properties compared to composites prepared with biphenylene end-capped polyimide pre-polymers (Table 8).

To increase the crosslink density, a trifunctional amine monomer was used as a branching site. The pre-preg was prepared as before except 3 to 10 mole percent of 4,4'-diaminodiphenyl ether was replaced with 3,3',5,5'-triaminobenzophenone (20). The staged pre-preg was processed at 391°C



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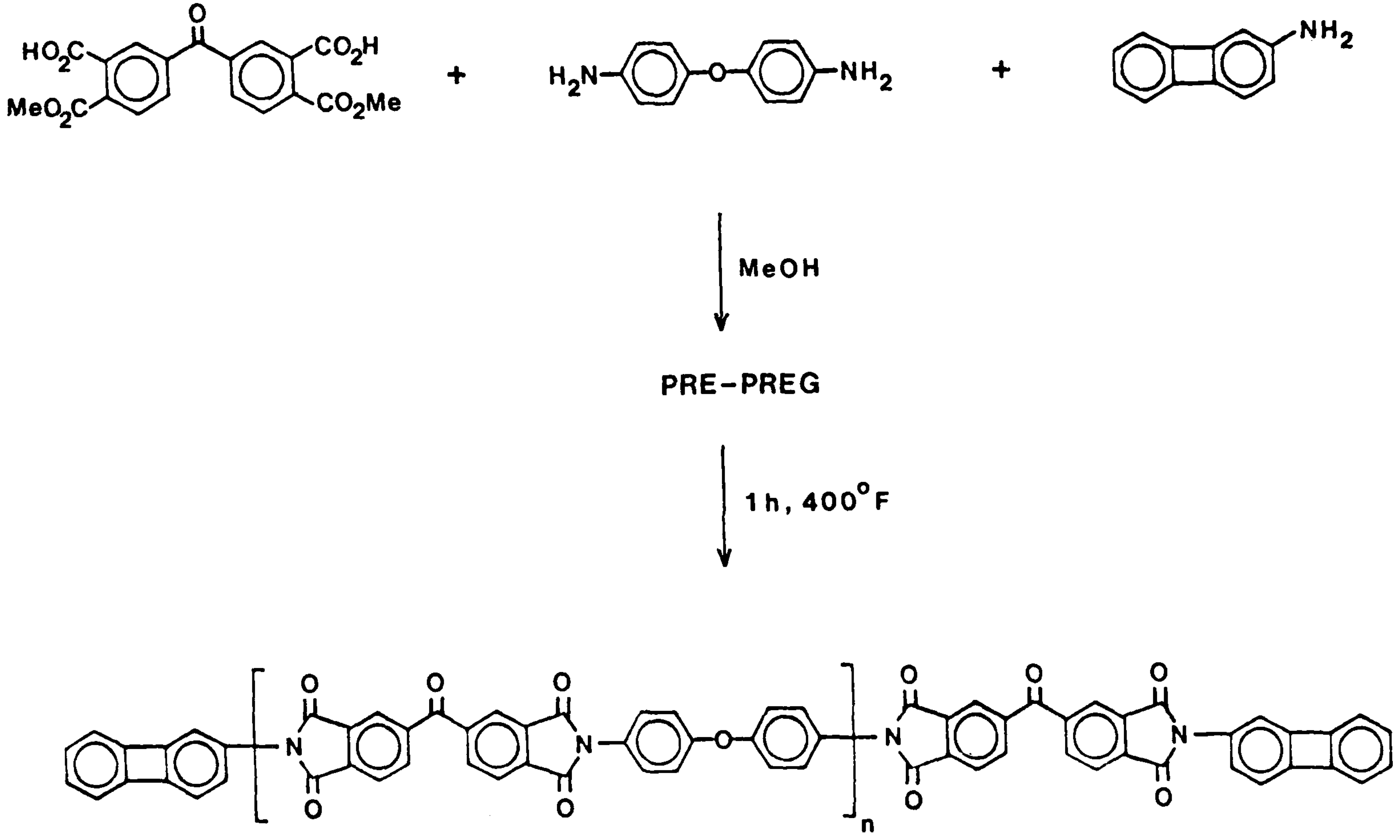

Figure 8. Pre-pregging of Biphenylene End-capped Polyimide Pre-polymers

Table 8

Properties of Composites Prepared from Polyimide Pre-polymers Celion®-6000 Unidirectional Graphite Fiber

End-Cap	Post-cure conditions[a] (h/Temperature)	Tg. °C(TMA)[b]	ILSS, psi		Flex Strength, psi		Flex Modulus, psi	
			RT	316°C(600°F)	RT	316°C(600°F)	RT	316°C(600°F)
Nadic[c]	16h/316°C (600°F)	332°C (630°F)	17,000	7300	250,000	140,000	17,400,000	16,200,000
Biphenylene[d]	-	263 (505°F)	14,000	-	287,000	90,000[e]	20,200,000	15,600,000[e]
Biphenylene[d]	50h/316°C (600°F)	-	-	6000[e]	270,000	156,000[e]	18,300,000	16,700,000[e]
Biphenylene	150h/316°C (600°F)	337 (639°F)	11,000	7000[e]	-	-	-	-
Phenyl	-	246 (475°F)	8700	3600[e]	-	-	-	-
Phenyl	47h/343°C (650°F)[e]	250 (482°F)	10,000	5700[e]	139,000[e]	-	12,300,000[e]	-

a. In circulating air.

b. Thermal mechanical analysis.

c. Properties of PMR-15 composites for comparison. PMR-15 employs 4,4'-methylene dianiline as the diamine monomer and has n = 2.09. The other composites were prepared using 4,4'-diaminodiphenyl ether as the diamine monomer and have n = 4.89. All composites were prepared using the dimethyl ester of 3,3'4,4'-benzophenonetetracarboxylic dianhydride as the acid-ester monomer.

d. 30% resin content by weight.

e. Thermoplastic (nonbrittle) breaks.

(735°F) under 2000 psi for 3 hours. The higher pressure (2000 psi compared to 1500 psi) was used since the branch site was expected to reduce polymer flow. The composites in which 3 and 5 mole percent of 4,4'-diaminodiphenyl ether had been replaced with **20** showed excellent mechanical properties both at room temperature and 316°C (600°F) (Table 9). All breaks were true thermoset (brittle) breaks which confirmed that a sufficient crosslink density had been achieved. Particularly interesting was the observation that replacement of 10 mole percent of 4,4'-diaminodiphenyl ether afforded a composite in which the deisred biphenylene reaction had been inhibited, as evidenced by the lower Tg and the thermoplastic ILSS break. This was attributed to the reduced mobility of the polymer chains due to the high branch site concentration and gave a polymer with a low crosslink density which was primarily chain extended through the branch site.

Athough composites with state-of-the-art initial properties had been prepared, loose surface fiber was observed in all composites prepared from biphenylene end-capped pre-polymers oxidatively aged for 50-100 hours at 316°C (600°F), even though the composite weight loss during aging was only 1 - 2.5 percent (polyquinoline and polyimide composites). Furthermore, aged composites no longer gave a metallic-like ring when dropped on a hard surface. These observations suggested that the biphenylene end-capped matrix resins were not particularly thermooxidatively stable. Photomicrographs of polyquinoline and polyimide composites before and after oxidative isothermal aging at 316°C (600°F) confirmed that the resins degraded during aging. Photomicrographs of composites prepared from biphenylene end-capped polyquinoline pre-polymer 11 ($\widetilde{DP} = 22$) containing 20 mole percent (based on biphenylene) of the Ni(0) catlayst showed the least degradative void formation even though the composite properties had diminished considerably

Table 9

Properties of Composites Prepared from Biphenylene End-capped Polyimide Pre-polymers Containing 3,3',5'-triaminobenzophenone

Mole % Diamine Replaced with Triamine	Post-cure Conditions[a] (h/temperature)	T_g,°C (TMA)[b]	ILSS, psi		316°C (600°F) Flex Strength, psi	316°C (600°F) Flex Modulus, psi
			RT	316°C (600°F)		
3	-	298 (568°F)	13,000	-	-	-
3	14h/343°C (650°F)	325 (617°F)	12,000	7300	-	-
5[c]	47h/316°C (600°F)	328 (622°F)	13,000	6800	186,000	17,300,000
10	43h/316°C (600°F)	310 (590°F)	9600[d]	5400[d]	-	-

a. In circulating air.

b. Thermal mechanical analysis.

c. 26% resin content by weight.

d. Thermoplastic (nonbrittle) break.

and the weight loss during aging was comparable to the other laminates. The composite also had the lowest amount of loose surface fiber after aging. While explaining the observations with certainty is not possible, the results suggest that the Ni(0) catalyst does not necessarily have a deleterious effect on the thermooxidative stability of the composites and actually may impart some desirable characteristics.

While the actual mechanism of degradation of the composites is not known, high energy aromatic radicals are undoubtedly involved due to the rapid and catastrophic nature of the degradation. In an effort to determine if unreacted biphenylene was responsible for the degradation, higher processing temperatures were employed in an attempt to complete the reaction of the biphenylene end-groups. However, polyimide composites melt processed at 427°C (800°F) for 3 h showed more rapid degradation when oxidatively aged at 316°C (600°F) than those processed at 391°C (735°F). A polyimide pre-polymer in which 25 mole percent of 4,4'-diaminodiphenyl ether was replaced with 4,4'-methylene dianiline also afforded an inferior composite. The benzylic hydrogens in methylene dianiline did not improve the thermooxidative stability by acting as a sink for high energy aromatic radicals. Finally, isothermal aging of a polyimide composite for 71 hours at 343°C (650°F) under a nitrogen atmosphere showed low composite weight loss and no loose surface fiber. However, aging of the resultant composite under oxidative conditions at 316°C (600°F) resulted in rapid and severe degradation.

The high thermooxidative stability of resins prepared from biphenylene end-capped polyquinolines and polyimides was not realized. Curing takes place primarily by a chain extension reaction in which biphenylene ends give tetrabenzocyclooetatetraene linkages. A limited amount of crosslinking takes place by attack of a biphenyl diradical (obtained from the opening of biphenylene) on the backbone of a neighboring polymer chain. The amount of crosslinking is sufficient to provide insolubility, but not sufficient to avoid thermoplastic breaks. Thus, the use of a small amount of trifunctional monomer to give some branched polymer containing three biphenylene ends was necessary to give sufficiently crosslinked resin.

The two most probable sources of degradation are the biphenylene end-caps, which remain unreacted during post-curing, and the product of the biphenylene chain-extension reaction, tetrabenzocyclooctatetraene. When biphenylene is pyrolyzed at 430-445°C, the yield of tetrabenzocyclooctatetraene decreases at the expense of polymeric products.[21,23] In this pyrolysis, either the biphenylene is leading to the polymeric products, or the initially formed tetrabenzocyclooctatetraene is undergoing further degradation to yield polymer. In the latter case, tetrabenzocyclooctatetraene may be the source of high energy radicals which, on aging, pick up oxygen from the air. Alternatively, because polymer chain motion is restricted as curing progresses the biphenylene ends may become isolated and be unable to undergo appreciable further reaction in the polymer matrix. As a result, on isothermal aging, the remaining biphenylene ends can react with oxygen and lead to rapid degradation.

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APPENDIX I

List of Publications

ARO Support 1980-1982

W. Vancraeynest and J.K. Stille, Macromolecules, 13, 1361 (1980). "Bisbiphenylenes: New Crosslinking Reagents for Thermally Stable Polymers".

J.K. Stille, R.M. Harris and S.M. Padaki, Macromolecules, 14, 486 (1981). "Polyquinolines Containing Fluorene and Authrone Cardo Units: Synthesis and Properties".

P.D. Sybert, W.H. Beever and J.K. Stille, Macromolecules, 14, 493 (1981). "Synthesis and Properties of Rigid-Rod Polyquinolines".

J.K. Stille, Macromolecules, 14, 870 (1981). "Polyquinolines".

S.M. Padaki and J.K. Stille, Macromolecules, 14, 888 (1981). "Dilute Solution Parameters for a Fluorene-Containing Cardo Polyquinoline".

J.K. Stille, J.P. Droske, W. Vancraeynest, J. Garapon, A. Recca and U.M. Gaik, Polymer Preprints, 22(2), 105 (1981). "Biphenylene Curing of Thermally Stable Polymers".

R.M. Harris and J.K. Stille, Macromolecules, 14, 1584 (1981). "A Cardo Polyquinoline from an AB Monomer".

F.A. Bottino, A. Mamo, A. Recca, J.P. Droske and J.K. Stille, Macromolecules, 15, 227 (1982). "Perfluoroalkylene-linked Polyquinolines and Related Model Compounds".

H.-J. Dussel, A. Recca, J. Kolb, D.O. Hummel and J.K. Stille, J. Anal. and Appl. Pyrolysis, 3, 307 (1982). "Pyrolysis-Field Ionization Mass Spectrometric Investigation of Polymeric Heterocycles I. Polyquinolines and Polyquinoxalines".

J.K. Stille, Contempory Topics in Polymer Science, Vol. 5, Plenum Press, N.Y., 1983. "New Developments in High Temperature and High Strength Polymers".

J.P. Droske and J.K. Stille, Polymer Preprints, 24(1) (1983). "All Aromatic Biphenylene End-Capped High Performance Composite Resins".

John P. Droske and J.K. Stille, Macromolecules, submitted for publication. "Biphenylene End-Capped Polyquinoline Prepolymers: Synthesis, Processing and Curing".

John P. Droske, U.M. Gaik and J.K. Stille, Macromolecules, submitted for publication. "Biphenylene End-Capped Aromtic Pre-Polymers: Polyimides, Poly(Ether-Keto-Sulfone)s and Polyquinoxaines".

John P. Droske and J.K. Stille, Macromolecules, submitted for publication. "Biphenylene End-Capped Polyquinolines and Polyimide Pre-Polymers as Matrix Resins for High Use-Temperature Composites".

APPENDIX 2

List of Participating Scientific Personnel

Principal Investigator: Dr. J. K. Stille

Post-Doctoral Research Associates:
- Dr. Akira Sekiya
- Dr. Akira Harada
- Dr. Jun-ichi Suenaga

Graduate Students:
- Dr. Sridhar Padaki (PhD, Colorado State, 1980)
- Dr. Rodney M. Harris (PhD, Colorado State, 1981)
- Dr. John P. Droske (PhD, Colorado State, 1982)
- Mr. Dirk Sutherlin
- Mr. Scott Tunney

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