Macromolecules 1981, *14*, 493-502

Table II
Elemental Analyses of "Cardo" Polyquinolines 31

polymer	calcd % C	calcd % H	calcd % N	found % C	found % H	found % N	residue %
31a	92.07	4.77	3.16	90.91	4.65	2.96	0.68
31b	90.57	4.63	3.06	89.23	4.54	2.98	
31c	90.56	4.62	3.06	89.45	4.53	3.01	0.25
31d	89.15	4.49	2.97	88.22	4.46	2.92	
31e	91.38	4.74	3.87	90.71	4.82	3.83	0.37
31f	89.40	4.64	3.79	87.83	4.70	3.48	0.54
31g	89.57	4.56	3.73	89.09	4.52	3.69	0.22
31h	87.71	4.47	3.65	87.09	4.37	3.57	
31i	91.38	4.74	3.88	91.22	4.72	3.74	
31j	89.41	4.64	3.79	88.67	4.61	3.69	
31k	89.82	4.31	3.74	88.29	4.56	3.65	
31l	87.71	4.47	3.65	87.12	4.34	3.51	

them to slowly evaporate in a dust-free chamber for 24 h. Peeling the film from the glass and drying it in between two glass plates in an oven at 100 °C for 12 h gave transparent tough flexible films of polymer **31j**.

Polymer Properties. Viscosity measurements of the polymers were determined in chloroform, *m*-cresol, sulfuric acid, or TCE at 25 ± 0.2 °C. For each polymer, the intrinsic viscosity was obtained from the intersection of plots of η_{inh} vs. C and η_{red} vs. C.

Thermal analyses were conducted with a Du Pont 990 differential thermal analyzer equipped with a differential scanning calorimeter (DSC) cell base module II and a 950 thermogravimetric analyzer (TGA). The DSC analyses were obtained on pressed powder samples at a heating rate of 10 °C/min under a flowing nitrogen atmosphere. Either powder or pressed powder samples were used for TGA analyses. The analyses were conducted at a heating rate of 5 °C/min in both flowing air and flowing nitrogen atmospheres. Dynamic thermomechanical analyses were performed by using a Rheovibron (Model DDV-II-C) on film samples as described.[19]

Acknowledgment. S.M.P. is thankful to P. D. Sybert for the sample of 4,4′-diamino-3,3′-dibenzoylbiphenyl. This research was supported by the U.S. Army Research Office, Durham, N.C. We also thank the Colorado State University Regional NMR Center.

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Synthesis and Properties of Rigid-Rod Polyquinolines

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ABSTRACT: The self-condensations of 5-acetyl-2-aminobenzophenone and 4-amino-4′-acetyl-3-benzoylbiphenyl and the copolymerization of these monomers were carried out in a *m*-cresol/di-*m*-cresyl phosphate medium to afford rigid-rod polymers that possessed high T_g's (330–415 °C), showed limited solubilities, and retained a relatively high percentage of mechanical properties above T_g. The condensation of 3,3′-dibenzoylbenzidine with a variety of diacetyl and diphenacetyl aromatic compounds also afforded rigid-rod polyquinolines that had limited solubilities, had high T_g's (340–370 °C), and retained a high percentage of mechanical properties above T_g. The analogous polymers containing a flexible ether linkage possessed improved solubilities, showed lower T_g's (260–330 °C), and lost a significant percentage of mechanical properties above T_g. The polymerization dope (1.0–1.5% solids) of poly[2,6-(*p*-phenylene)-4-phenylquinoline], which exhibited birefringence domains, could be spun into fibers which had moderate tensile strength (4.4 g/denier) and a high degree of crystallinity. The polymerization dopes from the rigid AA–BB monomers were also wet spun into fibers. Anisotropic solutions (18.5%) of poly[1,1′-(*p*,*p*-biphenyl)-6,6′-bis(4-phenylquinoline)] in *m*-cresol/di-*m*-cresyl phosphate (5:1 molar ratio) were jet-dry wet spun into fibers, which after heat treatment possessed tenacities and moduli of up to 9.0 and 340 g/denier, respectively.

Introduction

Flexible polymers containing either 2,6- or 2,4-quinoline units show excellent oxidative and thermal stabilities.[1–3] Although these amorphous polymers possess acceptable melt and solution properties for processing, they lose mechanical properties at T_g, $\sim$200–300 °C, a temperature well below the decomposition temperature (T_d = 550 °C). Increasing the degree of crystallinity from $\sim$10 to 15% in

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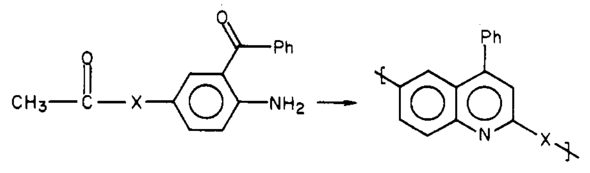
Table I
Properties of Polyquinolines 22



polymer	X	solubility[a]	$[\eta]$,[b] dL/g	reaction time, h	T_g, °C DSC	T_g, °C E''_{max}	T_m, °C	TGA,[c] °C air	TGA,[c] °C N_2	TGA,[c] °C % wt loss at 800 °C (N_2)
22a	nil	H_2SO_4	3.6	70	415	d	552	520[e]	570[e]	20[e]
22b	p-C_6H_4	H_2SO_4	11.6	24		383	580	605	610	20
22c	random 1:1 nil-p-phenylene	H_2SO_4 CF_3CO_2H	4.9	48	330	343	520	555	580	22

[a] Solubility defined as the ability to dissolve 5% by weight of polymer. [b] Intrinsic viscosities measured in concentrated sulfuric acid at 25 °C. [c] Onset of weight loss from decomposition. [d] Suitable film not obtained. [e] From ref 3.

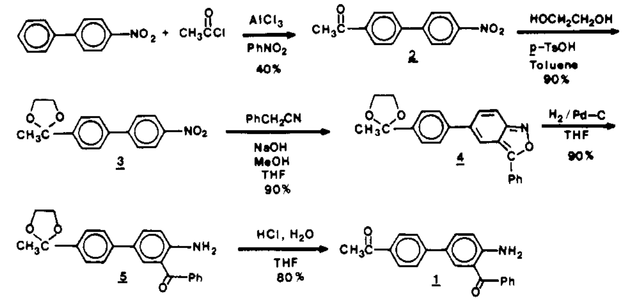


Figure 1. Synthesis of 4-amino-4′-acetyl-3-benzoylbiphenyl (**1**).

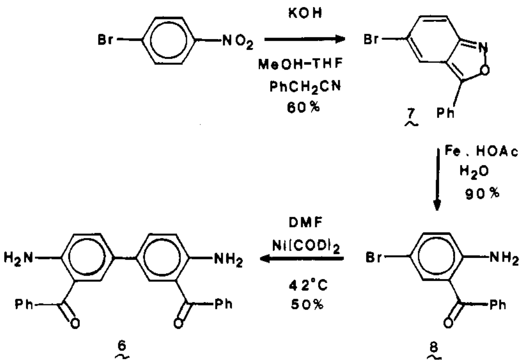


Figure 2. Synthesis of 3,3′-dibenzoylbenzidine (**6**).

these largely amorphous materials could raise the effective use temperature to the crystalline transition temperatures; however, all attempts to increase the degree of crystallinity of these flexible polymers did not produce materials with a significantly higher crystallinity.[3] Polymers containing 3,6-quinoline units in the main chain could be annealed to develop sufficient crystallinity to raise the use temperature up to T_m.[4]

In an effort to combine the excellent oxidative and thermal properties of polyquinolines, the effective use temperature of a highly crystalline polymer, and the high-strength/high-modulus properties of highly oriented fibers, we synthesized a series of rigid-rod polyquinolines.

Results and Discussion

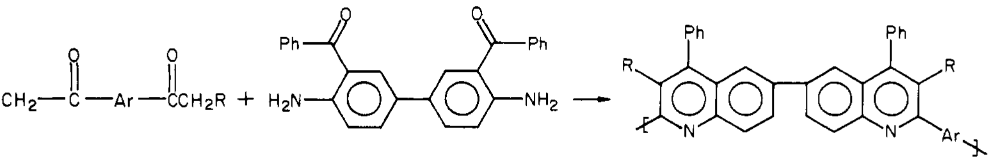
Monomer Synthesis. The AB monomer 4-amino-4′-acetyl-3-benzoylbiphenyl (**1**) was synthesized by the acylation of 4-nitrobiphenyl in nitrobenzene to give 4-acetyl-4′-nitrobiphenyl (**2**) in a 40% yield.[5] Protection of the ketone and the reaction of the ketal **3** with phenylacetonitrile in basic methanol and tetrahydrofuran (THF) gave a 90% yield of 5-[p-(2-methyl-1,3-dioxolan-2-yl)-phenyl]-3-phenyl-2,1-benzisoxazole (**4**). The benzisoxazole ring was then hydrogenated to the o-amino ketone **5** (Figure 1). Acid hydrolysis of **5** afforded a quantitative yield of **1**.

Synthesis of the bis(o-amino ketone) monomer **6** has been described,[6,7] but due to the low yields and difficulty in obtaining monomer-pure product, a new synthesis was devised (Figure 2). The bromobenzisoxazole **7** was prepared in a 60% yield by treatment of p-bromonitrobenzene with phenylacetonitrile in basic methanol[8] and THF. Reduction of **7** with iron and acetic acid[8] gave **8** which was readily purified through the amine hydrochloride. Coupling[9] of **8** was promoted by bis(1,5-cyclooctadiene)nickel(0) [Ni(COD)$_2$] in N,N-dimethylformamide (DMF) and the crude product was subjected to column chromatography followed by recrystallization to afford monomer-grade **6**.

Monomer **9** has been prepared by the addition of benzylmagnesium chloride to 4,4′-dicyanobiphenyl followed by acid hydrolysis of the resultant imine.[10] In our hands, however, a mixture of side products was obtained, which could not be removed by normal purification methods due to their low solubilities in common organic solvents. A better method for synthesis of **9** was through the coupling of pure **10**, using Ni(COD)$_2$. Since the only side product of this reaction was phenacetylbenzene, purification was readily accomplished. Acylation of bromobenzene using phenacetyl chloride gave crude **10**,[11,12] which, through repeated fractional recrystallization, was obtained suitably pure (Figure 3). No attempt was made to optimize the reaction conditions. The p,p‴-diacetylquaterphenyl monomer **11** was prepared by the coupling of **12**, using Ni(COD)$_2$ in DMF (Figure 3). 4-Acetyl-4′-bromobiphenyl (**12**) was prepared by the acylation of 4-bromobiphenyl with acetyl chloride in carbon disulfide, using aluminum chloride.[13] The remaining monomers **14**–**21** were prepared according to known procedures (Experimental Section).

Polymer Synthesis. The self-polymerizations of 5-acetyl-2-aminobenzophenone (**14**)[14] and 4-amino-4′-acetyl-3-benzoylbiphenyl (**1**) along with the copolymerization of **14** and **1** were conducted in a m-cresol/di-m-cresyl phosphate medium[15] at 135 °C for 24–48 h to afford polymers **22a**–**c** (Table I). As the polymerization proceeded, the reactions were diluted as necessary with m-cresol to ensure adequate stirring. Polymer **22b**, for example, required a 15-fold dilution before the polym-

Table II
Properties of Polyquinolines 23 and 24



			solubility[a]			T_g, °C			TGA,[d] °C		
polymer	R	Ar	H_2SO_4	CF_3SO_3H	$[\eta]$,[b] dL/g	DSC[c]	E''_{max}	T_m, °C	air	N_2	% wt loss at 800 °C (N_2)
23a	H	$p\text{-}C_6H_4$	PS	S	7.0	350 (365)	395		570	595	24
23b	H	$(p\text{-}C_6H_4)_2$	I	S	14.5-26.0	340 (350)	360	500	570	580	24
23c	H	$(p\text{-}C_6H_4)_3$	I	S	22.0	345 (360)	350	504	525	600	23
23d	H	$(p\text{-}C_6H_4)_4$	I	I	*e*	350 (360)	*f*		580	600	22
24a	Ph	$p\text{-}C_6H_4$	I	S	17.0	370 (365)	400	555[g]	580	590	30
24b	Ph	$(p\text{-}C_6H_4)_2$	PS	S	22.0	360 (365)	420		570	595	25

[a] S = ability to dissolve 0.5% by weight of polymer, 0 < PS < 0.5%, *I* = insoluble. [b] Intrinsic viscosities measured in trifluoromethanesulfonic acid at 25 °C. [c] Samples first heated to 450 °C at 50 °C/min and then quenched with liquid nitrogen before the DSC was recorded. Values in parentheses obtained from samples with no thermal treatment. [d] Onset of weight loss from decomposition. [e] Insoluble in all solvents tried. [f] Suitable film not obtained. [g] Appears to be a first-order transition due to crystalline melt but may be onset of decomposition.

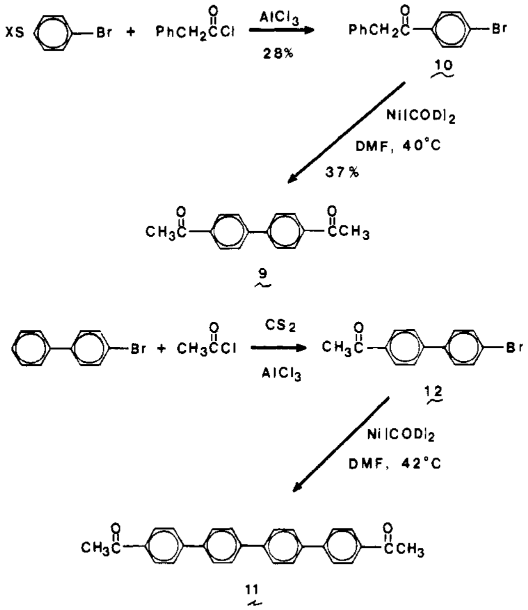


Figure 3. Synthesis of 4,4′-diphenacetylbiphenyl (9) and 4,4‴-diacetylquaterphenyl (11).

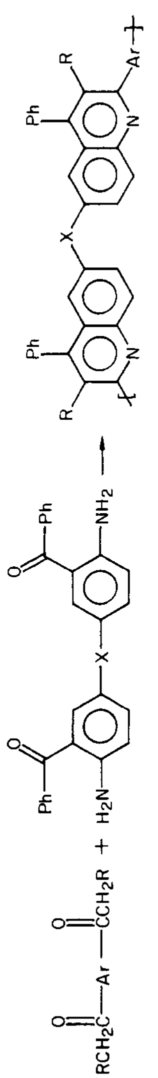
erization was complete. The polymer dope was then either used for the preparation of films and fibers directly or precipitated into ethanol-triethylamine. Polymers **22a** and **22b** were soluble only in the polymerization medium and sulfuric acid, whereas **22c** was also soluble in trifluoroacetic acid (**22b** precipitated from the polymerization medium on standing at ambient temperature). Random copolymerization of two rigid monomers to afford a rigid copolymer, such as **22c**, is known to increase the solubility of the copolymer over the corresponding homopolymer.[16,17] Thus, either by the fabrication of films and fibers directly from the polymerization medium or by the preparation of soluble **22c** an otherwise intractable material could be processed. The relatively low viscosities of **22a** and **22c** compared to that of **22b** were probably due to impurities in monomer **14**, which softened at 160.5 °C and finally melted at 162.0–163.5 °C.

The polymerizations of 3,3′-dibenzoylbenzidine (**6**) with various diacetyl and diphenacetyl *p*-phenylene monomers were run for 48 h as described for polymers **22** to yield rigid-rod polymers **23** and **24** (Table II). Polymers **23a–c** and **24** were diluted as necessary with *m*-cresol to ensure adequate stirring. These polymers were soluble in the polymerization medium and trifluoromethanesulfonic acid, while polymer **23d** precipitated from the reaction mixture and was insoluble in all solvents tried. By a similar procedure the appropriate diacetyl or bisphenacetyl monomers were allowed to react with either 3,3′-dibenzoylbenzidine (**6**) or 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**21**). These semirigid polyquinolines (**25**), containing ether links, remained in solution throughout the polymerization (Table III). Except for polymer **25d**, these and other flexible 2,6-polyquinolines[2] show enhanced solubility over the rigid analogues.

Phase Transition Temperatures. Pressed powder and film samples of polyquinolines were analyzed by differential scanning calorimetry (DSC) and dynamic thermomechanical analysis (Tables I–III). The glass transition temperatures of polymers **22a** and **22b** ranged from 383 °C (Rheovibron; not detectable by DSC) to 415 °C, with the copolymer **22c** having a significantly lower T_g (330–343 °C). The T_g values [as loss (E'') maximum] determined by thermomechanical analysis of films on a Rheovibron were in close agreement with the values obtained by DSC.

Polymers **23a–d** had T_g's as measured by DSC of 345 ± 5 °C, which indicated that variations in the "–Ar–" group have little affect on T_g (Table II). Polymers **24a** and **24b** had T_g's of 365 ± 5 °C. As expected, the flexible polymers had lower T_g's, ranging from 270 to 330 °C. Powder samples annealed in the DSC above their T_g showed an increase in their T_g of 10–20 °C after cooling and rerunning the samples. A similar dependence of T_g on the thermal

Table III
Properties of Semirigid Polyquinolines 25



polymer	X	R	Ar	solubility[a] TCE	solubility[a] m-cresol	solubility[a] H_2SO_4	solubility[a] CF_3SO_3H	$[\eta]$, dL/g	T_g, °C DSC[b]	T_g, °C E''_{max}	TGA,[c] °C air	TGA,[c] °C N_2	TGA,[c] °C % wt loss at 800 °C (N_2)
25a[d]	nil	H	p-C_6H_4O-p-C_6H_4	I	S	S	S	3.4 (m-cresol)	305 (270)	285	548	565	30
25b	nil	Ph	p-C_6H_4O-p-C_6H_4	I	I	PS	S	10.5 (CF_3SO_3H)	330 (270)	*e*	550	575	25
25c	O	H	$(p$-$C_6H_4)_3$	S	S	S	S	3.5 (TCE)	260–275[f] (280)	300	540	540	15
25d	O	H	$(p$-$C_6H_4)_4$	I	I	I	I	*g*	270–290[f] (305)	310	520	560	20

[a] S = ability to dissolve 0.5% by weight of polymer, 0 < PS < 0.5%, I = insoluble; TCE = *sym*-tetrachloroethane. [b] Samples first heated to 450 °C at 50 °C/min and then quenched with liquid nitrogen before DSC was recorded. Values in parentheses obtained from samples with no thermal treatment. [c] Onset of weight loss from decomposition. [d] Polymer 25a has been reported previously; however, it was not characterized and appeared to contain a small degree of cross-linking.[7] [e] Suitable film not obtained. [f] Due to the shape of the curve for the second-order transition an accurate value was not obtained. [g] Insoluble in all solvents tried.

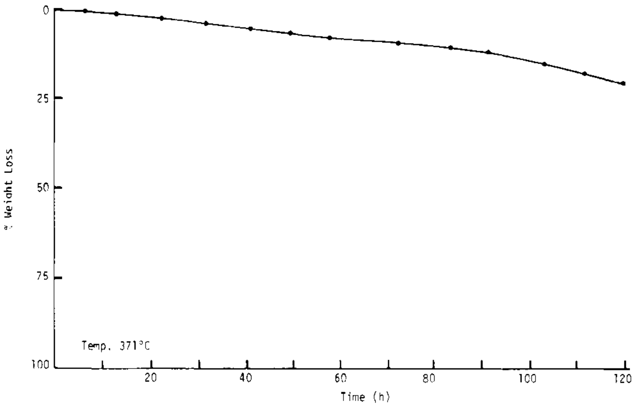


Figure 4. Isothermal aging data on rigid-rod polyquinoline **23b**.

history of other polyquinolines has been described.[18] The values for T_g determined by Rheovibron for polymers **23**, **24**, and **25** in most cases were substantially higher than those obtained by DSC; these results are not uncommon[18] and are probably due to a higher degree of crystallinity and/or orientation in the film.

Polymers **22a–c** exhibited crystalline transition temperatures by DSC ranging from 520 to 580 °C, whereas with polymers **23** and **24** only **23b** and **23c** exhibited T_m's. Polymers **23a** and **23d** probably undergo decomposition before the crystalline transitions occur, since powder samples of **23a** and **23c** had a higher degree of crystallinity than **23b**, which had an observable T_m. None of the polymers containing ether links exhibited crystalline transition temperatures.

Thermal Stabilities. These polyquinolines showed excellent thermal and thermooxidative stabilities in nitrogen and air atmospheres (Tables I–III). Thermogravimetric analysis (TGA) showed weight losses occurring between 520 and 605 °C in air and between 540 and 610 °C in a nitrogen atmosphere, with 15–30% weight loss at 800 °C in a nitrogen atmosphere. This type of thermal stability is typical of all polyquinolines.[3,4] Rigid-rod polyquinoline **23b**, however, showed only a 15% weight loss at 371 °C after 100 h (Figure 4), whereas the flexible ether-containing polyquinoline had shown a 48% weight loss after 100 h.[2]

Solution Properties. The following criteria must be met in order to attain a high degree of orientation in solution (anisotropic solutions): (1) The polymer must take on a rigid or extended-chain conformation in solution. (2) The polymer must exceed some minimum molecular weight (increasing the concentration may compensate to some degree for a lower molecular weight). (3) The polymer must be sufficiently soluble to exceed a critical concentration which is dependent on the axial ratio of the polymer.[19,20]

Polymer **23b** was selected for solution studies because of its rodlike characteristics, high molecular weight, and good solubility.

Polymer solutions were obtained by heating the polymer at 135 °C in a solution of m-cresol/di-m-cresyl phosphate (5:1 molar ratio) for 3–4 h, after which time no undissolved polymer was detected by microscopy. Polymer solutions of 2–7% (w/v) when examined under a microscope were found to be completely isotropic by the lack of depolarization of plane-polarized light. Flow birefringence was observed under shear, however. The clear reddish brown solution continued to get very viscous and gellike as more polymer was added. At approximately 9%, as the solution was cooled, it became gold in color and appeared turbid. To avoid orientation due to shear, a thin film of the so-

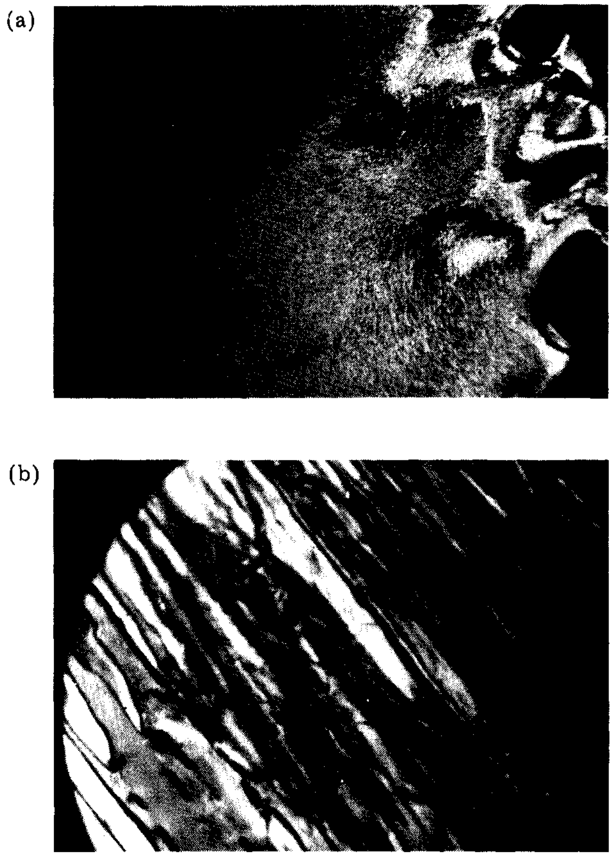


Figure 5. A 9% solution of **23b** at rest (a) and under shear (b) as viewed through crossed polarizers at 240× magnification.

lution was first heated between a microscope slide and cover glass to approximately 135 °C, during which time the solution again became clear, and was then allowed to cool to room temperature. Samples prepared in this manner were highly birefringent and appeared to be completely anisotropic at rest (Figure 5a). The turbid solution also exhibited complete boundary mobility under shear, thus indicating the absence of undissolved material (Figure 5b). Solutions of 18.5% (w/w) were obtained, but no noticeable drop in bulk viscosity up to this concentration was noted. A detailed study of the solution properties of **23b** is currently under way and will be reported separately.

The polymerization dopes (~1.5% solids) of polymers **22b** and **22c** also exhibited flow birefringence as described for **23b**. Polymer **22b** showed a small amount of birefringence at rest at 1.5% solids (Figure 6). The polymerization dope of **22b**, however, solidified on standing.

Films and Fibers. Clear tough light yellow or orange flexible films of polymers **22b,c**, **23a,b**, and **24a** could be cast directly from the polymerization dope (0.5–1.5% solids). Polymer dopes of **23c** and **24b** produced tough flexible translucent films while polymer **23d** gave thin weak inhomogeneous films due to the insolubility of the higher molecular weight polymer. Polymer **22a** afforded brittle films characteristic of a lower molecular weight polymer. Flexible polymers **25c** and **25d** gave opaque white films from the polymerization dope, which appeared to contain microvoids. Polymers **25a** and **25b** did not give suitable films from the polymerization dope; however, clear yellow flexible films of **25a** could be obtained from *m*-cresol. The polymerization dopes used for casting films were isotropic and the properties characteristic of anisotropic solutions were not observed during slow evaporation of the *m*-cresol. After extraction and drying, however, the rigid-rod polymer films showed birefringence and retention of a high percentage of their mechanical properties above T_g, typical of crystalline and/or oriented polymers.

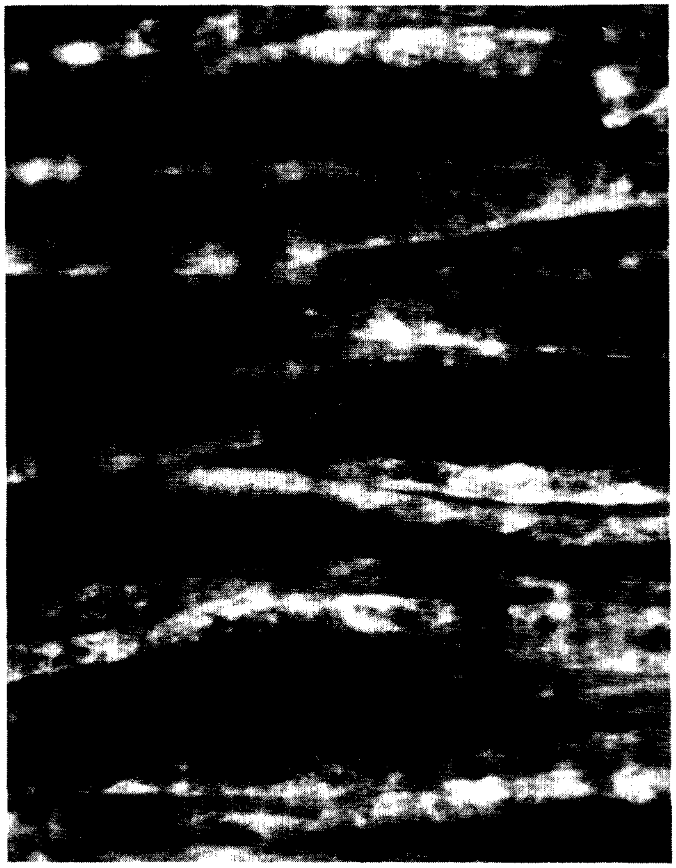


Figure 6. A 1.5% solution of **22b** at rest as viewed through crossed polarizers at 160× magnification.

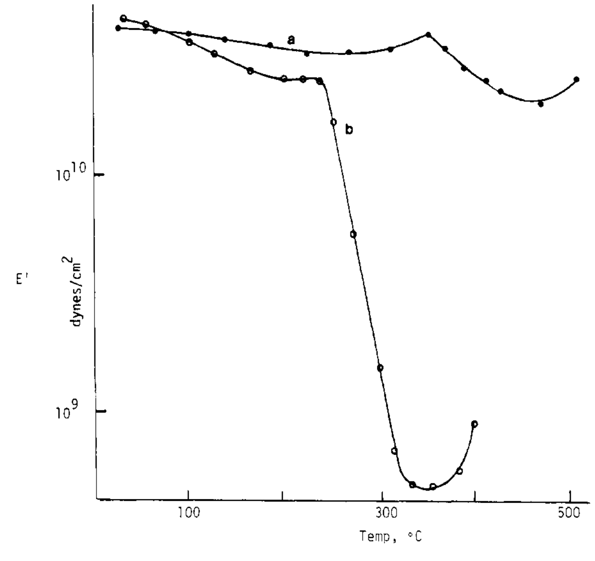


Figure 7. Dynamic storage modulus as a function of temperature for rigid-rod polymer **23a** vs. flexible amorphous polymer **25a**.

The drop in dynamic modulus (E') when the T_g is traversed has been correlated with the degree of crystallinity in polymer films.[21,22] The difference in the thermomechanical properties of a film of a rigid-rod polymer and an amorphous flexible polymer is evident from a plot of the dynamic storage modulus vs. temperature (Figure 7). Other rigid- and semirigid-rod polyquinolines behave similarly (Table IV). Polymers **23a–d** when precipitated from the reaction dope, however, exhibited low to little or no crystallinity by X-ray analysis. By contrast, polymer

Table IV
Dynamic Thermomechanical Properties of Polyquinolines

polymer[a]	E',[b] dyn/cm^2	E',[c] dyn/cm^2
22b	4.2×10^{10}	3.6×10^{9} (480)
22c	3.1×10^{10}	5.2×10^{9} (355)
23a	4.2×10^{10}	1.9×10^{10} (425)
23b	3.9×10^{10}	1.8×10^{9} (440)
23c	2.5×10^{10}	4.2×10^{9} (442)
24a	2.5×10^{10}	1.9×10^{9} (502)
24b	1.7×10^{10}	1.8×10^{9} (515)
25a	5.5×10^{10}	4.2×10^{8} (428)
25c	3.7×10^{9}[d]	9.7×10^{7} (376)
25d	8.4×10^{9}[d]	2.0×10^{8} (427)

[a] Suitable films of **22a**, **23d**, and **25b** could not be obtained. [b] At 25 °C. [c] Temperature in parentheses. [d] These lower values are probably due to poor film quality.

22b that had been precipitated from the polymerization solution in powder form or wet spun from the polymerization medium possessed a high degree of crystallinity in both the polymer precipitated from solution (Figure 8) and fiber samples. It appears then that in the process of casting the films and/or the treatment of the film under conditions (heat and mild stress) necessary to measure the dynamic storage modulus, crystallization is induced to the degree that the properties above T_g of **23a–c** are comparable to those of highly crystalline **22b**.

The success of the preparation of high-strength/high-modulus fibers from rigid-rod polymers has been credited to the ability of solutions of these polymers to form a high degree of orientation of the extended polymer chains along the long fiber axis before coagulation. Maximum tensile properties have been achieved by using high polymer concentrations of anisotropic spin dopes and elongational flow after the spinneret but before coagulation. Although fibers spun in this manner have shown good tensile properties as spun, normally the modulus and tenacity can be greatly improved by further thermal treatment.

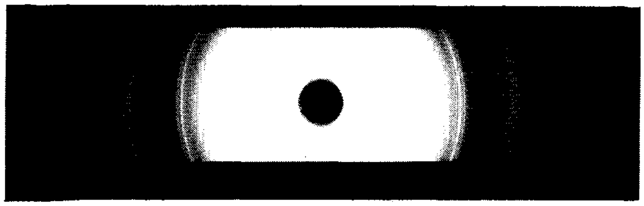


Figure 8. X-ray diffraction pattern for powder samples of **22b**.

Fortuitously, the best solvent for the wet spinning of rigid-rod polyquinolines was the polymerization medium. Fibers were wet spun directly from the polymerization dopes (~1.5–2.3% solids) of **22b,c**, **23a–d**, and **24a** into an ethanol/triethylamine bath via a syringe. Unfortunately, although fibers prepared in this manner exhibited birefringence characteristic of orientation, they possessed relatively low tensile properties and high elongations to break (Table V). The removal of the needle from the coagulation bath caused the fiber to break in the air gap.

Polymer **23b** was also dry-jet wet spun from anisotropic solutions with orifice diameters of 270 and 5 mils. Elongational flow of the free-falling fiber was crudely controlled by the distance of the orifice from the nonsolvent and the rate of extrusion. As expected, the tensile properties of the "as-spun" fibers were improved by using a 9% (w/w) anisotropic spin dope with an air gap. Although elongational flow could not be controlled accurately without careful control of extrusion rates and takeup spools, an increase in the tensile properties was noted with a longer air gap (Table V). The use of an 18.5% (w/w) anisotropic spin dope with a 63.0-cm air gap also showed an increase in the fiber tensile properties over the corresponding fibers from the 9.0% anisotropic solution. Fibers spun with an 81.5-cm air gap and an 18.5% anisotropic solution exhibited a dramatic increase in the tensile properties for the "as-spun" fibers (Table V). The large difference in tenacities for the different air gaps indicates the importance

Table V
Fiber Properties of Rigid-Rod Polyquinolines

polymer	spinning dope[a]	spinning conditions[b]	heat treatment[c]	denier, g (Tex)	tenacity, g/d (N/T)	elongation to break, %	modulus, g/d (N/T)	toughness, g/d (N/T)
22a	I (1.5)	N	50/120/1 min	51 (5.7)	4.4 (0.39)	23	100 (9.2)	0.73 (0.065)
23a	I (0.5–1.0)	N	as spun	190 (21)	0.84 (0.074)	47	17 (1.5)	0.34 (0.030)
23a	I (0.5–1.0)	N	25/120/30 s	160 (17)	1.2 (0.11)	29	35 (3.1)	0.23 (0.025)
23b	I (0.5–1.0)	N	as spun	360 (40)	1.5 (0.13)	115	11 (0.94)	1.1 (0.098)
23b	I (0.5–1.0)	N	25/120/30 s	300 (34)	1.8 (0.16)	41	52 (4.5)	0.58 (0.051)
23b	A (9)	G (21.5)	as spun	500 (55)	2.7 (0.23)	20	47 (4.2)	0.28 (0.024)
23b	A (9)	G (21.5)	100/380/1 h	350 (39)	4.2 (0.37)	2.2	170 (15)	0.046 (0.0041)
23b	A (9)	G (63.0)	as spun	350 (39)	3.8 (0.34)	12	98 (8.7)	0.29 (0.026)
23b	A (9)	G (63.0)	100/380/1 h	240 (27)	6.8 (0.60)	2.6	280 (25)	0.093 (0.0082)
23b	A (18.5)	G (63.0)	as spun	27 (3.0)	4.8 (0.42)	5.4	150 (13)	0.15 (0.0013)
23b	A (18.5)	G (63.0)	10/380/1 h	27 (3.0)	4.6 (0.41)	1.8	260 (23)	0.04 (0.0039)
23b	A (18.5)	G (81.5)	as spun	25 (2.8)	8.5 (0.75)	7.7	160 (14)	0.34 (0.0030)
23b	A (18.5)	G (81.5)	20/380/1 h	23 (2.6)	9.0 (0.79)	2.5 (0.11)	340 (30.2)	0.11 (0.0098)

[a] A, dope exhibited anisotropic behavior at this concentration; I, dope exhibited isotropic behavior at this concentration. Numbers in parentheses indicate concentration of polymer in spinning dope (% w/w). [b] N, orifice was immersed in the nonsolvent bath; G, orifice was above the bath and fiber was allowed to free fall. Numbers in parentheses indicate the distance in cm between the orifice and the nonsolvent. [c] Weight used for drawing in grams/temperature (°C)/time.

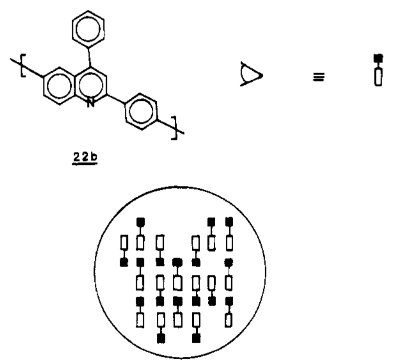


Figure 9. Polymer chain ordering in the crystalline regions of polymer 22b.

of the elongational flow on the fiber properties. Significant improvement in tenacities and dramatic improvements in the moduli were observed by drawing the fibers at elevated temperatures (Table V). Fibers obtained from heat treatment of fibers from the 18.5% spin dope and 63.0-cm air gap showed a slight decrease in the tensile properties. These results are probably due to imperfections in the fibers, since large deviations in the properties were noted: T/E/M, 2.9–6.0 gpd/1.6–2.1%/230–300 gpd.

Although the tensile properties are still somewhat lower than expected, improvement probably could be realized by careful control of elongational flow and by improved heat treatment conditions.

A fiber of **22b** which had been annealed at 430 °C for 3.5 h showed sharp diffraction lines due to crystalline regions at *d* spacings of 10.23, 10.30, and 10.31 Å. From X-ray analysis the chains of polymer **22b** are believed to be ordered in the crystalline regions as shown schematically in Figure 9. The pendant phenyl rings are depicted as closed boxes and the quinoline ring as an open box. The picture drawn is what would be seen when the fiber is viewed collinear with its long fiber axis. X-ray studies on fibers of **23b** are in progress and will be reported separately.

Although rigid-rod polymers **22**, **23**, and **24** have very limited solubilities and high transition temperatures, they can be fabricated into films and fibers from the polymerization medium. These polymers not only exhibit excellent thermooxidative properties but also show a high retention of their mechanical properties above T_g. Thus, their use temperature is only limited by the T_m and PDT (≤500 °C).

Experimental Section

4-Nitro-4′-acetylbiphenyl (2). To an ice-cooled solution of 125 g (0.940 mol) of anhydrous aluminum chloride and 170 g (0.850 mol) of *p*-nitrobiphenyl in 700 mL of dry nitrobenzene was added dropwise 73.8 g (0.940 mol) of freshly distilled acetyl chloride. The red solution was then stirred for 17 h at room temperature and for 24 h at 50 °C. The resultant dark brown solution was poured onto a mixture of ice and concentrated hydrochloric acid. The organic layer was separated and the nitrobenzene was removed by steam distillation. The dark brown solid obtained was continuously extracted for 72 h with 3 L of ethanol. The ethanol solution was then allowed to cool to room temperature and 122 g of a dark yellow powder was obtained. After two recrystallizations from acetone followed by one recrystallization from ethanol, 80 g (40%) of gold fibrous needles was obtained: mp 155–156 °C (lit.[5] mp 153–154 °C). Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81. Found: C, 69.54; H, 4.51; N, 5.72.

4-Nitro-4′-(2-methyl-1,3-dioxolan-2-yl)biphenyl (3). A rapidly stirred solution of 225 g (0.933 mol) of **2**, 164 mL (2.94 mol) of ethylene glycol, and 1.5 g (8.9 mmol) of *p*-toluenesulfonic acid in 1.4 L of toluene was heated at reflux for 44 h in a 5-L flask equipped with a Dean–Stark trap. The brown solution was diluted with 5.5 L of toluene and washed three times with 300 mL of a 10% aqueous sodium hydroxide solution and once with 700 mL of water. The toluene solution was concentrated to one-third of its original volume and allowed to cool. The yellow crystals obtained were collected by filtration and the filtrate was concentrated to afford additional product. A total of 230 g (87%) of yellow crystals were obtained: mp 146.0–146.5 °C; IR (KBr) 1500, 1330 (NO_2), absence of 1675 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6 (s, 3 H), 3.88 (A_2B_2, 4 H), 7.86 (dd, 8 H). Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.24; H, 5.22; N, 4.74.

5-[*p*-(2-Methyl-1,3-dioxolan-2-yl)phenyl]-3-phenyl-2,1-benzisoxazole (4). A total of 181 g (4.53 mol) of powdered sodium hydroxide was added to 1035 mL of methanol and the rapidly stirring mixture was allowed to cool to room temperature. To this solution were added 212 g (218 mL, 1.81 mol) of benzyl cyanide and 259 g (0.908 mol) of **3** along with 520 mL of tetrahydrofuran. The green mixture was stirred at room temperature for 1 h and then for 24 h at 65 °C. After the resulting mixture was cooled in ice, 900 mL of water was added and the orange powder was collected by filtration. The powder was washed well with water and then with methanol until the washings were clear, leaving 290 g (89%) of **4** as fine yellow needles: mp 135 °C; IR (KBr) 1620 (C=N), absence of 1500, 1330 (NO_2) cm^{-1}. Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.48; H, 4.38; N, 3.81.

4-Amino-3-benzoyl-4′-(2-methyl-1,3-dioxolan-2-yl)biphenyl (5). To a solution of 290 g (0.811 mol) of **4** in 2.9 L of tetrahydrofuran and 95 mL of triethylamine was added 27.1 g of 5% palladium on carbon. The vigorously stirred suspension was flushed with hydrogen and stirred at room temperature under 1 atm of hydrogen until the absorption of hydrogen ceased. The catalyst was removed by filtration through a bed of Celite and the solvent was removed under reduced pressure to afford yellow crystals. Recrystallization from 5:1 ethanol/tetrahydrofuran afforded 260 g (89.2%) of gold-colored crystals melting at 161–162 °C: IR (KBr) 3450 and 3330 (NH_2), 1620 (C=O) cm^{-1}. Anal. Calcd for $C_{23}H_{21}NO_3$: C, 76.86; H, 5.89; N, 3.90. Found: C, 76.69; H, 5.97; N, 3.71.

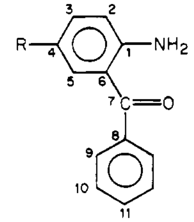
4-Amino-4′-acetyl-3-benzoylbiphenyl (1). A solution of 265 g (0.736 mol) of **5** in 2.5 L of tetrahydrofuran and 1 L of 0.6 N hydrochloric acid was stirred at room temperature for 6 h and then 1 L of water was added. The tetrahydrofuran was removed under reduced pressure, at which time a yellow precipitate formed in the water layer. The yellow precipitate was collected by filtration and washed with water until the washings were no longer acidic. The precipitate was then dissolved in chloroform and washed with a 10% aqueous sodium bicarbonate solution followed by water. The chloroform was removed by distillation, affording 230 g (99.1%) of bright yellow crystals. After one recrystallization from carbon tetrachloride, 190 g (81.8%) of pure **1** was obtained: mp 142–143 °C; IR (KBr) 3450, 3300 (NH_2), 1670 ($CH_3C{=}O$), 1620 (PhC=O) cm^{-1}; ^1H NMR (Me_2SO) δ 2.58 (s, 3 H), 3.44 (s, 2 H), 6.9–8.0 (m, 12 H); see Table VI for ^{13}C NMR data. Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44. Found: C, 80.00; H, 5.44; N, 4.36.

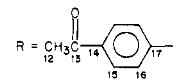
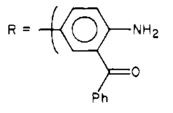
3-Phenyl-5-bromo-2,1-benzisoxazole (7). To a stirred solution of 148 g (2.27 mol) of potassium hydroxide in 300 mL of methanol at ice bath temperature was added 16.7 mL (0.126 mol) of phenylacetonitrile. To the colorless solution was added a solution of 25.4 g (0.126 mol) of *p*-bromonitrobenzene in 100 mL of tetrahydrofuran and 200 mL of methanol, at which time the solution turned dark purple. After 4.5 h at ice bath temperature the reaction mixture was precipitated into 1 L of water and the gold-colored needles were isolated by suction filtration to afford 29 g (86%) of **7**: mp 108–111 °C. Recrystallization from methanol afforded 20.5 g (59.4%) of **7**: mp 117.5–118.2 °C (lit.[8] mp 116–118 °C).

2-Amino-5-bromobenzophenone (8). Following a procedure for reduction of 5-chloro-3-(*p*-methoxyphenyl)-2,1-benzisoxazole[8] with iron and acetic acid, **7** was reduced and purified through the amine hydrochloride to afford 35 g (90%) of **8**: mp 110.0–112.0 °C (lit.[24] mp 110 °C).

Bis(1,5-cyclooctadiene)nickel(0). Bis(1,5-cyclooctadiene)nickel(0) was prepared according to the published procedure[25] and was used without further purification.

Table VI
Carbon-13 Shifts for Monomers 5 and 6



				
carbon	calcd[a]	obsd	calcd[a]	obsd
1	147.0	151.1	147.0	149.3
2	115.4	117.7	115.4	117.3
3	131.9	131.5	131.9	131.9
4	131.6	126.6	131.6	130.9
5	130.0	*c*	130.0	128.9
6	125.0	118.1	125.0	118.1
7		*b*		198.4
8	137.9	139.7	137.9	139.6
9	130.2	*c*	130.9	127.8
10	128.3	128.2	128.3	127.6
11	132.1	134.8	132.1	131.4
12	30.0	26.5		
13		*b*		
14	136.4	134.9		
15	129.0	129.0		
16	127.4	125.8		
17	145.8	144.7		

[a] Chemical shift values calculated on the basis of the additivity of the chemical shift parameters based on monosubstituted benzene as outlined in ref 23. [b] Two carbonyl peaks were observed at 197.5 and 198.7 ppm. [c] These two carbons were not resolved; only one peak was observed at 129.2 ppm.

3,3′-Dibenzoylbenzidine (6). To a stirred slurry of 22.5 g (81.5 mmol) of bis(1,5-cyclooctadiene)nickel(0)[25] in 200 mL of dry oxygen-free DMF under an argon atmosphere was added via syringe a solution of 15 g (54 mmol) of **8** in 150 mL of dry oxygen-free DMF. The slurry was stirred for 15 min at 25 °C and then heated to 42 °C for 90 h, after which time the slurry was cooled and poured into 500 mL of 2% hydrochloric acid. The aqueous mixture was extracted with methylene chloride. The organic phase was filtered to remove the nickel salts, washed with water, and dried with magnesium sulfate, and the solvent was removed under reduced pressure. The crude product was coated onto silica gel (1 g/5 g of SiO_2), placed onto a dry column (1 g of crude product/70 g of silica gel), and eluted with 2% ethyl acetate in methylene chloride. Recrystallization from benzene afforded 5 g (50%) of **6** as yellow crystals: mp 195.0–196.0 °C (lit.[6,7] mp 198 °C); IR (KBr) 3460, 3340 (NH_2), 1635 (*o*-amino C═O) cm^{-1}; see Table VI for ^{13}C NMR data. Anal. Calcd for $C_{26}H_{20}N_2O_2$: C, 79.57; H, 5.14; N, 7.14. Found: C, 79.67; H, 5.23; N, 7.19.

***p*-Bromophenacetylbenzene (10).** A mixture of 10 g (65 mmol) of phenacetyl chloride, 9.5 g (71 mmol) of aluminum chloride, and 150 mL of bromobenzene was stirred at room temperature for 9 h while nitrogen was bubbled through the mixture.[11,12] The reaction mixture was poured onto a mixture of crushed ice and concentrated hydrochloric acid. The organic layer was separated and washed three times with 3 N sodium hydroxide and twice with water. The excess bromobenzene was removed in vacuo and the resultant product was recrystallized several times from a solution of 90% ethanol–10% water to afford 4.9 g (27%) of **10** as white crystals: mp 113.5–114.0 °C; ^1H NMR ($CDCl_3$) δ 4.16 (s, 2, $PhCH_2$), 6.9–7.9 (m, 9, aromatic); ^{13}C NMR ($CDCl_3$) (calcd) δ 45.5 (51.6), 126.9 (125.6), 128.1 (126.6), 128.6 (128.4), 129.2 (129.2), 130.0 (131.7), 131.8 (131.9), 134.0 (136.3), 135.2 (137.4), 196.2. Anal. Calcd for $C_{14}H_{11}BrO$: C, 61.11; H, 4.03; Br, 29.04. Found: C, 61.59; H, 4.06; Br, 29.11.

4,4′-Diphenacetylbiphenyl (9). Under an argon atmosphere 7.0 g (25 mmol) of bis(1,5-cyclooctadiene)nickel(0), 6.88 g (25.0 mmol) of **10**, and 100 mL of dry oxygen-free DMF were mixed and stirred at 42 °C for 30 h. The reaction mixture was poured into 3% hydrochloric acid solution, filtered, and washed with a saturated sodium bicarbonate solution followed by ether. The product was then extracted from the undissolved nickel in a Soxhlet extractor with methylene chloride. Two recrystallizations from methylene chloride afforded 1.8 g (37%) of **9** as small white platelets: mp 232.0–233.5 °C (lit.[10] mp 226–227 °C). A second crop afforded 1.8 g (73% total) of **9**.

4-Acetyl-4′-bromobiphenyl (12). Acylation of 4-bromobiphenyl with acetyl chloride and aluminum chloride[13] followed by column chromatography (SiO_2) and recrystallization from carbon tetrachloride gave **12** as white crystals: mp 128.5–130.0 °C (lit.[13] mp 131 °C); IR (KBr) 1680 (C═O), 815 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.6 (s, 3 H), 7.1–8.0 (m, 8 H); ^{13}C NMR ($CDCl_3$) (calcd) δ 26.2 (29.5), 122.4 (121.8), 131.8 (132.3), 128.7 (129.1), 138.4 (140.0), 144.2 (145.8), 126.8 (127.4), 128.5 (129.0), 135.8 (136.4), 197.2. Anal. Calcd for $C_{14}H_{11}BrO$: C, 61.11; H, 4.03; Br, 29.04. Found: C, 60.84; H, 3.75; Br, 29.11.

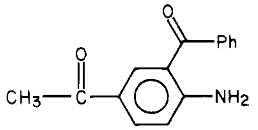
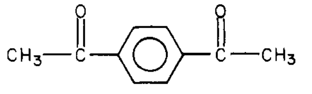
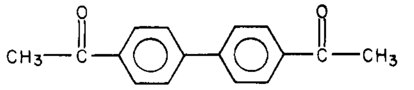
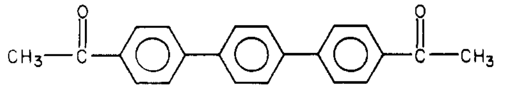
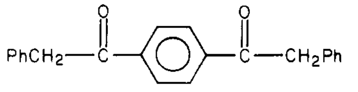
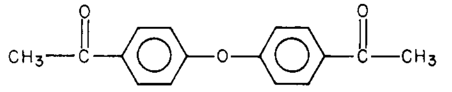
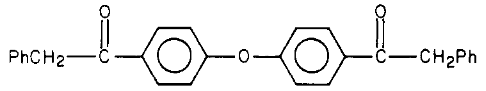
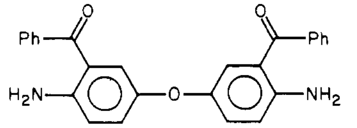
4,4‴-Diacetylquaterphenyl (11). To a stirred slurry of 5.6 g (20 mmol) of bis(1,5-cyclooctadiene)nickel(0)[25] in 60 mL of dry oxygen-free DMF under an argon atmosphere was added a solution of 7.0 g (26 mmol) of 4-acetyl-4′-bromobiphenyl (**12**) in 40 mL of DMF. After 15 min of stirring at 25 °C, the temperature was raised to 42 °C and maintained for 67 h. The mixture was cooled and poured into 100 mL of 3% hydrochloric acid and stirred for 5 min. The gray solid was removed by suction filtration and washed with 3% hydrochloric acid, water, and ether. Two recrystallizations from DMF afforded 2.3 g (45%) of **11** as off-white platelets: mp 347.5–349.0 °C; IR (KBr) 1680, 1270, 810 cm^{-1}. A suitable solvent was not found for NMR due to the low solubility. Anal. Calcd for $C_{28}H_{22}O_2$: C, 86.13; H, 5.68. Found: C, 85.39; H, 5.59.

Other Monomers (14–21). A list of the other monomers used in the polymerizations is given in Table VII.

Polymerizations. The synthesis of poly[2,6-(*p*-phenylene)-4-phenylquinoline] (**22b**) is given below as a general procedure for the polymerization of the remaining AB monomers. To a resin flask were added 3.1537 g (10.000 mmol) of 4-amino-4′-acetyl-3-benzoylbiphenyl, 33 g (12 mmol) of di-*m*-cresyl phosphate,[14] and 11 mL of freshly distilled *m*-cresol. The resin flask was purged with nitrogen and the solution was stirred for 24 h under a static nitrogen atmosphere at 140 °C. A total of 111 mL of additional *m*-cresol was added in portions during the 24 h to keep the solution viscosity low enough to permit efficient stirring of the reaction. The deep red polymerization solution was slowly poured into a stirred solution of 1.8 L of ethanol and 200 mL of triethylamine. The resultant yellow fibrous powder was chopped in a blender, continuously extracted with a solution of ethanol and triethylamine for 24 h, and dried at 115 °C under reduced pressure for 21 h to afford yellow fibrous polymer (see Table VIII for elemental analyses).

The preparation of poly[2,2′-(*p*,*p*′-biphenyl)-6,6′-bis(4-phenylquinoline)] (**23b**) is given below as a general procedure for the polymerization of the AA and BB monomers. To a resin flask were added 3.000 g (7.6440 mmol) of **6**, 1.8215 g (7.6440 mmol) of **16**, 51.1 g (184 mmol) of di-*m*-cresyl phosphate, and 17 mL of *m*-cresol. The resin flask was purged with nitrogen and the solution was stirred for 48 h at 140 °C under a static nitrogen atmosphere. A total of 100 mL of additional *m*-cresol was added in 10-mL portions during the 48 h to ensure efficient stirring. The resultant polymerization dope was worked up as previously described (see Table VIII for elemental analyses). Films were obtained from the polymerization dope by the following procedure. The polymerization dope was poured directly from the reaction flask onto a glass plate and was smoothed with a doctor's knife. The polymer-coated glass plate was then heated at 95 °C for 5–6 h in a vacuum oven and then allowed to cool to room temperature, after which time it was placed in a 10% solution of triethylamine in ethanol to release the film from the plate and extract the remaining di-*m*-cresol phosphate from the polymer. After 10–12 h the film was removed from the solution, clamped between two glass plates, and dried at 95 °C for 7–8 h in vacuo.

Table VII
Miscellaneous Monomers 14-21

monomer		mp, °C (lit. mp, °C)	ref
14		softened at 160.5 °C 162.0-163.5 (159.0-161.0)	2
15		113.0-114.5 (114)	*a*, 26
16		195.0-196.0 (190-191)	27
17		283.0-284.0 (268.0-269.0)	28
18		178.5-181.5 (172-174)	29
19		102.0-103.0 (102-103)	30
20		173.0-174.0 (169-170)	2, 10
21		(157.5-158.5)	2, 31

[a] Monomer 15 was obtained from Aldrich Chemical Co.

Table VIII
Elemental Analyses of Polyquinolines

	calcd			found			
polymer	% C	% H	% N	% C	% H	% N	residue
22b	90.30	4.69	5.01	88.86	4.87	4.72	0.00
22c	89.60	4.59	5.80	88.02	4.89	5.80	0.00
23a	89.60	4.59	5.80	88.92	4.73	5.84	0.21
23b	90.30	4.69	5.01	89.45	4.86	5.04	0.16
23c	90.82	4.76	4.41	89.62	4.70	4.36	0.29
23d	91.24	4.82	3.94	90.21	4.84	4.19	<0.10
24a	90.82	4.76	4.41	89.02	4.63	4.37	0.30
24b	91.24	4.82	3.94	89.73	4.90	3.73	0.77
25a	87.77	4.57	4.88	87.80	4.80	4.83	0.00
25b	89.23	4.71	3.85	88.49	4.78	3.87	0.33
25c	88.59	4.65	4.30	86.99	4.64	4.19	0.62
25d	89.23	4.71	3.85	88.72	4.76	3.80	0.14

Isotropic solutions of polymers **22b,c**, **23**, and **24a** were wet spun directly from the polymerization medium by the following method. The hot polymerization dope (135 °C) was poured into a 10-mL Ideal Vaco metal plunger veterinary syringe (ID 123) equipped with a $^3/_4$-in, 22- or 25-ga needle. The syringe was then mounted in a hand-crank device and the dope was spun into an ethanol/triethylamine bath. The fiber was allowed to fall to the bottom without tension. After soaking for at least 24 h the fibers were dried at ambient temperatures with a ~0.5-g weight attached (as-spun fibers) or in an oven at 120 °C with a 25-g weight attached. Tensile properties for fibers of polymers **22b** and **23a,b** are given in Table V. Fibers failed to form when the needle was removed from the nonsolvent.

The preparation of anisotropic solution **23b** and the jet-dry wet spinning of these solutions were conducted as follows.

To a 25-mL flask containing a nitrogen inlet and a mechanical stirrer was added 1.058 g of **23b**. The flask was flushed with nitrogen and 5.68 g of a solution of 3.69 g of *m*-cresol and 1.99 g of di-*m*-cresyl phosphate was added. The flask was heated to 135 °C under a static nitrogen atmosphere, and the mixture was stirred occasionally by hand. After 3-4 h solution was complete. On cooling to room temperature, the solution was extremely viscous and appeared turbid. On examination of the gold-colored solution under a microscope, no undissolved particles could be detected.

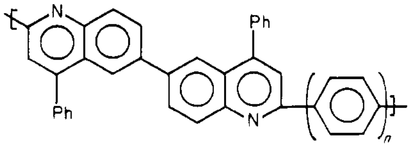
A Greeneid Arbor sodium press was modified for the jet-dry wet spinning experiments. The sodium die apparatus was fitted with a staninless steel airtight plunger. Two dies were also made containing orifice diameters of 5 or 270 mils.

An anisotropic solution of 9% (w/w) of **23b** at ambient temperature, which was prepared as described above, was placed in the die assembly (equipped with a 270-mil orifice) and mounted in the press. The spinning dope was then extruded from the spinning apparatus and into an ethanol/triethylamine bath. The polymer solution was bright gold in the air gap before entering the coagulation bath. Air gap distances of 21.5 and 63.0 cm were used. The elongational flow was dependent on the air gap distance and the rate of extrusion. At very low extrusion rates, however, the forming fiber would break in the air gap. The fibers were allowed to soak in the ethanol/triethylamine bath for 24 h, after which time they were dried at ambient temperature with a ~0.5-g weight attached for 24 h to afford the "as-spun" fibers.

Fiber samples were heat treated above T_g to increase the tensile properties by the following procedure. A fiber of approximately 6 cm with a 100-g weight attached to one end was suspended in a glass tube under a static argon atmosphere. The tube was then heated in a preheated oven to 380 ± 5 °C for 1 h. After the tube cooled, fibers from both 21.5- and 63.0-cm air gaps exhibited draw ratios of 1.1 and enhanced tensile properties (Table V).

Anisotropic solutions of 18.5% (w/w) of **23b** were also jet-dry wet spun, using a 5-mil orifice and air gap distances of 63.0 and 81.5 cm. Heat treatment of the fibers was accomplished as above with a 10- and 20-g weights for fiber samples obtained from a 63.0- and 81.5-cm air gaps, respectively. Draw ratios of 1.0-1.1 were

Table IX
X-ray Data on Powder Samples of Polyquinolines **23**[a]



polymer	n	d spacing,[a] Å	impurity spacing, Å
23a	1	4.9 (h), 5, 34 (m)	
23b	2	4.9 (h)	
23c	3	4.9 (m), 6.0 (m)	
24d	4	4.9 (m), 4.9 (h)	3.39 (s)

[a] s = sharp diffraction ring, m = medium sharp diffraction ring, h = halo diffraction ring.

obtained. Tensile properties of the "as-spun" and heat-treated fibers are listed in Table V.

Polymer Properties. Viscosity measurements of the polymers were determined in *sym*-TCE, *m*-cresol, concentrated sulfuric acid, or trifluoromethanesulfonic acid at 25.0 ● 0.2 °C, using a Cannon-Ubbelohde viscometer. The intrinsic viscosity was obtained from the intersection of plots of η_{inh} vs. C and η_{red} vs. C.

Thermal analyses were conducted with a Du Pont 990 differential thermal analyzer equipped with a differential scanning calorimeter (DSC) cell base module II and a 950 thermogravimetric analyzer (TGA). The DSC analyses were obtained on pressed powder samples (10 °C/min) that had first been heated at 50 °C/min under a flowing nitrogen atmosphere to 450 °C and then quenched with liquid nitrogen. Thermogravimetric analyses were obtained with a heating rate of 50 °C/min on pressed powder samples in both flowing air and nitrogen atmospheres.

Dynamic thermomechanical analyses were obtained on film specimens with a Rheovibron (Model DDV-II-C) as described previously.[4] A frequency of 35 Hz was used with an approximate heating rate of 5–10 °C/min in a flowing nitrogen atmosphere.

X-ray diffraction patterns were carried out by Dr. J. B. Lando and D. R. Day, Department of Macromolecular Science, Case Western Reserve University, on powder samples of **23a–d** (Table IX) and fibers of **22b**, using a Statton powder camera with Cu Kα radiation. X-ray data on powder samples of **22b** were carried out by Dr. N. Baenziger, University of Iowa, using a Debye-Scherrer powder camera with Cu Kα radiation.

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Synthesis of (*R*)-Cyclohexylmethyl-*p*-styrylphosphine and the Preparation of Polymer-Bound Optically Active Phosphines

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ABSTRACT: Synthesis of (*R*)-cyclohexylmethyl-*p*-styrylphosphine (**1**) was accomplished through the resolution of (S_P)-menthyl methyl-*p*-tolylphosphinate (**2a**). The free radical copolymerization of **1** with hydroxyethyl methacrylate and ethylene dimethacrylate afforded cross-linked polymer **14** containing ~0.42 mequiv of optically active monophosphine per gram of polymer. Optically active phosphines such as this polymer-bound cyclohexylmethylphenylphosphine can be used as ligands for rhodium-catalyzed asymmetric syntheses.

Introduction

The use of polymer-bound catalysts for effecting organic reactions has progressed to a point such that the capabilities of the method and the limitations—at least with the present catalytic systems and supports—have been recognized. The unique features and advantages of binding a homogeneous transition-metal complex to an insoluble polymer are evident.[1] When the catalytic reaction is an

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