Macromolecules

Volume 17, Number 1 January 1984

Biphenylene End-Capped Polyquinoline Prepolymers: Synthesis, Processing, and Curing Reactions

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Received March 8, 1983

ABSTRACT: Biphenylene end-capped polyquinoline prepolymers of $\overline{\mathrm{DP}}$ = 3, 11, and 22 were prepared by adjusting the stoichiometry of the bis(amino ketone) monomer, 4,4′-diamino-3,3′-dibenzoyldiphenyl ether, the bis(ketomethylene) monomer, 4,4′-diacetyldiphenyl ether, and the ketomethylene end cap, 2-acetylbiphenylene. Melt processing of the prepolymers in the presence of bis(triphenylphosphine)dicarbonylnickel(0) was carried out at 325–340 °C under 500 psi to give high-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% insoluble, had increased T_g's, and showed improved mechanical properties both above and below the T_g as compared with the uncured resins. On the basis of model reactions and the observation that the degree of cross-linking in the cured resins was essentially independent of the $\overline{\mathrm{DP}}$ of the prepolymer, chain extension by conversion of biphenylene end caps to tetrabenzocyclooctatetraene linkages was proposed to be the major reaction of the biphenylene end groups, with cross-linking occurring to a lesser extent after the chain length increased and the concentration of biphenylene ends decreased.

Introduction

Polymers of the highest thermal stability are those constructed of aromatic carbocyclic and heterocyclic units linked to yield a conjugated chain.[1-4] 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 chemically alter a processable polymer after or during fabrication to give a material with improved properties. Any chemical reaction intended for this purpose should fulfill the following requirements: (1) the reaction should proceed without the evolution of volatile byproducts in order to prevent the formation of voids, which decrease the strength of fabricated components, (2) the temperature necessary for the reaction should be above the T_g 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.

Cross-linking the polymer after or during processing affords a means of improving the properties of processable thermally stable polymers. Highly cross-linked polymers show desirable properties such as excellent dimensional stability with low creep rates, high resistance to solvents, increased softening temperatures, and improved thermal stability over the analogous un-cross-linked polymers.[3,5] The cross-linking site may be introduced to the polymer 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 cross-linking sites have been used to improve the properties of readily processable thermally stable polymers. For example, acetylene[6] and nadic (bicyclo[2.2.1]hept-4-ene-2,3-dicarboxylic anhydride)[7-11] end groups are currently being used in commercially available imide prepolymers. While these prepolymers give cross-linked 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.[12,13] Thus, a reactive end group that would yield wholly aromatic cross-link 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,[14-16] depending on the reaction conditions, to afford primarily tetrabenzocyclooctatetraene, aromatic polymer, or stable

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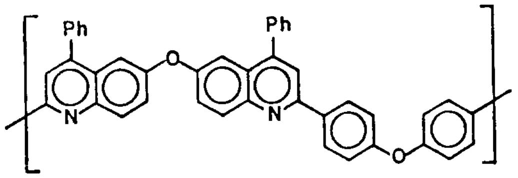
adducts with aromatic compounds. This "inner-ring chemistry" of biphenylene was the basis for the use of biphenylene as a cross-linking site for thermally stable polymers, because it was expected that any structures formed as a result of biphenylene inner-ring chemistry would be aromatic and would show stability comparable to that of the parent polymer. Furthermore, volatile products would not be generated during cross-linking, thereby allowing void-free processing.

The first application of biphenylene as a cross-linking site was the incorporation of biphenylene into the main chain of various high molecular weight polyquinolines.[17,18] After curing, the polymers were insoluble, showed higher T_g's, and demonstrated improved mechanical properties both above and below the T_g compared to the uncured polymers. Similar results were observed with aromatic polyamides, polyquinoxalines, and a polybenzimidazole containing biphenylene units in the main chain.[19] The viability of biphenylene as a cross-linking site for thermally stable polymers was further demonstrated by the preparation of bisbiphenylene compounds as cross-linking additives in which the group linking the biphenylenes was a structural unit similar to that contained in the polymer to be cross-linked.[20] Solutions of polymer and cross-linking additive were cast into films that were thermally cured to give insoluble polymers.

This paper reports the synthesis of biphenylene end-capped low molecular weight polyquinoline prepolymers, the neat resin processing of the prepolymers, and the properties of the resultant films. The thermolysis of biphenylene in the presence of suitable model compounds for polyquinolines also is reported.

Results and Discussion

Ether-linked polyquinolines (1) showed the most desirable processing characteristics when compared to other polyquinolines.[21] High-quality films cast from solutions of the polymer in common organic solvents showed no weight loss after oxidative isothermal aging for 100 h at 300 °C.[22] 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.[23] This combination of high thermal stability and good processability indicated that 1 was particularly well suited for the preparation of biphenylene end-capped polyquinoline prepolymers.



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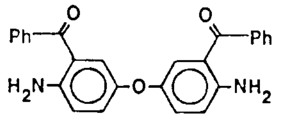
A preliminary investigation of the flow characteristics of 1 was carried out to identify the upper molecular weight limit for adequate flow under typical melt-processing conditions for thermally stable polymers. Aliquots were withdrawn periodically during a polymerization to give 1, in order to obtain samples of 1 with different molecular weights. A powder sample obtained from the polymerization mixture after 2 h formed a good, transparent film when melt processed at 340 °C under 500 psi. The intrinsic viscosity of this sample of 1 was determined to be 0.47 dL/g (chloroform, 25.0 °C). Substitution of the viscosity into the Mark–Houwink equation gave a number-average molecular weight ($\overline{M}_n$) of 13 000 ($K = 9.0 \times 10^{-4}$ and $a = 0.66$ for polyquinolines, membrane osmometry)[22] for the sample, which corresponded to a number-average $\overline{DP}$ of 22. Samples withdrawn in excess of 2 h showed restricted flow under the melt-processing conditions. Thus, in order to be melt processable under typical conditions, biphenylene end-capped polyquinoline prepolymers with $\overline{DP} \leq 22$ were desired.

Table I
Molecular Weight Distributions of Polyquinolines Prepared via Different Approaches to the Control of Molecular Weight

	GPC[a]			
polymer	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
1[b]	12 000	40 000	62 000	3.3
phenyl end capped[c]	15 000	37 000	65 000	2.5

[a] Relative to polystyrene standards. [b] Exact monomer balance but polymerization quenched after 2 h. [c] Excess 4,4'-diamino-3,3'-dibenzoyldiphenyl ether used to control molecular weight.

Synthesis and Prepolymer Properties. For the preparation of end-capped polyquinoline prepolymers, a polymerization was run in which 4,4'-diamino-3,3'-dibenzoyldiphenyl ether (2) was added in excess relative to



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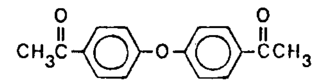

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4,4'-diacetyldiphenyl ether (3), utilizing the relationship $\overline{DP} = (1 + r)/(1 + r - 2rp)$ such that $r = 0.9308$ and $p = 0.99$[24] to yield a polymer of $\overline{DP} = 22$. Acetophenone was added to the polymerization medium after 12 h to effect the end capping. Gel permeation chromatography of the phenyl end-capped polyquinoline prepolymer gave a molecular weight distribution similar to that of polyquinoline 1 prepared with an exact monomer balance but quenched after 2 h (Table I). Thus, the agreement between the molecular weight distribution of the phenyl end-capped polyquinoline (calculated $\overline{DP}$ of 22) and the molecular weight distribution of polyquinoline 1 (experimentally determined $\overline{DP}$ of 22, from viscosity) confirmed the usefulness of an imbalance in the monomer stoichiometry in preparing polyquinoline prepolymers of desired $\overline{DP}$'s.

A series of biphenylene end-capped polyquinoline prepolymers (6) with $\overline{DP}$ = 3, 11, and 22 were prepared by overbalancing with an appropriate amount of 2 relative to 3 to give prepolymers with the desired $\overline{DP}$ (Figure 1). To effect end capping, 2-acetylbiphenylene—prepared in 70% yield from acetic anhydride and biphenylene under Friedel–Crafts conditions—was added after 24 h to the polymerization medium containing the preformed polymers. The completeness of the end-capping reaction was verified by the lack of an appreciable ketone absorption in the infrared spectra of the prepolymers. Furthermore, the ^{13}C NMR spectrum of 6 ($\overline{DP}$ = 3) was consistent with the calculated chemical shifts and the ^{13}C NMR spectra of polyquinolines containing biphenylene units in the main chain[17] and did not show the presence of a carbonyl carbon (Table X).

Excellent agreement between the $\overline{DP}$ calculated on the basis of monomer imbalance and the $\overline{DP}$ obtained from molecular weight determination (viscometry) was realized (Table II). Biphenylene end-capped polyquinoline 6 prepared via a calculated imbalance of the monomers to give $\overline{DP}$ = 22 had an intrinsic viscosity of 0.47 dL/g

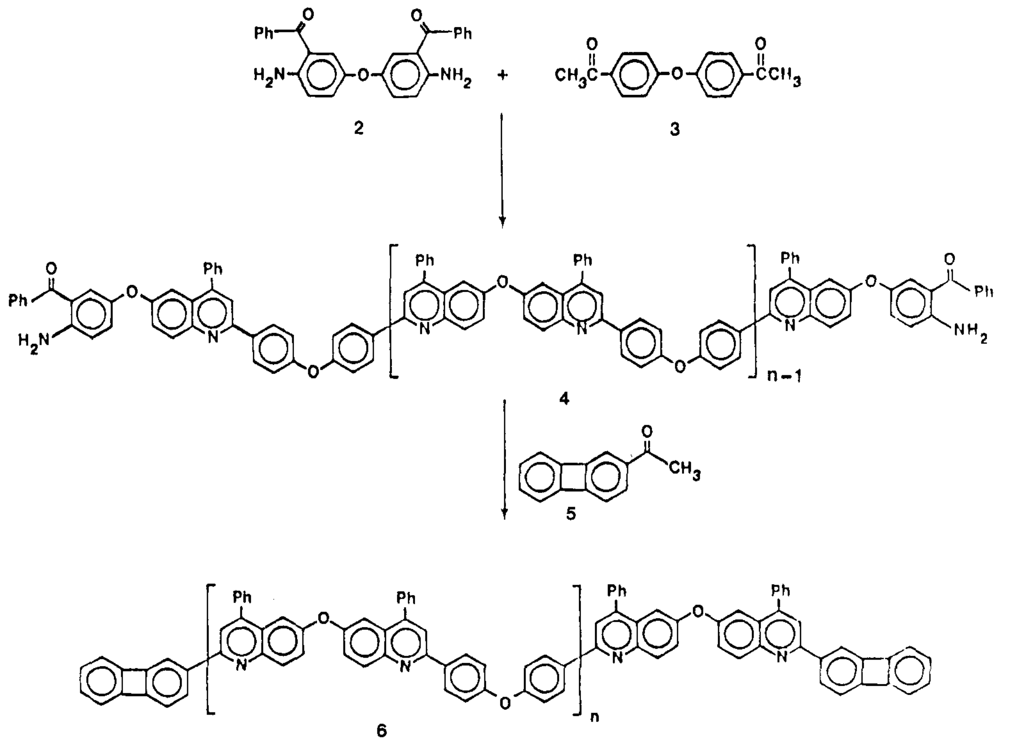


Figure 1. Synthesis of biphenylene end-capped polyquinoline prepolymers.

Table II
Comparison of Calculated and Observed Degrees of Polymerization for Biphenylene End-Capped Polyquinoline Prepolymers 6

calcd		obsd		
$\overline{\mathrm{DP}}^a$	$\overline{M}_n{}^b$	$[\eta]$, dL/g	$\overline{\mathrm{DP}}^c$	$\overline{M}_n{}^c$
3	1 800	0.09	2	1 100
11	6 500	0.25	8	5 000
22	13 000	0.47	22	13 000

[a] $\overline{\mathrm{DP}} = (1 + r)/(1 + r - 2rp)$. [b] $\overline{M}_n = \overline{\mathrm{DP}} \times 590$. [c] $[\eta] = K\overline{M}_n{}^a$

(chloroform, 25.0 °C), which corresponded to $\overline{\mathrm{DP}} = 22$ (obtained from the Mark–Houwink equation). The viscosity also was identical with the viscosity of the sample of 1 obtained from a 2-h reaction time with an exact monomer balance. The results were quite reproducible; in three different preparations of 6 ($\overline{\mathrm{DP}} = 22$) intrinsic viscosities of 0.45, 0.47, and 0.51 dL/g were obtained. The slight discrepancy between the calculated and observed $\overline{\mathrm{DP}}$'s (3 and 11) for 6 (Table II) was not surprising, since the Mark–Houwink equation has been shown to be suspect at very low degrees of polymerization.[25]

The molecular weight distributions of the biphenylene end-capped polyquinoline prepolymers were determined by gel permeation chromatography (GPC). Even though absolute values of the average molecular weights ($\overline{M}_n$), ($\overline{M}_w$), and ($\overline{M}_z$) 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 III). The GPC of polymer 6 ($\overline{\mathrm{DP}} = 11$ and $\overline{\mathrm{DP}} = 22$) gave statistical distributions of molecular weights, as do high polymers, while prepolymer 6 ($\overline{\mathrm{DP}} = 3$) was clearly oligomeric (Figure 2).

The T_g of the prepolymers as determined by differential scanning calorimetry (DSC) was a function of the molecular weight (Table IV).

Table III
Comparison of the Molecular Weights of Biphenylene End-Capped Polyquinoline Prepolymers Determined by Viscosity and Gel Permeation Chromatography

polymer 6	viscosity^a	GPC^b			
$\overline{\mathrm{DP}}$	$\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
3	1 100	600	3 300	12 000	5.7
11	5 000	6 500	19 000	34 000	2.9
22	13 000	12 000	36 000	56 000	2.9

[a] $[\eta] = K\overline{M}_n{}^a$. [b] Relative to polystyrene standards.

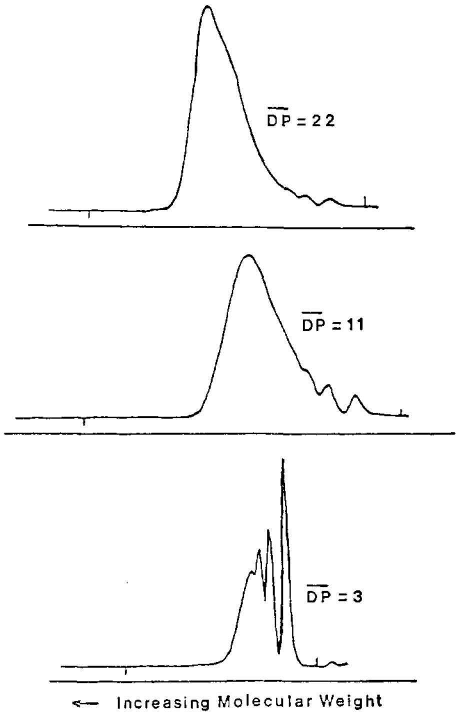


Figure 2. Molecular weight distributions of biphenylene end-capped polyquinoline prepolymers.

Table IV
Dependence of the T_g on the $\overline{M}_n$ of Biphenylene End-Capped Polyquinoline Prepolymers

polymer	$\overline{M}_n$[a]	T_g, °C (DSC)	T_m, °C (DSC)
6 ($\overline{DP}$ = 3)	1 100	153	230
6 ($\overline{DP}$ = 11)	5 000	212	c
6 ($\overline{DP}$ = 22)	13 000	232	c
1[d]	40 000	266	448[b]
1[d]	100 000	266	448[b]

[a] From viscosity. [b] Not observed after annealing at 300 °C. [c] Not observed. [d] No end cap.

Prepolymer Processing and Properties of Cured Polymer. The polymer melt temperature[26] of prepolymer 6 ($\overline{DP}$ = 22) was approximately 300 °C, which indicated that melt processing of the prepolymers 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 6, which showed an exotherm with a 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.[17,18] The addition of 0.5 mol % (norbornadiene)chlororhodium(I) dimer (based on biphenylene) to 6 lowered the ring opening maximum to 365 °C (DSC). Melt processing of 6 containing the Rh(I) catalyst was conducted at 340 °C (the temperature at which the ring-opening exotherm was approximately half of the maximum) under 500 psi and afforded films of various cross-link densities, depending on the processing time (Table V). In all cases, 6 processed in the presence of the Rh(I) catalyst gave films that showed improved Young's modulus (E') both above and below T_g and partial or complete insolubility in chloroform, a good solvent for the resin. Curing of 6 containing the Rh(I) catalyst for 1 h or longer gave films with a higher T_g than the T_g of the uncured resin. As a control experiment, phenyl end-capped polyquinoline prepolymer ($\overline{DP}$ = 22) was melt processed under the same conditions in the presence of the rhodium catalyst. Even after curing for 1 h, the resultant film was completely soluble and showed no increase in the T_g. Thus, in the presence of the Rh(I) catalyst, the biphenylene end-capped polyquinoline prepolymer 6 underwent cross-linking/chain extension in the melt to give a cured polymer with improved properties compared to the uncured resin. However, another catalyst was desired since the (norbornadiene)chlororhodium(I) dimer was expensive and had been implicated in the acceleration of resin degradation under oxidative aging at elevated temperatures.[27]

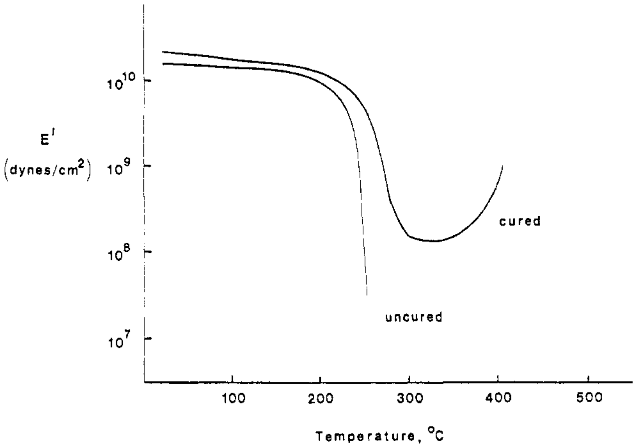


Figure 3. Young's modulus as a function of temperature for 6 ($\overline{DP}$ = 22) cured for 15 min at 340 °C under 500 psi in the presence of bis(triphenylphosphine)dicarbonylnickel(0).

The addition of 20 mol % (based on biphenylene) of bis(triphenylphosphine)dicarbonylnickel(0) to polymers containing bisbiphenylene additives has been shown to effectively catalyze the cross-linking reaction.[20] Thus, prepolymer 6 was melt processed as above in the presence of 20 mol % (based on biphenylene) of the Ni(0) catalyst. The resultant transparent, high-quality films were completely insoluble and showed increased T_g's as well as improved mechanical properties both above and below the T_g (Figure 3, Table VI). Most striking was the observation that curing for only 15 min in the presence of the Ni(0) catalyst gave a film with properties nearly identical with 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

Table V
Properties of 6 ($\overline{DP}$ = 22) Melt Processed at 340 °C under 500 psi in the Presence of (Norbornadiene)chlororhodium(I) Dimer

processing time, min	T_g, °C (DSC) (after processing)	solubility[a]	$E'_{25°C}$, dyn/cm^2	$E'_{\text{above } T_g}/T$,[b] (dyn/cm^2)/°C
15[c]	235	100	2.3×10^{10}	d
15	235	100	2.6×10^{10}	4.0×10^7/320
60	243	73	3.2×10^{10}	8.0×10^7/(310–341)
120	247	1	2.8×10^{10}	1.0×10^8/(320–332)
60[e]	232	100		

[a] Percent soluble after 24 h in chloroform. [b] $E'_{\text{above } T_g}$ is the lowest value of the storage modulus obtained above T_g. The temperature at which the modulus obtained is also given. [c] Without catalyst. [d] Not measurable even at the highest sensitivity of the instrument (Rheovibron). [e] Phenyl end-capped polyquinoline prepolymer 6 ($\overline{DP}$ = 22).

Table VI
Film Properties of 6 Melt Processed at 340 °C under 500 psi

wt % $(PPh_3)_2Ni(CO)_2$	processing time, min	T_g, °C (DSC)	solubility[a]	$E'_{25°C}$, dyn/cm^2	$E'_{\text{above } T_g}/T$,[b] (dyn/cm^2)/°C
	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] $E'_{\text{above } T_g}$ is the lowest value of the storage modulus obtained above T_g. The temperature at which the modulus was observed is also given. [c] Not measurable even at the highest sensitivity of the instrument.

Table VII
Comparison of Film Properties of 6 Melt Processed at 340 °C under 500 psi

prepolymer 6, $\overline{\mathrm{DP}}$	wt % biphenylene	wt % $(PPh_3)_2$-$Ni(CO)_2$	T_g, °C (DSC) after processing	ΔT_g, °C	solubility[b]	$E'_{25°C}$, dyn/cm²	$E'_{\text{above } T_g}/T$,[c] (dyn/cm²)/°C
3	23	7.0	217	+64		*e*	*e*
3[d]	23	7.0	235	+82	26	*e*	*e*
11	7.5	4.2	243	+31	0	2.8×10^{10}	1.4×10^{8}/(285-335)
22	3.5	2.5	243	+11	0	2.8×10^{10}	1.0×10^{8}/(291-330)

[a] ΔT_g is the difference in T_g between the cured and uncured resins (see Table IV). [b] Percent soluble after 24 h in chloroform. [c] $E'_{\text{above } T_g}$ is the lowest value of the storage modulus obtained above T_g. The temperature at which the modulus was observed is also given. [d] Melt processed for 45 min. All others melt processed for 15 min. [e] Film quality not sufficient for modulus measurement.

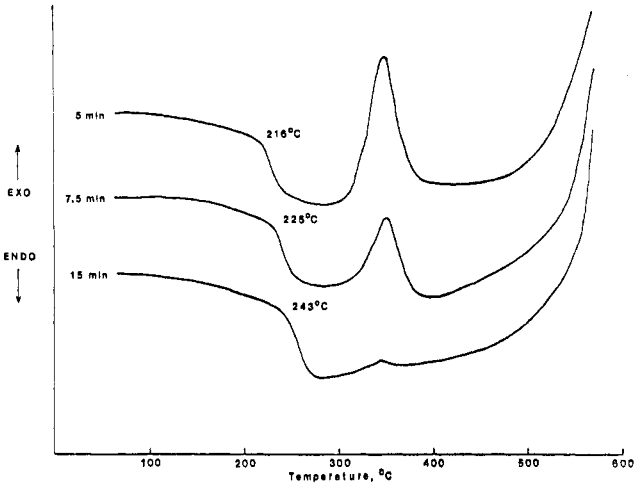


Figure 4. Differential scanning calorimetry of 6 ($\overline{\mathrm{DP}}$ = 11) melt processed in the presence of bis(triphenylphosphine)dicarbonylnickel(0) for various times at 340 °C under 500 psi.

demonstrated by the DSC of films prepared by melt processing 6 ($\overline{\mathrm{DP}}$ = 11) under the same conditions in the presence of the Ni(0) catalyst for 5, 7.5, 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 4). Thus, curing biphenylene end-capped polyquinoline prepolymers in the presence of the Ni(0) catalyst afforded high-quality, cross-linked films in very short cure times.

Although cured polymer 6 ($\overline{\mathrm{DP}}$ = 11) contained a higher concentration of biphenylene end groups than polymer 6 ($\overline{\mathrm{DP}}$ = 22), the resulting films had nearly identical Young's moduli above T_g, indicating an equal cross-link 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. Cross-linking occurred only when the biphenylene ends became inaccessible to one another. Since this would be expected to occur at approximately the same $\overline{\mathrm{DP}}$, the same cross-link density was observed in both films. Prepolymer 6 ($\overline{\mathrm{DP}}$ = 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 prepolymer clearly underwent cross-linking/chain extension during processing, as indicated by the increase in T_g and the considerable insolubility of the cured polymer (Table VII), the film quality was only fair. Apparently, the processing "window" in the case of 6 ($\overline{\mathrm{DP}}$ = 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 prepolymers 6 ($\overline{\mathrm{DP}}$ = 3 and $\overline{\mathrm{DP}}$ = 11) at 340 °C in the absence of added catalyst did not afford coherent films, and the resultant polymers remained completely soluble. At this melt-processing temperature, in the absence of catalyst, biphenylene reactions do not take place and these polymers do not have high enough molecular weight to give coherent films. The involvement of biphenylene end groups in cross-linking/chain extension was unambiguously demonstrated by the melt processing of phenyl end-capped polyquinoline prepolymer ($\overline{\mathrm{DP}}$ = 22) containing the Ni(0) catalyst. The resultant film was completely soluble and showed no increase in the glass transition temperature after processing.

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

polymer	% wt loss
phenyl end capped ($\overline{\mathrm{DP}}$ = 22)[a]	8.2
6 ($\overline{\mathrm{DP}}$ = 22)	1.9
6 ($\overline{\mathrm{DP}}$ = 22)[b]	2.6
6 ($\overline{\mathrm{DP}}$ = 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 mol % (based on biphenylene) bis(triphenylphosphine)dicarbonylnickel(0). [c] Cast film of 1 ($\bar{M}_n$ = 45 000). [d] Powder sample of very high molecular weight 1 ($\bar{M}_n$ = 220 000).

Oxidative isothermal aging of polyquinoline films was conducted at 300 °C (Table VIII). Melt-processed films prepared from biphenylene end-capped prepolymers showed thermooxidative stability compared to a phenyl end-capped polyquinoline prepolymer ($\overline{\mathrm{DP}}$ = 22) but showed higher weight loss than a cast film of 1 ([η] = 1.06, $\bar{M}_n$ = 45 000) and a powder sample of very high molecular weight 1 ([η] = 3.0, $\bar{M}_n$ = 220 000). The weight loss of prepolymers 6 ($\overline{\mathrm{DP}}$ = 11 and $\overline{\mathrm{DP}}$ = 22) melt processed in the presence of the bis(triphenylphosphine)dicarbonylnickel(0) catalyst cannot be compared directly to 6 ($\overline{\mathrm{DP}}$ = 22) melt processed without added catalyst, since the latter did not undergo cross-linking/chain extension under the melt-processing conditions (340 °C, 500 psi). While the weight loss of cured polymers prepared from the biphenylene end-capped prepolymers 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.

Mechanism of Cross-Linking/Chain Extension via Biphenylene End Groups. The dimerization of biphenylene end groups to tetrabenzocyclooctatetraene linkages would afford only chain extension and not cross-linking. Since the properties of cured biphenylene end-capped prepolymers clearly showed moderate degrees of cross-linking, the biphenylene end group must be able to react with aromatic units in adjacent polymer chains

Table IX
Major Fragments in the Mass Spectra of 2,4-Diphenylquinoline and the Adduct 9

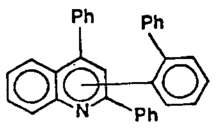
2,4-diphenylquinoline		adduct	
m/*e*	intensity	*m*/*e*	intensity
202	24	354	24
204	13	356	28
280	100	432	100
281 (M^+)	74	433 (M^+)	91
282	16	434	27

to form cross-link 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.[14,16] These conditions are quite different from 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)dicarbonylnickel(0)-catalyzed reactions (10 mol % 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 equiv 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 (7), fluorenone (8), 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 cross-linking 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 equiv of 2,4-diphenylquinoline 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 9 of the addition of biphenylene to 2,4-diphenylquinoline (Table IX). A full characterization of the compound was not possible due to the small quantity of 9 and difficulties in separation of the complex product mixture; based on HPLC, the adduct consists of a mixture of isomers. 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 9, and the total ion intensity of 9 in the product mixture from the thermal reaction was greater than the total ion intensity of 9 in the product mixture from the Ni(0)-catalyzed reaction. The lack of tetrabenzocyclooctatetraene (7) 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 3 equiv or more of anthracene.[15]



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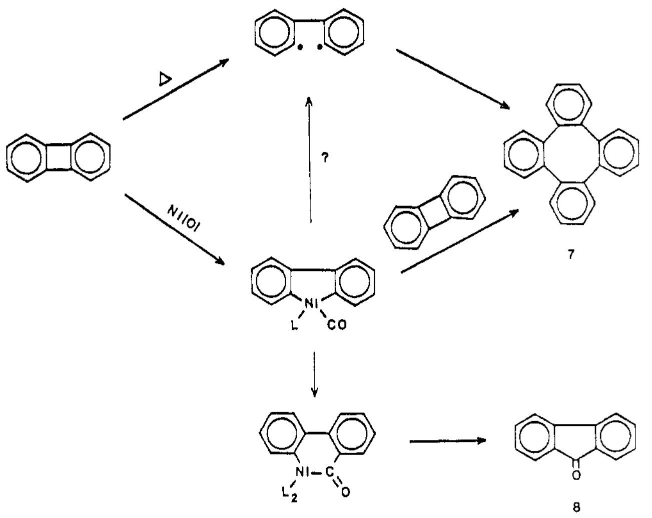


Figure 5. Mechanisms for the reactions of biphenylene.

The Ni(0)-catalyzed reaction of biphenylene with 10 equiv of diphenyl ether gave recovered biphenylene, fluorenone (8), and biphenyl (GCMS). Only a trace of tetrabenzocyclooctatetraene (7) was detected, in contrast to the Ni(0)-catalyzed reactions of biphenylene with benzene-d_6 and 2,4-diphenylquinoline, in which 7 was the major product. This observation was not readily explained, since the thermal reaction of biphenylene with 10 equiv of diphenyl ether afforded primarily 7, residual biphenylene, and biphenyl. Quenching was not observed in this reaction even though 10 equiv of diphenyl ether was present. No addition product of biphenylene to the diphenyl ether was detected.

The conclusions from this model study are as follows: (1) The dimerization of biphenylene to tetrabenzocyclooctatetraene (7) occurs under both Ni(0)-catalyzed and uncatalyzed conditions. However, in agreement with previous reports,[14–16] the formation of 7 is quite dependent on the reaction conditions. (2) Biphenylene does react with 2,4-diphenylquinoline to give 9 as a minor product under both Ni(0)-catalyzed and uncatalyzed conditions but apparently does not react with benzene or diphenyl ether under the same conditions. (3) The cross-linking of polyquinolines probably occurs via the reaction of biphenylene with quinoline groups in the polymer chain. (4) The presence of fluorenone (8) in the product mixtures from the catalyzed reactions confirms that Ni(0) inserts into the biphenylene inner ring via an oxidative addition, analogous to the rhodium(I) insertion into cubane.[28] While the thermal reactions of biphenylene have been postulated to involve a biradical intermediate,[14–16] 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 5).

The results of the model study are consistent with the results observed with the biphenylene end-capped prepolymers. Since tetrabenzocyclooctatetraene (7) formation is a major reaction of biphenylene, chain extension via the formation of 7 would be expected to be an important reaction of the biphenylene end group. Cross-linking 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 cross-linking on the degree of polymerization of the prepolymers. Prepolymers of low DP would chain extend via the formation of 7 to give prepolymers with increased DP's. At some DP, the collision frequency of the end groups would be severely diminished and biphenylene reaction with aromatic nuclei would then prevail and result in the formation of cross-link structures. Thus, decreasing the DP (ergo, increasing the concentration of biphenylene end groups) only facilitates the chain extension reaction, and similar cross-link densities are observed for the cured polymer irrespective of the DP of the biphenylene end-capped prepolymer.

Experimental Section

All melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were measured with a Varian EM-360 spectrometer and a JEOL FX-100 Fourier transform spectrometer, respectively. All chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Infrared spectra were determined with a Beckman AccuLab 3 spectrometer. Elemental analyses were performed by Micro-Tech Laboratories.

Dilute solution viscosity measurements of polymer solutions were obtained with Cannon-Ubbelohde microdilution viscometers no. 50 (chloroform) and 200 (sulfuric acid). Gel permeation chromatography was done in chloroform at a flow rate of 2.5 mL/min with a Waters GPC equipped with a 6000 A pump, U6K injector, R401 RI detector, 730 data module, and 500-, 10^3-, 10^4-, and 10^5-Å μ-Styragel columns.

Thermal analyses were performed with a DuPont 990 thermal analyzer equipped with a differential scanning calorimeter (DSC) cell base (heating rate 10 °C/min). Dynamic thermomechanical analyses were obtained on a Rheovibron DDV-II-C dynamic viscoelastometer (frequency 35 Hz). Oxidative isothermal aging was performed in a circulating-air oven. Unless otherwise noted, all starting materials, reagents, and solvents were obtained from commercial suppliers and used without further purification. The monomers 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (2)[22] and 4,4′-diacetyldiphenyl ether (3)[29,30] were prepared as described.

Biphenylene.[31] Biphenylene was obtained in 20–25% yields from anthranilic acid and was purified by flash chromatography[32] (230–400-mesh silica gel, methylene chloride) followed by sublimation of the solid at 70 °C (0.2 mmHg) afforded product as a nearly white solid: mp 113.0–115.0 °C (lit.[31] mp 109–112 °C). 2,4-Diphenylquinoline was prepared as described.[33]

2-Acetylbiphenylene (5). To a slurry of 12.7 g of aluminum chloride in 42 mL of dry methylene chloride cooled to 0 °C was added dropwise 4.6 mL (5.0 g, 4.9 mmol) of dry distilled acetic anhydride. After stirring for 1 h at 0 °C, the mixture was cannulated over 30 min into a solution of 6.3 g (41 mmol) of biphenylene in 55 mL of dry methylene chloride cooled to −30 °C. The mixture was stirred at −30 °C for 1.5 h and then allowed to warm to room temperature. The mixture was poured into 300 g of ice and 200 mL of hydrochloric acid and extracted with 3 × 200 mL of methylene chloride. The methylene chloride extracts were combined and washed with water, saturated sodium bicarbonate, again with water, and finally with saturated sodium chloride. The solution was dried over sodium sulfate. Removal of the solvent under reduced pressure afforded a solid, which was purified by flash chromatography[32] (230–400-mesh silica gel, 25% hexane in methylene chloride). Sublimation at 100 °C (0.05 mmHg) afforded 5.8 g (73%) of 2-acetylbiphenylene as bright yellow crystals: mp 136.5–137.0 °C (lit.[34] mp 134–135 °C); IR (KBr) 1680 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.5 (s, 3, CH$_3$), 6.6–7.6 (m, 7, aromatic).

Preparation of Polyquinoline 1 To Determine a $\overline{\mathrm{DP}}$ Suitable for Melt Processing. A mixture of 5.1 g of P$_2$O$_5$ and 12 mL of freshly distilled *m*-cresol was stirred for 2 h at 130 °C under a static nitrogen atmosphere in a resin kettle equipped with a mechanical stirrer. The solution was allowed to cool to room temperature, and 1.2254 g (3.000 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether and 0.7629 g (3.000 mmol) of 4,4′-diacetyldiphenyl ether were added. The solution was heated to 135–137 °C and maintained during the polymerization at 2, 3.25, and 5 h and immediately quenched by pouring into a vigorously stirred solution of 120 mL of ethanol and 10 mL of triethylamine. Each mixture was transferred to a Waring blender, ground up at high speed, and suction filtered. The resulting powders were continuously extracted for 24 h with 300 mL of ethanol and 20 mL of triethylamine. The polymer samples were dried at 110 °C (0.05 mmHg) for 24 h. The molecular weight distribution of the 2-h sample 1 is given in Table I.

Phenyl End-Capped Polyquinoline Prepolymer ($\overline{\mathrm{DP}}$ = 22). A procedure similar to that above was followed except 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether and 0.7629 g (3.000 mmol) of 4,4′-diacetyldiphenyl ether were added to the catalyst mixture. After 12 h, 65 μL (67 mg, 0.56 mmol, 25% excess) of purified acetophenone was added and heating was continued for 3 h before quenching. The molecular weight distribution is given in Table I.

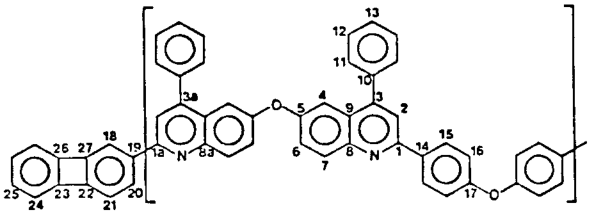
Biphenylene End-Capped Polyquinoline (6 ($\overline{\mathrm{DP}}$ = 22)). To a resin kettle equipped with a mechanical stirrer were added 0.7629 g (3.000 mmol) of 4,4′-diacetyldiphenyl ether (3), 1.3165 g (3.223 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (2), 21.5 g (77.4 mmol) of di-*m*-cresyl phosphate,[24] and 6.9 g of distilled *m*-cresol. The solution was heated at 135–137 °C under a static nitrogen atmosphere for 24 h and then cooled slightly, and 0.1082 g (0.5577 mmol, 25% excess) of 2-acetylbiphenylene (5) was added. Heating at 135–137 °C under a static nitrogen atmosphere was resumed for an additional 24 h, at which time the dark red solution was poured into a vigorously stirred solution of 360 mL of ethanol and 30 mL of triethylamine. The mixture was ground up at high speed in a blender and suction filtered. The resulting yellow powder was continuously extracted for 62 h with 300 mL of ethanol and 25 mL of triethylamine and then dried at 110 °C (0.01 mmHg) for 48 h to afford 1.8 g (85%) of 6: $[\eta]_{\mathrm{inh}}$ = 0.47 dL/g (25.0 °C, chloroform). (The yield of 6 was increased to 93% when the polymerization was run on a larger scale.) Anal. Calcd: C, 85.64; H, 4.41; N, 4.70. Found: C, 85.01; H, 4.40; N, 4.54. The prepolymer properties are reported in Tables II–IV.

Biphenylene End-Capped Polyquinoline (6 ($\overline{\mathrm{DP}}$ = 11)). The above procedure was followed except 1.4435 g (3.534 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether, 0.7629 g (3.000 mmol) of 4,4′-diacetyldiphenyl ether, 23.5 g of di-*m*-cresyl phosphate,[24] 7 mL of distilled *m*-cresol, and 0.2590 g (1.335 mmol, 25% excess) of 2-acetylbiphenylene were used. The yield of 6 was 1.8 g (85%): $[\eta]_{\mathrm{inh}}$ = 0.25 dL/g (25.0 °C, chloroform). Anal. Calcd: C, 85.91; H, 4.45; N, 4.63. Found: C, 84.93; H, 4.07; N, 4.48. The prepolymer properties are reported in Tables II–IV.

Biphenylene End-Capped Polyquinoline (6 ($\overline{\mathrm{DP}}$ = 3)). The above procedure was followed except 1.2254 g (3.000 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether, 0.3814 g (1.500 mmol) of 4,4′-diacetyldiphenyl ether, 20.2 g of di-*m*-cresyl phosphate,[24] 7 mL of distilled *m*-cresol, and 0.6410 g (3.300 mmol, 10% excess) of 2-acetylbiphenylene were used. Due to the fineness of the resulting powder, the workup was modified as follows: After pouring of the blood red polymerization mixture into 360 mL of ethanol and 30 mL of triethylamine, the resultant fine powder was isolated by centrifugation. The powder was extracted with 5 × 60 mL of hot ethanol and 6 mL of triethylamine by stirring the prepolymer in ethanol/triethylamine, followed by centrifugation and removal of the supernatant liquid. The yellow powder was dried at 110 °C (0.1 mmHg) for 18 h to afford 1.9 g (95%) of 6: $[\eta]_{\mathrm{inh}}$ = 0.09 dL/g (25.0 °C, chloroform). Anal. Calcd: C, 86.58; H, 4.45; N, 4.49. Found: C, 87.61; H, 4.32; N, 4.34. The ^{13}C NMR spectrum of 6 is reported in Table X. The prepolymer properties are given in Tables II–IV.

Reactions of Biphenylene. NMR-grade benzene-d_6 (Norrell, 99.5% isotopic purity) containing 1% tetramethylsilane (Me$_4$Si) was used. Integration of the aromatic and Me$_4$Si resonances substantiated the isotopic purity of the benzene-d_6. The concentration of Me$_4$Si was significantly decreased (as followed by ^{1}H NMR) by bubbling argon through the solution for 5 min to prepare the benzene-d_6 for use as a reagent. Diphenyl ether was purified by a known procedure.[38] The purification of 2,4-diphenylquinoline was effected by recrystallization from methanol

Table X
^{13}C NMR of Polyquinoline Prepolymer



carbon no.	calcd shift,[a] ppm	obsd shift,[b] ppm	previously obsd shift,[c-e] ppm
1	164.3	154.9	155.3[c]
1a	164.3	155.3	156.0[d]
2	119.4	122.6 (d)	122.9[c]
3	149.5	148.2	148.3[d]
3a	149.5	147.9	148.3[c]
4	119.4	112.3 (d)	112.5[c]
5	156.1	154.4	154.6[c]
6	120.3	119.1 (d)	119.3[c]
7	131.4	131.8 (d)	132.1[c]
8	144.7	145.5	146.0[d]
8a	144.7	145.7	146.0[d]
9	128.0	126.4	126.5[c]
10	141.5	137.8	138.1[c]
11	127.4	128.9[f]	129.1[c]
12	129.0	129.1[f]	129.4[c]
13	127.5	128.5[f]	128.7[c]
14	136.2	134.6	135.0[c]
15	128.8	128.5[f]	128.7[c]
16	119.6	119.1 (d)	119.3[c]
17	156.7	157.9	158.2[c]
18	116.7	116.2 (d)	117.8[e]
19	141.4	139.4	128.4[e]
20	127.3	128.5[f]	128.4[e]
21	118.3	117.6 (d)	117.8[e]
22	150.7	151.7	151.7[e]
23	151.7	150.6	151.7[e]
24	117.8	117.2 (d)	117.8[e]
25	128.4	128.0[f]	128.4[e]
26	151.7	150.5	151.7[e]
27	152.2	152.3	151.7[e]

[a] Chemical shift values calculated on the basis of the additivity of chemical shift parameters.[35,36] [b] 100-MHz FT NMR; doublets, as determined by off resonance, are indicated by (d). [c] Reference 17. [d] Chemical shift reported for 6-oxybis(2,4-diphenylquinoline).[22] [e] Chemical shift reported for unsubstituted biphenylene.[37] [f] Assignments may be reversed due to proximity of peaks. Off resonance indicated doublets but overlap hindered accurate assignment.

containing a small amount of triethylamine. Bis(triphenylphosphine)dicarbonylnickel(0) (Aldrich) was used without further purification. A Parr reactor was modified for use as a furnace by placing a thin-walled copper pipe wrapped with flexible heating tape (Briskeat no. BIH-21) in the center of the reactor. Packing of the dead volume with glass wool afforded adequate insulation. Temperatures were maintained to 5 °C as measured by a thermocouple attached to the glass reaction tubes. All tubes were sealed under reduced pressure (0.05 mmHg); liquid reagents were subjected to two freeze–pump–thaw cycles (under an argon atmosphere during thawing) before the reaction tubes were sealed. Mass spectra (70 eV) obtained at Colorado State University were done on a V.G. Micromass 16F mass spectrometer equipped with a Perkin-Elmer Sigma 3 gas chromatograph (GCMS). Other mass spectra (70 eV) were obtained from the Midwest Center for Mass Spectrometry, Lincoln, NB, and the U.S. Geological Survey, Wheatridge, CO. All components were identified by comparison with standard spectra.[39,40]

Bis(triphenylphosphine)dicarbonylnickel(0)-Catalyzed Reactions. (a) Biphenylene and Benzene-d_6. To a glass tube was added 96 mg (0.15 mmol) of bis(triphenylphosphine)dicarbonylnickel(0), using 0.5 mL of benzene-d_6 to ensure complete

Table XI
Mass Spectral Data for the Product Mixtures from the Ni(0)-Catalyzed Reactions of Biphenylene with Model Compounds

model compd	% of total ion intensity; m/e					
	biphenylene	biphenyl	fluorenone	tetraphenylene	triphenylphosphine	others
benzene-d_6[a]		18%; m/e 155 (13.01), 154 (M$^+$, 100), 153 (28.79), 152 (31.33), 77 (11.55), 76 (14.89)	24%; m/e 181 (14.32), 180 (M$^+$, 100), 152 (26.86), 151 (13.94), 76 (19.56)	41%; m/e 305 (24.63), 304 (M$^+$, 100), 303 (56.83), 302 (47.98), 152 (15.43), 151 (34.25), 150 (17.54)	7%; m/e 262 (M$^+$, 2.03), 261 (20.44), 260 (100), 259 (22.73), 183 (41.17)	10%, b
diphenyl ether[c,d]	65%; m/e 153 (14), 152 (M$^+$, 100), 151 (30), 150 (15), 76 (11)	12%; m/e 155 (15), 154 (M$^+$, 100), 153 (45), 152 (31), 77 (12), 76 (23)	16%; m/e 181 (14.20), 180 (M$^+$, 100), 152 (70.10), 151 (35.21), 76 (44.08)	trace; 305 (25.93), 304 (M$^+$, 100), 303 (76.19), 302 (66.67), 226 (41.27), 151 (21.69), 150 (24.34)	6%; m/e 262 (M$^+$, 100), 261 (16.49), 260 (5.32), 183 (42.24)	1%, b
2,4-diphenylquinoline[c]		21%; m/e 155 (14), 154 (M$^+$, 100), 153 (41), 152 (28), 77 (8), 76 (19)	26%; m/e 181 (19), 180 (M$^+$, 100), 152 (29), 151 (20), 76 (18)	38%; m/e 305 (22), 304 (M$^+$, 100), 303 (75), 302 (53), 151 (40), 150 (38)	15%; m/e 263 (22), 262 (M$^+$, 100), 261 (18), 183 (82)	e

[a] Analysis done at Colorado State University. [b] See detailed Experimental Section. [c] Analysis done at U.S. Geological Survey, Wheatridge, CO. [d] Analysis done by Midwest Center for Mass Spectrometry, Lincoln, NB. [e] Adduct **66** (<5% of the total ion intensity) was detected by direct-insertion probe mass spectrometry; see Table IX.

Table XII
Mass Spectral Data for the Product Mixtures from the Uncatalyzed Reactions of Biphenylene with Model Compounds

	% of total ion intensity; *m/e*			
model compd	biphenylene	biphenyl	tetraphenylene	others
diphenyl ether[a]	30%; *m/e* 153 (11), 152 (M^+, 100), 151 (19), 150 (12), 76 (5)	10%; *m/e* 152 (M^+)[b]	60%; *m/e* 305 (25.00), 304 (M^+, 100), 303 (73.24), 302 (59.42), 152 (25.08), 151 (48.00), 150 (33.63)	
2,4-diphenylquinoline[c]	53%; *m/e* 153 (12), 152 (M^+, 100), 151 (30), 150 (15), 76 (10)	32%; *m/e* 155 (12), 154 (M^+, 100), 153 (42), 152 (28), 77 (5), 76 (14)		15%, *d*

[a] Analysis done by Midwest Center for Mass Spectrometry, Lincoln, NB. [b] Only *m/e* for parent reported. [c] Analysis done at U.S. Geological Survey, Wheatridge, CO. [d] Adduct **9** (15% of the total ion intensity) was detected by direct-insertion probe mass spectrometry; see Table IX.

transfer. A solution of 228 mg (1.50 mmol) of biphenylene in 1.0 mL of benzene-d_6 was then added, using 0.5 mL of benzene-d_6 to rinse any residual material into the tube (total benzene-d_6: 2.0 mL, 1.8 g, 21 mmol). The tube was sealed under reduced pressure and heated at 200 °C for 1.5 h. The resultant brown-black solution was filtered through a Celite pad to afford a clear, yellow solution. (The dark color of the solution before filtering is probably attributable to precipitated nickel(0) black.) The solution was analyzed by GCMS using an SE-54 capillary column and a temperature program of 180 → 300 °C at 6 °C/min to effect the separation of the components in the product mixture. In addition to the major components reported in Table XI, trace amounts of the following were also detected: triphenylene (3% of the total ion intensity), *m/e* 229 (20), 228 (M^+, 100), 227 (12), 226 (31), 113 (23), 112 (20); *o*-quaterphenyl (3% of total ion intensity), *m/e* 307 (33), 306 (M^+, 100), 305 (17), 229 (21); *o*-terphenyl (1% of the total ion intensity), 231 (26), 230 (M^+, 100), 229 (61), 228 (38), 227 (20), 226 (20); triphenylphosphine oxide (1% of the total ion intensity), *m/e* 279 (15), 278 (M^+, 55), 277 (100); an unidentified component (2% of the total ion intensity), *m/e* 261 (23), 260 (100), 259 (24).

(b) Biphenylene with Diphenyl Ether. A solution of 152 mg (1.00 mmol) of biphenylene in 1.0 mL of diphenyl ether was added to a glass tube. To this solution, 63.9 mg (0.100 mmol) of bis(triphenylphosphine)dicarbonylnickel(0) was added, using 0.6 mL of diphenyl ether to ensure complete transfer (total diphenyl ether: 1.6 mL, 1.7 g, 10 mmol). The tube was sealed under reduced pressure and heated at 200 °C for 1.5 h. The resultant orange solution containing a black precipitate (probably nickel(0) black) was filtered through a Celite pad to afford a clear, bright yellow solution. The solution was analyzed by GCMS using a 3% SE-30 packed column and a temperature program of 180 → 300 °C at 6 °C/min to effect separation of the components in the mixture. In addition to the components reported in Table XI, a trace amount (1% of the total ion intensity) of triphenylphosphine oxide was detected: *m/e* 279 (8), 278 (M^+, 32), 277 (100).

(c) Biphenylene with 2,4-Diphenylquinoline. A solution of 1.40 g (5.00 mmol) of 2,4-diphenylquinoline, 0.152 g (1.0 mmol) of biphenylene, and 0.064 g (0.10 mmol) of bis(triphenylphosphine)dicarbonylnickel(0) in a minimum amount of methylene chloride was added to a glass tube. The methylene chloride was removed, and the tube was sealed under reduced pressure. The tube was heated at 200 °C for 1.5 h to afford a black, tarry product. The mixture was dissolved in methylene chloride and filtered through a Celite pad to give a clear, orange-red solution. The product mixture was analyzed, as described above, by GCMS (see Table XI). Direct-insertion probe mass spectrometry (70 eV), at a probe temperature of 300 °C, revealed the presence of a component tentatively identified as the product of the addition of biphenylene to 2,4-diphenylquinoline, **9** (see Table IX). The adduct, **9**, could not have formed during electron bombardment since all residual biphenylene was volatilized prior to the appearance of **9**.

Uncatalyzed Reactions. (a) Biphenylene with Diphenyl Ether. A solution of 152 mg (1.00 mmol) of biphenylene in 1.6 mL (1.7 g, 10 mmol) of diphenyl ether was added to a glass tube. The tube was sealed under reduced pressure and heated at 400 °C for 1 h to afford a clear, yellow solution. The solution was analyzed by GCMS, as described above (see Table XII).

(b) Biphenylene with 2,4-Diphenylquinoline. A solution of 1.40 g (5.00 mmol) of 2,4-diphenylquinoline and 0.152 g (1.00 mmol) of biphenylene in a minimum amount of chloroform was added to a glass tube. The chloroform was removed under reduced pressure. The tube was sealed and heated at 400 °C for 1 h to afford a black, tarry product mixture. (Neat 2,4-diphenylquinoline subjected to the same conditions afforded a product mixture of similar appearance.) The mixture was dissolved in methylene chloride and analyzed by GCMS, as described above (see Table XII). Direct-insertion probe mass spectrometry at a probe temperature of 300 °C again demonstrated the presence of **9** (see Table IX).

Neat Resin Processing. The appropriate amount of bis(triphenylphosphine)dicarbonylnickel(0) (Aldrich) or (norbornadiene)chlororhodium(I) dimer (Strem) was added to the prepolymer swelled in benzene. The mixture was stirred for 1 h, the solvent was removed under reduced pressure, and the resulting powder was dried at 75 °C and 0.05 mmHg for 18 h.

A modified Wabash hydraulic press (Model 12 10) fitted with Carver heated platens (no. 2102) was used for the neat resin processing. A 170-mg sample of the prepolymer powder was placed in a small pile between 2–6 in. × 6 in. pieces of copper foil (0.005-in. thick, Baker no. 1-1714) with a 0.005-in. copper foil spacer. The assembly was placed in the hydraulic press and melt processed at 300–371 °C (572–700 °F) under 500–1000 psi for various times. Plunging of the assembly into cold water immediately after processing facilitated removal of the film from the copper foil. Any residual copper that adhered to the surface of the film was removed by placing the film in concentrated ammonium hydroxide for 30 min, followed by thorough rinsing with water. The specific melt-processing conditions and cured polymer properties for each biphenylene end-capped prepolymer are given in Tables V–VIII and Figure 3.

Acknowledgment. This research was supported by a grant from the Army Research Office, Research Triangle, NC. We thank Phillips Petroleum Co. for a fellowship to J.P.D.

Registry No. **6**, 85884-44-2; **5**, 779-26-0; biphenylene, 259-79-0; benzene-d_6, 1076-43-3; diphenyl ether, 101-84-8; 2,4-diphenylquinoline, 1039-51-6; bis(triphenylphosphine)dicarbonylnickel, 13007-90-4.

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Biphenylene End-Capped Aromatic Prepolymers: Polyimides, Poly(ether–keto–sulfones), and Polyquinoxalines

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Received March 8, 1983

ABSTRACT: Biphenylene end-capped polyimide, poly(ether–keto–sulfone), and poly(phenylquinoxaline) prepolymers were synthesized. The polyimide prepolymer of $\overline{DP}$ = 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 T_g 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 prepolymer. Poly(phenylquinoxaline) prepolymers 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 to give an insoluble film with a T_g of 291 °C and improved mechanical properties above T_g.

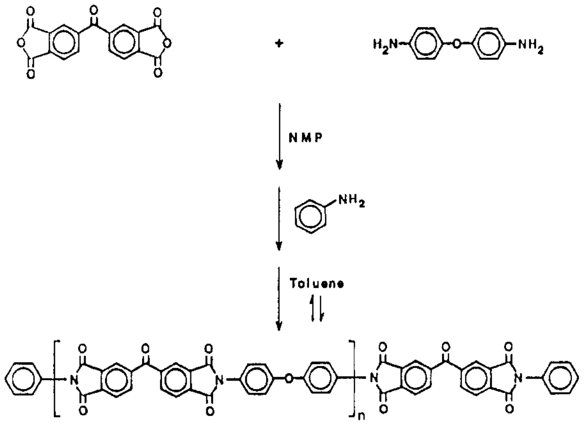
Introduction

In the preceding paper, the preparation and processing of biphenylene end-capped polyquinoline prepolymers were described. These prepolymers underwent chain extension and cross-linking in the melt to yield high-quality cross-linked films. Thus, the extension of this approach to other types of thermally stable polymers was undertaken in an effort to determine the scope of this prepolymer curing reaction. Polyimides are one of the most industrially important thermally stable polymers[1] while certain poly(ether–sulfones) and poly(phenylquinoxalines) have potential for commercial application. Consequently, the preparation and cross-linking/chain extension reactions of biphenylene end-capped prepolymers of these types were carried out.

Results and Discussion

Polyimides. The poor melt flow of high molecular weight polyimides necessitated the determination of a $\overline{DP}$ suitable for melt processability. Thus, phenyl end-capped polyimide prepolymers[1] 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 (Scheme I).

Scheme I



1 a n = 3
b n = 11

0024-9297/84/2217-0010$01.50/0