Sample no. 2 was then dissolved in 350 ml of chloroform and the original procedure followed to give three samples of decreasing molecular weight. These three samples were used for measurement of the osmotic pressure of polymer 13a as a function of concentration and molecular weight.

Molecular Weight Determination. The molecular weights in Table III were obtained with a Hewlett-Packard high-speed membrane osmometer using a cellophane superdense membrane at 20 °C in chloroform. The concentrations of the solutions ranged from 9.12 to 1.0 g/l.

Thermogravimetric Analysis. The thermal stability of **13a** was measured on a Du Pont 950 thermogravimetric analyzer by heating continuously weighed polymer films in air at 300 and 360 °C for 100 h (Figure 2) and by heating continuously weighed polymer films in both air and nitrogen from 25 to 800 °C at a rate of 5 °C/min (Figure 3).

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Synthesis and Solution Properties of Phenylated Polyquinolines. Utilization of the Friedländer Reaction for the Synthesis of Aromatic Polymers Containing 2,6-Quinoline Units in the Main Chain

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ABSTRACT: The condensation of 4,4'-diamino-3,3'-dibenzoyldiphenyl ether with a series of diacetyl and bis(phenylacetyl) aromatic monomers afforded a series of new high molecular weight polyquinolines. The polymers were prepared in solvents consisting of a premixed solution of *m*-cresol and either polyphosphoric acid or phosphorus pentoxide and, after isolation, were soluble in phenolic and chlorinated hydrocarbon solvents, although the polymers tended to crystallize from the latter solvents. Clear, tough, flexible films could be cast from 15–30 wt % solutions, and all the polymers showed outstanding thermal and oxidative stability.

Polyquinoxalines (1, R = H) and polyphenylquinoxalines^{1,2} (1, $R = C_6H_5$) which show excellent thermal and oxidative stability as determined by isothermal aging, are totally amorphous. This is due, in part, to the random geometrical arrangement with respect to the catenation at the quinoxaline



ring which is a result of the ring-forming polymerization reaction. Both the polyquinoxalines and polyphenylquinoxalines have glass transition temperatures ranging from 195 to 325 °C, well below the decomposition temperature of the polymers (550-570 °C). Thus, the use temperature of these polymers has been limited by the relatively low glass transition temperatures.

With the ultimate goal of increasing the use temperature of the polyphenylquinoxalines and at the same time retaining solubility, several efforts to increase both chain rigidity and aggregate rigidity have been reported.^{3–5} However, the most feasible method of extending the use temperature range of polymers like the polyphenylquinoxalines would be to modify the polymer backbone to increase the symmetry of the repeat unit, thus allowing the development of crystallinity. The combination of a high degree of crystallinity and a high crystalline transition temperature would raise the ultimate use temperature to the crystalline transition temperature, or the polymer decomposition temperature, whichever is lower.



Substituted quinolines of only one geometrical isomer are prepared in high yield by the Friedländer reaction.⁶ This reaction involves the condensation of an o-aminocarbonyl (2) with an active methylene carbonyl compound (3) to afford the substituted quinoline (4). Classically, the reaction has been base catalyzed,^{7,8} although several reports have shown that the condensation proceeded smoothly under acid catalysis.9,10 The preparation of high molecular weight, thermally stable aromatic polymers by the Friedländer condensations of 4,6-dibenzoyl-1,3-phenylenediamine or 2,5-dibenzoyl-1,4phenylenediamine with a series of diacetyl aromatics to afford a series of polyanthrazolines and polyisoanthrazolines¹⁰ demonstrated that the reaction was effective for the synthesis of aromatic polymers. This condensation reaction has now been explored for the synthesis of polyquinolines structurally similar to the known series of polyquinoxalines.

Results and Discussion

Monomers. Since the synthesis of phenylated polyquinolines utilizing the Friedländer synthesis as the polymerization reaction required both diacetylaromatic and bis-*o*-aminobenzophenone monomers, a bis-*o*-aminobenzophenone monomer, 4,4'-diamino-3,3'-dibenzoyldiphenyl ether (5), was synthesized by two different pathways. One synthetic method involved the direct benzoylation of 4-aminophenyl ether under vigorous conditions to give a 6–13% yield of 5 which was difficult to suitably purify for polymerizations.



Another synthetic scheme which requires the hydrogenation of an intermediate 2,1-benzisoxazole is outlined in Figure 1. The synthesis of 4,4'-dinitrodiphenyl ether (6) was accomplished by the reaction of *p*-nitrophenol with *p*-fluoronitrobenzene in dimethyl sulfoxide (DMSO).¹¹ The reaction of 6 with phenylacetonitrile in basic methanol afforded 5,5'-oxybis(3-phenyl-2,1-benzisoxazole) (7). Hydrogenation of 7 in tetrahydrofuran solvent with hydrogen over a 5% palladium catalyst afforded a quantitative yield of 5. After two recrystallizations, an 85% yield of monomer pure 5 was obtained.

An AB monomer of high purity should afford the highest molecular weight polymer as a result of perfect functional group balance. Such an AB monomer 5-acetyl-2-aminobenzophenone (8) suitable for polyquinoline formation has been reported.¹²

Polymer Synthesis. The polymerization of 4,4'-diamino-



Figure 1. Synthesis of 4,4'-diamino-3,3'-dibenzoyldiphenyl ether (5).



3,3'-dibenzoyldiphenyl ether (5) with 4,4'-diacetyldiphenyl ether (9a) was carried out under a variety of conditions. The solubility characteristics and viscosity measurements on the resulting poly[2,2'-(p,p'-oxydiphenylene)-6,6'-oxybis(4-phenylquinoline)] (10a) were used as an indicator of the rel-



ative molecular weights of the polymers prepared under each set of conditions. The results, summarized in Table I, indicate that acid catalysis, as expected,¹⁰ generally afforded higher molecular weight polymers. However, the polymerization in polyphosphoric acid (PPA), a strong acidic solvent, gave low

Table I
Polymerization of 4,4'-Diamino-3,3'-dibenzoyldiphenyl
Ether (5) with $4,4'$ Diacetyldiphenyl Ether $(9a)$ under
Various Conditions

Polymerizati	Polymer			
Solvent	Catalysta	$\overline{Solubility^b}$	[η]	
Sulfolane Sulfolane/diphenyl	H ₃ PO ₄ H ₃ PO ₄	CHCl ₃ CHCl ₃	0.4 - 1.36 0.63 - 1.6	
PPA HMPA Pyridine	КОН	CHCl ₃ CHCl ₃ Insoluble	$\begin{array}{c} 0.32\\ 0.15\end{array}$	
m-Cresol/PPA ^c m-Cresol/P ₂ O ₅ ^d	nom	CHCl ₃ CHCl ₃	0.92 - 1.0 1.6-1.8	

^a Catalyst concentration of 1-5% by weight of solvent. ^b Polymers soluble in CHCl₃ are also soluble in *m*-cresol. ^c 25 wt % PPA. ^d 22 wt % P₂O₅.



Figure 2. Degree of polymerization as a function of polymerization time for polymer 10a.



Figure 3. Plots for determinations of molecular weight of polymer 10a.

molecular weight polymer. When the polymerization was conducted in sulfolane, the polymer began to precipitate from the reaction medium after only a few hours of reaction. If a mixture of sulfolane and diphenyl sulfone (1:1 by weight) was used as the polymerization solvent, the polymer remained in solution throughout the polymerization reaction. However, the viscosities of the resulting polymers varied greatly, and high molecular weight polymer was not consistently obtained under these conditions. The best polymerization conditions involved the use of a premixed, homogeneous solution of *m*-cresol and either PPA or phosphorus pentoxide (P_2O_5). Polymerizations conducted in these solvent mixtures invariably afforded high molecular weight, chloroform-soluble polymers.

The inconsistent results obtained in PPA, sulfolane, and sulfolane/diphenyl sulfone solvents can be accounted for by the known, acid-catalyzed trimerization of acetylaromatic compounds affording 1,3,5-triarylbenzenes.^{13,14} Thus, under



strongly acidic conditions (polyphosphoric acid), the monomer balance could be upset as a result of the trimerization of the diacetyl monomer, and only low molecular weight polymer would be obtained. In the sulfolane and sulfolane/diphenyl sulfone solvents, the viscosity and molecular weight of the polymer varied as did the extent of the trimerization reaction. Moderation of the acid strength by the use of *m*-cresol/PPA and *m*-cresol/P₂O₅ solvents apparently greatly decreased the trimerization reaction.

Macromolecules

Table II Effect of Monomer Balance on Intrinsic Viscosity of Polymer 10a

Mole ratio 5/9a	[η]	
1.01/1.00 1.00/1.00 1.00/1.01	0.91 1.00 1.04	

Table III Summary of Molecular Weight Determinations on Polymer 10a

[η]	M _n	DP	Γ, cm³/g
1.50	72 300	122	0.056
1.24	60 400	102	0.046
1.08	44 500	75	0.029



Figure 4. Determination of Mark-Houwink constants for polymer 10a.

The polymerization kinetics of 5 with 9a in both *m*-cresol/ PPA and m-cresol/P₂O₅ were followed by withdrawing aliquots, isolating the polymer, and measuring solution viscosity. The number average molecular weight (M_n) and the degree of polymerization (DP) was calculated for each sample. Plots of DP as a function of time for the polymerizations in both solvents are linear during the initial stages of the polymerization (Figure 2), indicating that the polymerization is first order with respect to each monomer, second order overall. Both polymerizations deviated from linearity after 13–15 h of reaction, and the polymers showed little increase in molecular weight after 20 h of reaction. Since this decrease in the rate of polymerization can be ascribed to imperfect monomer balance, the difference in the ultimate attainable molecular weight in the two solvents must reflect a difference in the occurrence of side reactions. The extents of reaction in the two cases, 99.3% (*m*-cresol/PPA) and 99.7% (*m*-cresol/ P_2O_5), mean that, as an upper limit, only 0.4% of the acetyl end groups need be involved in the cyclotrimerization reaction to account for the differences in molecular weights attained in the two solvents. This amount of a side reaction, too low to be detected





Figure 5. Differential distribution curve for polymer 10a.

in the kinetic plots, would affect the attainable molecular weights.

The effect of monomer balance on the intrinsic viscosity of polymer 10a obtained from three polymerizations in m-cresol/PPA showed that a slight excess of aminoketone 5 severely limited the viscosity and molecular weight, while a slight excess of diacetyl 9a slightly increased the viscosity and molecular weight of the polymer (Table II). These results are consistent with the view that trimerization of the diacetyl monomer consumes acetyl end groups in the acid-catalyzed polymerizations.

A sample of polymer 10a $([\eta] = 0.94 \text{ dl/g})$ was fractionated from a 1% chloroform solution using absolute ethanol as the precipitant. Fractions chosen for molecular weight determinations had intrinsic viscosities of 1.50, 1.24, and 1.08 dl/g. The results of number average molecular weight (M_n) determinations (chloroform solutions) by membrane osmometry are summarized in Table III. The molecular weight of each of the

 Table V

 Thermogravimetric Analysis of Polyquinolines

	Air	Nitrogen		
Polymer	Break	Break	% wt loss at 800 ° C	
10a	545	565	16	
10b	540	575	22	
10c	530	555	15	
10d	530	555	26	
10e	535	545	25	
10f	540	545	19	
11	520	570	20	
		300*		
20-		37,1*	~	
ş 40				



Figure 6. Isothermal aging curves for polymer 10a.

three fractions was determined from plots of π/c vs. c (Figure 3) using the standard relationship:

$$\frac{\pi}{c} = \frac{RT}{M_{\rm n}} + \frac{RT\Gamma c}{M_{\rm n}}$$

The molecular weight of each sample was determined from the intercept of each line, and the second viral coefficient was calculated from the slope of each line. The low Γ values show that chloroform at 25 °C is very nearly a theta solvent for this polymer; thus, the polymer-solvent interaction is minimal. A plot of ln [η] as a function of ln M_n (Figure 4) from the three samples was linear, and provided the Mark-Houwink relationship:

		Diacetyl an R	d Bis(phenylacetyl) Monomers O O ∥ ∥ ∥ .CH ₂ CArCCH ₂ R						
	9								
	Ar	R	Recrystallization solvent	Mp, °C (lit. mp, °C)	Ref				
a		Н	95% ethanol	103-104 (102-103)	17, 18				
b	-	Н	95% ethanol (sublimed)	114-115 (114)	19, 20 <i>ª</i>				
с		Н	Benzene	191-192 (190-191)	21, 22				
d		C_6H_5	Toluene	174-175 (169-170)	23				
e	-0-	C_6H_5	Benzene	180-181 (172-174)	23				
f	-	C_6H_5	Methylene chloride	235-236 (226-227)	24				

Table VI

^a Available from Aldrich Chemical Co.

$[\eta] = (9.0 \times 10^{-4})(M_{\rm n})^{0.66}$

The value of 0.66 for a is lower than might be expected for a rigid aromatic polymer; however, this value in chloroform is consistent with a minimal polymer–solvent interaction resulting in a tightly coiled polymer conformation.

Gel permeation chromatography of polymer 10a provided a number average molecular weight (M_n) of 51 600 and a weight average molecular weight (M_w) of 193 000 (based on polystyrene standards), in reasonable agreement with the M_n value of 40 500 calculated by the Mark-Houwink equation for this sample. The differential distribution curve for 10a in chloroform is shown in Figure 5. The dispersity of this polymer sample (M_w/M_n) is 3.75.

Polymerization of 4,4'-diamino-3,3'-dibenzoyldiphenyl ether (5) with other bisketomethylene monomers 9b-f were carried out in *m*-cresol/PPA and *m*-cresol/ P_2O_5 as outlined in Table IV. The polymerizations were conducted at 130-135 °C for 21–122 h; however, the polymerization reactions were essentially complete at this temperature after 20-24 h. Polymers 10a, b, and d were readily soluble in chloroform, but precipitated from concentrated chloroform solutions upon prolonged standing. Polymers 10c, e, and f would only swell in chloroform, but did dissolve in tetrachloroethane. However, concentrated solutions of polymers 10c, e, and f in tetrachloroethane precipitated on prolonged standing. Polymer sample which had precipitated from either chloroform or tetrachloroethane could be dissolved in m-cresol, and after precipitation from *m*-cresol into ethanol, the polymer sample again dissolved in the chlorinated hydrocarbon.

Tough flexible films of all the polyquinolines were cast from 15-25 wt % solutions in either chloroform (polymers 10a, b, and d) or 3:1 tetrachloroethane:*m*-cresol (polymers 10c, e, and f). Casting polymer 10a from 15-20 wt % chloroform solutions onto glass plates with the aid of a doctor knife and allowing the chloroform solvent to quickly evaporate afforded clear, tough, flexible films. However, when the glass plate was loosely covered and the chloroform was allowed to slowly evaporate over a period of 24-48 h, the resulting film was very tough and flexible, but was translucent. The translucent films did not dissolve in chloroform, as did the clear films, but dissolved in *m*-cresol and, after precipitation from *m*-cresol, dissolved in chloroform again. Although this type of behavior is charac-

Table VII Carbon-13 Spectra of o-Aminoketones



^a Chemical shift values calculated on the basis of the additivity of the chemical shift parameters based on monosubstituted benzenes as outlined in ref 25. ^b Indicates a singlet resonance in off-resonance proton decoupling experiments. Unless otherwise noted, all other resonances in off-resonance coupling experiments are doublets. ^c Indicates a quartet on off-resonance proton decoupling experiments.

Table VIII					
Carbon-13 Spectra	of Polyquinoline 10a and	l a Model Compound			

			ł				54 15
Carbon No.	Obsd $(Calcd)^a$	Carbon No.	$\begin{array}{c} \text{Obsd} \\ (\text{Calcd})^a \end{array}$	Carbon No.	Obsd (Calcd) ^a	Carbon No.	Obsd $(Calcd)^a$
1	$156.0 (s)^b$ (164.6)	10	138.1 (s) (141.6)	1	155.3 (s) (164.6)	10	138.1 (s) (141.6)
2	122.8 (119.5)	11	128.8 (127.4)	2	`122.9´ (119.5)	11	129.1 (127.4)
3	148.3 (s) (149.7)	12	129.4 (128.9)	3	148.4 (s) (149.7)	12	129.4 (128.9)
4	112.5 (114.1)	13	128.6 (127.3)	4	112.5 (114.1)	13	128.7 (127.3)
5	154.7 (s) (158.4)	14	139.5 (s) (141.6)	5	154.6 (s) (158.4)	18	135.0 (s) (133.9)
6	119.8 (115.5)	15	127.4 (127.4)	6	119.3 (115.5)	19	128.7 (128.4)
7	132.2 (131.3)	16	128.6 (128.9)	7	132.1 (131.3)	20	119.3 (114.5)
8	146.0(s) (149.1)	17	127.4 (127.3)	8	146.0 (s) (149.1)	21	158.2 (s) (158.7)
9	126.6 (s) (128.9)		(/	9	126.5 (s) (128.9)		(/

^a Chemical shift values calculated on the basis of the additivity of the chemical shift parameters based on monosubstituted benzenes as outlined in ref 25. ^b Indicates a singlet resonance in off-resonance proton decoupling experiments. Unless otherwise noted, all other resonances in off-resonance coupling experiments are doublets.

teristic of polymers which crystallize from solution,¹⁵ both the clear and the translucent films showed only a diffuse x-ray pattern, indicating less than 20% crystallinity. Thermal treatment of the clear film, including either heating it under an inert atmosphere or drawing it over a preheated metal bar, afforded a white, translucent film that again showed reversible solubility in chloroform.

Allowing the chloroform solvent to evaporate slowly during the casting of films of polymers **10b** and **10d** did not result in the formation of a translucent film, but rather provided a coating exhibiting a strong adherance to the glass. Attempts to remove the film from the glass resulted in the separation of the top surface of the glass before the polymer-glass adhesion was broken.

The self-condensation polymerization of 5-acetyl-2-aminobenzophenone (8) was carried out in *m*-cresol/PPA or in *m*-cresol/P₂O₅ at 120–130 °C to afford poly[2,6-(4-phenylquinoline)] (11). The polymer, which began to precipitate from the polymerization solutions after 24–30 h, had intrinsic viscosities of 1.3–2.2 dl/g (sulfuric acid). After isolation, 11



dissolved only in strong acids (concentrated sulfuric acid, methanesulfonic acid). X-ray powder patterns of 11 showed distinct reflections indicating the crystalline character of the polymer. From plots of intensity as a function of 2θ , the degree of crystallinity in powder samples of 11 has been estimated to be ~65%. Fibers could be wet spun directly from the polymerization solution into ethanol containing triethylamine.

As expected, the polyquinolines showed outstanding thermal stability both in inert atmospheres as well as in air.

Table IX Elemental Analyses of Polyquinolines

Poly.	Calcd, %			Found, %			
mer	С	Н	N	C	Н	N	
10a	85.40	4.44	4.74	84.78	4.46	4.70	
10b	86.72	4.45	5.62	85.72	4.31	5.49	
10c	87.78	4.56	4.87	86.23	4.50	4.72	
10d	87.31	4.61	3.77	86.86	4.62	3.47	
10e	88.59	4.65	4.30	86.95	4.60	4.10	
10f	89.23	4.71	3.85	88.78	4.62	3.89	
11	88.65	4.46	6.89	72.94^{a}	4.47	5.83	

^a 14.61% residue after combustion.

Thermogravimetric analysis (TGA) of polymers 10a–f and 11 (Table V) showed breaks in air at 530-545 °C, with breaks in nitrogen at 530-570 °C and only 15–26% weight loss at 800 °C under nitrogen. In general, the polymers having four pendent phenyl groups per repeating unit showed breaks at temperatures 5–15 °C lower than the structural analogue having only two pendent phenyl groups per repeat unit. Isothermal aging curves for polymer 10a (Figure 6) showed no weight loss after 100 h at 300 °C, and 48% weight loss after 100 h at 371 °C.

Detailed comparisons of thermal transition temperature data on polyquinolines 10a-f and 11 and the results of dynamic mechanical testing of polymer 10a are presented in an accompanying paper.¹⁶

Experimental Section

Diacetyl and Bis(phenylacetyl) Monomers (9). A list of the diacetyl and bis(phenylacetyl) monomers used in the polymerizations is given in Table VI.

5-Acetyl-2-aminobenzophenone (8). The synthesis of AB monomer 8 was conducted as described previously.¹² Recrystallization from 95% ethanol afforded light yellow needles: mp 159–161 °C (lit.¹² mp 152–154 °C); ir (KBr) 3280 and 3400 (NH), 1610 and 1660 cm⁻¹

	Polymerizations in <i>m</i> -Cresol/PPA Solvent System							
		Solvent, g		Polymerization		<i>M</i>		
Polymer	Monomers (mmol)	PPA	m-Cresol	Temp, °C	Time, h	version	[η]	
10a	5 , 9a (5)	10	35	125	65	96	0.92	
	(10)	20	60	135	87	92	0.92	
	(50)	100	300	130	48	91	0.94	
	(25)	50	150	130	49	a	1.0	
	5(5.05), 9(5.00)	10	30	130	48	95	0.91	
	5 (5.00), 9 (5.05)	10	30	130	48	96	1.04	
10b	5,9b (5)	10	30	135	122	90	0.60	
10c	5 , 9c (5)	10	30	135	23	94	1.7	
	(5)	10	30	135	41	91	2.0	

 Table X

 Polymerizations in m-Cresol/PPA Solvent System

^a Samples withdrawn for kinetic information, so total % conversion not determined.

Table XI Data on the Polymerization Rate of 5 with 9a in *m*-Cresol/PPA

Sample No.	Polymerization time, h	[η]	M _n ^a	DP ^b
1	3	0.30	6 600	22.2
2	6	0.47	12 900	46
3	8.5	0.58	17 800	60
4	13.5	0.79	28 400	96
5	23.5	0.96	37 800	128
6	32.5	0.98	39 300	133
7^c	49	1.00	40 500	137

^a Calculated from Mark–Houwink equation: $[\eta] = (9.0 \times 10^{-4})M_n^{\circ.66}$. ^b Calculated from M_n . ^c Remainder of polymerization solution.

(C=O); NMR (CHCl₃) δ 2.37 (s, 3, CH₃), 6.5 (s, 2, NH₂), and 6.6–8.2 (m, 8, aromatic); see Table VII for the ¹³C NMR spectra.

Anal. Calcd for C₁₅H₁₃NO₂: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.11; H, 5.55; N, 5.71.

4,4'-Dinitrodiphenyl Ether (6). A stirred solution of 100 g (0.709 mol) of p-fluoronitrobenzene, 98.6 g (0.709 mol) of p-nitrophenol, and 141 g (1.50 mol) of potassium fluoride monohydrate in 375 ml of dimethyl sulfoxide was heated to the reflux temperature and maintained at reflux for 25 min. The solution was cooled to room temperature and the resulting crystals were filtered and washed well with water. Recrystallization from benzene afforded 160 g (86.7%) of white needles: mp 147-148 °C (lit.¹¹ 143-144 °C); ir (KBr) 1580, 1510, 1490, 1340, and 1240 cm⁻¹.

5.5'-Oxybis(3-phenyl-2,1-benzisoxazole) (7). To a vigorously stirred solution of 150 g (3.75 mol) of sodium hydroxide in 750 ml of absolute methanol at 25 °C was slowly added 88.5 g (0.750 mol) of phenylacetonitrile. After solution was complete, 97.5 g (0.375 mol) of 4,4'-dinitrodiphenyl ether (6) was slowly added. The resulting dark solution was warmed to 65–70 °C and maintained at this temperature for 9 h. The dark slurry was cooled to room temperature, diluted with 250 ml of 50% methanol, and cooled in an ice bath. The resulting dark precipitate (72%) was filtered and washed with cold methanol until the methanol washings were clear. Recrystallization from toluene

afforded 53.6 g (39.4%) of orange crystals: mp 207–208 °C; ir (KBr) 1640, 1470, 1265, and 1215 cm⁻¹.

Anal. Calcd for $C_{26}H_{16}N_2O_3$: C, 77.22; H, 3.99; N, 6.93. Found: C, 77.19; H, 4.14; N, 6.84.

4,4'-Diamino-3,3'-dibenzoyldiphenyl Ether (5) from 5,5'-Oxybis(3-phenyl-2,1-benzisoxazole) (7). A total of 3.0 g of 5% palladium on powdered charcoal was added to a suspension of 37.0 g (91.6 mmol) of 5,5'-oxybis(3-phenyl-2,1-benzisoxazole) (7) in 375 ml of dry tetrahydrofuran (THF) and 10 ml of triethylamine. The vigorously stirred suspension was flushed with hydrogen gas and was stirred at room temperature under a hydrogen atmosphere until absorption of hydrogen ceased (approximately 92–96% of molar amount; 8-10 h). The catalyst was removed by filtration through a bed of Celite and the solvent was removed under reduced pressure. The resulting oil was crystallized from benzene-Skelly B (10:1) to afford 30.8 g (83.2%) of orange crystals: mp 156-157 °C. Recrystallization from methanol afforded 26.8 g of yellow needles: mp 157.5-158.5 °C; ir (KBr) 3480, 3360 (N-H), 1635 (C=O), and 1250 cm⁻¹ (C-O-C); NMR (CHCl₃) δ 5.83 (s, 4, NH₂) and 6.5–7.5 (m, 16, aromatic); see Table VII for ¹³C NMR spectra.

Anal. Calcd for $\rm C_{26}H_{20}N_2O_3:$ C, 76.46; H, 4.94; N, 6.86. Found: C, 76.20; H, 4.95; N, 6.84.

4,4'-Diamino-3,3'-dibenzoyldiphenyl Ether (5) from 4-Aminophenyl Ether. A total of 28 g (0.14 mol) of 4-aminophenyl ether was slowly added to 150 ml of refluxing benzoyl chloride. The resulting slurry was vigorously stirred and a total of 46 g (0.34 mol) of anhydrous zinc chloride was slowly added. Heating was continued until evolution of hydrogen chloride gas ceased (2.0–2.5 h). The dark slurry was cooled to room temperature, 500 ml of water was slowly added, and the slurry was heated to the reflux temperature. The aqueous portion was then decanted. This extraction was repeated three times. The remaining dark residue was dissolved in hot 60% sulfuric acid, and the acid solution was maintained at 135–140 °C for 18 h. The hot acid was then poured onto 2 kg of cracked ice. The aqueous suspension was diluted to a volume of 3 l. by the addition of water, and was extracted three times with 1-l. portions of methylene chloride. The methylene chloride extracts were combined and washed with 1-l. portions of 10% sodium hydroxide (three times) and water (two times). The methylene chloride was removed under reduced pressure. The resulting residue was dissolved in hot 50% aqueous ethanol. Upon cooling, $7.5 ext{ g}$ (13%) of 5 precipitated. The crude product was chromatographed on silica gel using benzene as the eluent and was recrystallized three times from

Table XIIPolymerization in m-Cresol/P2 O5 Solvent System

			Solvent, g		Polymerization		97 40 10	
Polymer	Monomers	(mmol)	P_2O_5	<i>m</i> -Cresol	Temp, °C	Time, h	version	$[\eta]$
10a	5. 9a	(5)	8.5	30	130	48	95	1.6
	-,	(50)	85	300	130	$\overline{24}$	а	1.8
		(100)	170	600	130	24	98	1.8
10b	5. 9b	(10)	17	60	130	48	96	1.1
10c	5, 9c	(10)	17	60	130	48	100	3.1
10d	5. 9d	(10)	17	60	130	24	94	2.0
10e	5. 9e	(10)	17	60	130	21	98	3.4
10f	5. 9f	(10)	17	60	130	21	100	4.1

^a Samples withdrawn for kinetic information, so total % conversion not determined

Table XIII Data on the Polymerization Rate of 5 with 9a in m-Cresol/P. O.

Sample No.	Polymeri- zation time, h	[η]	M _n ^a	DP b	
1	2	0.34	8 000	27	
2	3	0.48	$13\ 100$	45	
3	4.5	0.71	23 900	81	
4	6	0.89	34 000	115	
5	7.5	1.04	43 000	146	
6	9	1.20	53 400	181	
7	11	1.37	65 200	221	
8	14	1.57	80 200	272	
9 c	24	1.77	96 000	325	

^a Calculated from Mark-Houwink equation: $[\eta] = (9.0 \times 10^{-4})M_n^{0.66}$. ^b Calculated from M_n . ^c Remainder of polymerization solution.

Table XIV Polymerizations of 5 and 9a in Sulfolane

Run No.	Heating schedule Temp, °C (time, h)	% con- version	$[\eta], dl/g$
1	125 (10); 140 (10); 165 (35); 175 (20); 195 (74)	63	0.24
2	265 (24)	86	0.36
3	128 (8); 155 (5); 175 (17); 185 (24)	87	0.51
4	130 (21); 155 (3); 180 (3); 190 (47)	85	1.4

benzene to afford 3.5 g (6.1%) of 5: mp 156.5–157.0 °C; ir (KBr) 3480 and 3366 (N–H), 1625 (C=O), and 1245 cm⁻¹ (C–O–C); ¹³C NMR spectra is given on Table VII.

Anal. Calcd for C₂₆H₂₀N₂O₃: C, 76.46; H, 4.94; N, 6.86. Found: C, 76.62; H, 5.09; N, 6.91.

6,6'-Oxybis(2,4-diphenylquinoline). A mixture of 10 g of commercial PPA and 20 ml of *m*-cresol was stirred under a nitrogen atmosphere and was heated at 140 °C for 2 h. The homogeneous solution was allowed to cool to room temperature, and 2.0423 g (5.0000 mmol) of aminoketone 5 and 1.3241 g (11.000 mmol) of acetophenone were added to the solution. An additional 10 ml of *m*-cresol was used to assure complete transfer of the reactants. The solution was poured into 500 ml of aqueous methanol, and the tan precipitate was collected by filtration and was washed well with water. Recrystallization from methanol afforded 2.5 g (89%) of colorless crystals: mp 229-230 °C; ir (KBr) 1610, 1590, 1230, and 1200 cm⁻¹; see Table VIII for ¹³C NMR data.

Anal. Calcd for $C_{42}H_{28}N_2O$: C, 87.47; H, 4.89; N, 4.86. Found: C, 87.77; H, 4.88; N, 4.85.

Polymerizations. Elemental analyses for polymers 10a-f and 11 are given in Table IX. A general procedure for the polymerization reaction in each solvent system follows.

Polymerizations in m-Cresol/Polyphosphoric Acid. The polymerization solvent was prepared from the amount of polyphosphoric acid (PPA) and two-thirds of the m-cresol indicated in Table X. The *m*-cresol/PPA slurry was stirred under a static nitrogen atmosphere and was heated to 140 °C for 2 h. The resulting homogeneous solvent was cooled to room temperature, and the appropriate quantities of monomers were added. The remaining one-third of the m-cresol was used to assure complete transfer of the monomers. The reaction vessel was purged with nitrogen, and the solution was stirred under a static nitrogen atmosphere and was heated at the temperatures for the times indicated in Table X. The solution was slowly poured into a large volume (1.5 l./100 ml of polymerization solution) of a vigorously stirred solution consisting of 5-10% triethylamine in 95% ethanol. The fibrous white polymer was collected by filtration, washed well with ethanol, and continuously extracted with 95% ethanol in a Soxhlet extractor for 12-24 h. The polymer was air dried and then the chloroform-soluble polymers were dissolved in chloroform. The chloroform solution was slowly poured into an excess of 95% ethanol, and the resulting fibrous polymer was filtered and dried at 100-120 °C under reduced pressure. Chloroform-insoluble polymers were dried

Table XV				
olymerizations of 5 and 9a in Sulfolane/Diphenyl Sulfone				

			1	
Run No.	Catalyst	Heating schedule Temp, °C (time, h)	% con- version	$[\eta], dl/g$
1	1 drop of 1 M H ₃ PO ₄	285 (42)	76	0.72
2	6 drops of concd H₃PO₄	140 (18); 160 (28); 165 (18); 190 (8)	92	0.63
3	5 drops of concd H ₃ PO ₄	120 (3); 150 (36); 175 (123)	56	1.6

immediately after extraction with ethanol.

Several aliquots of polymer 10a were withdrawn from the polymerization of 5 and 9a, 25 mmol scale, in order to study the rate of polymerization. Each sample was approximately 10 ml in size, and each was precipitated into ethanol-triethylamine and was reprecipitated from chloroform into 95% ethanol. After drying the sample at 100 °C under reduced pressure, the intrinsic viscosity of a chloroform solution of each sample was determined. The reaction time, viscosity, M_{n} , and DP for each sample are shown in Table XI.

Polymerizations in m-Cresol/Phosphorus Pentoxide. The polymerization solvent was prepared from the amount of phosphorus pentoxide and two-thirds of the m-cresol indicated in Table XII. The m-cresol/P₂O₅ slurry was stirred under a nitrogen atmosphere and was heated to 140 °C for 2-3 h. The homogeneous solution was allowed to cool to room temperature, and the appropriate quantities of monomers were added. The remaining one-third *m*-cresol was used to assure complete monomer transfer. The reaction vessel was purged with nitrogen, and the solution was stirred under a static nitrogen atmosphere and was heated at the temperatures for the times indicated. The polymer was isolated by precipitating the polymerization solution into a large volume (1.5 l./100 ml of polymerization solution) of a vigorously stirred solution of 5-10% triethylamine in 95% ethanol. The resulting white fibrous polymer was filtered, washed well with ethanol, and continuously extracted with 95% ethanol in a Soxhlet extractor for 12-24 h. The polymer was air dried and the chloroform-soluble polymers were dissolved in chloroform. The chloroform solution was slowly poured into an excess of 95% ethanol, and the resulting fibrous polymer was filtered and dried at 100-120 °C under reduced pressure. Chloroform-insoluble polymers were dried immediately after extraction with ethanol.

Several aliquots were withdrawn from the polymerization of 5 with 9a, 50 mmol scale, in order to study the rate of polymerization. Each aliquot was approximately 10 ml in size, and each was precipitated into ethanol-triethylamine and then was reprecipitated from chloroform into 95% ethanol. Each sample was dried at 100-120 °C under reduced pressure. The intrinsic viscosity of a chloroform solution of each sample was determined. The reaction time, intrinsic viscosity, M_n , and DP for each sample are shown in Table XIII.

Poly[2,2'-(p,p'-oxydiphenylene)-6,6'-oxybis(4-phenylquinoline)] (10a). Polymerizations of aminoketone 5 and diacetyl 9a were conducted under various conditions as outlined in the following.

Polymerizations in Sulfolane. A mixture of 0.8169 g (2.000 mmol) of bisaminoketone 5 and 0.5085 g (2.000 mmol) of 4,4'-diacetyldiphenyl ether (9a) in 11.5 ml of sulfolane in a resin flask was stirred and heated under a static nitrogen atmosphere. After all monomers had dissolved, two drops of 85% phosphoric acid were added to the solution, and the solution was heated with stirring for the times and temperatures outlined in Table XIV. The polymerization mixture was poured into 300 ml of vigorously stirred ethanol. The resulting precipitate was washed well with ethanol, filtered, and air dried. The polymer was dissolved in chloroform, reprecipitated into ethanol, filtered, and dried under reduced pressure at 100 °C for 12 h.

Polymerizations in Sulfolane/Diphenyl Sulfone. A stirred suspension of 2.0423 g (5.0000 mmol) of bisaminoketone 5, 1.2714 g (5.0000 mmol) of diacetyl 9a, 15.5 g of diphenyl sulfone, and 15.5 g (13 ml) of sulfolane was heated under a static nitrogen atmosphere to 100 °C at which temperature the mixture became a homogeneous solution. The phosphoric acid catalyst was added and the solution was stirred and heated as indicated in Table XV. The polymerization solvent was slowly poured into vigorously stirred acetone. The resulting precipitate was washed well with acetone and was dissolved in chloroform. The chloroform solution was slowly poured into vigorously stirred acetone. The resulting precipitate was filtered and dried at 100 °C under reduced pressure.

Table XVI Data Used for Determination of Molecular Weight

Comon «I					
$\pi \pi/c$	$20.14 \\ 10.15 \\ 0.5040$	12.08 4.79 0.397	7.25 2.50 0.345	4.35 1.28 0.294	0 0.236 ^a
Concn, g/l. π π/c	20.26 11.09 0.547	$12.16 \\ 5.36 \\ 0.441$	7.29 2.75 0.377	$4.38 \\ 1.49 \\ 0.341$	0 0.282ª
Concn, g/l. π π/c	20.48 12.53 0.612	12.29 6.35 0.517	7.37 3.44 0.467	4.42 1.95 0.441	0 0.383 ^a
	π π/c Concn, g/l. π π/c Concn, g/l. π π/c π π/c	Content, g/l. 20.14 π 10.15 π/c 0.5040Content, g/l.20.26 π 11.09 π/c 0.547Content, g/l.20.48 π 12.53 π/c 0.612	Cohen, g/l.20.1412.08 π 10.154.79 π/c 0.50400.397Cohen, g/l.20.2612.16 π 11.095.36 π/c 0.5470.441Cohen, g/l.20.4812.29 π 12.536.35 π/c 0.6120.517	Cohen, g/l.20.1412.087.25 π 10.154.792.50 π/c 0.50400.3970.345Cohen, g/l.20.2612.167.29 π 11.095.362.75 π/c 0.5470.4410.377Cohen, g/l.20.4812.297.37 π 12.536.353.44 π/c 0.6120.5170.467	Content, g/l.20.1412.087.254.35 π 10.154.792.501.28 π/c 0.50400.3970.3450.294Concn, g/l.20.2612.167.294.38 π 11.095.362.751.49 π/c 0.5470.4410.3770.341Concn, g/l.20.4812.297.374.42 π 12.536.353.441.95 π/c 0.6120.5170.4670.441

^a Values extrapolated to zero concentration from plots of data (Figure 3).

Polymerization in Hexamethylphosphoramide/Potassium Hydroxide. A solution of 0.8169 g (2.000 mmol) of bisaminoketone 5 and 0.5086 g (2.000 mmol) of diacetyl 9a in 15 ml of hexamethylphosphoramide was stirred under a static nitrogen atmosphere. A total of 10 drops of 10% potassium hydroxide in methanol was added and the solution was stirred and heated as follows: 100 °C for 23 h, 150 °C for 23 h, and 180 °C for 48 h. The polymerization solution was poured into 500 ml of vigorously stirred water, and the resulting precipitate was filtered, washed well with water, and air dried. The yellow powder was dissolved in chloroform, and the chloroform solution was reprecipitated into Skelly B. The resulting yellow polymer was filtered and dried at 100 °C under reduced pressure to afford 0.80 g (67%) of 10a. The intrinsic viscosity of the polymer was 0.15 dl/g in chloroform.

Polymerization in Pyridine/Potassium Hydroxide. A solution of 0.8169 g (2.000 mmol) of bisaminoketone 5, 0.6085 g (2.000 mmol) of diacetyl 9a, 10 drops of a 10% solution of potassium hydroxide in methanol, and 15 ml of pyridine was heated to the reflux temperature under a static nitrogen atmosphere. After heating for 1 h, the methanol was distilled from the solution, and reflux was maintained for 20 h. During this time, the yellow-brown polymer had precipitated from solution. The precipitated polymer was insoluble in chloroform, m-cresol, and sulfuric acid.

Polymerization in Polyphosphoric Acid. Polyphosphoric acid (PPA) was freshly prepared by the addition of 7.2 g of P_2O_5 to 5.0 g of 85% phosphoric acid. The resulting slurry was stirred under a nitrogen atmosphere and was heated to 160 °C for 6 h. The clear homogeneous PPA was cooled to room temperature, and 0.8169 g (2.000 mmol) of bisaminoketone 5 and 0.5086 g (2.000 mmol) of diacetyl 9a were added. The reaction flask was flushed with nitrogen, and the slurry was heated under nitrogen as follows: 110 °C for 13 h, 130 °C for 2 h, and 140 °C for 4 h. During this time, the polymerization mixture had become extremely viscous and rubbery making stirring very difficult. The mixture was cooled to 50 °C and 30 ml of 10% sodium hydroxide was slowly poured into the reaction flask, and the suspension was vigorously stirred. The resulting yellow powder was filtered, washed well with water, and suspended in 10% sodium hydroxide overnight. The yellow powder was collected by filtration, washed well with hot water, and air dried. The polymer was dissolved in chloroform, reprecipitated into Skelly B, and dried at 100 °C under reduced pressure. The resulting polymer (0.91 g, 77%) had an intrinsic viscosity of 0.32 dl/g in chloroform.

Poly[2,6-(4-phenylquinoline)] (11). The polymerization of 5acetyl- $\bar{2}$ -aminobenzophenone (8) was carried out in both m-cresol/ P_2O_5 and *m*-cresol/PPA solvent systems as follows.

Polymerization in m-Cresol/P₂O₅. The polymerization solvent was prepared from 17 g of P_2O_5 and 40 ml of *m*-cresol as previously described. After cooling the solution to room temperature, 4.7855 g (20.000 mmol) of 8 was added, and an additional 20 ml of *m*-cresol was used to assure complete transfer of the monomer. The solution was stirred under a static nitrogen atmosphere and was heated at 120 °C for 48 h. The solution was poured into 600 ml of a vigorously stirred solution of 10% triethylamine in 95% ethanol. The resulting fibrous precipitate was chopped and washed with ethanol in a Waring blender. The polymer was extracted with 95% ethanol in a Soxhlet extractor and was dried at 100 $^{\circ}\mathrm{C}$ under reduced pressure to afford 4.0 g (98%) of 11: $[\eta] = 2.2 \text{ dl/g}$ (sulfuric acid).

Polymerization in m-Cresol/PPA. The polymerization solvent was prepared from 10 g of commercial PPA and 20 ml of m-cresol as previously described. After the solution cooled to room temperature, 2.3928 g (10.000 mmol) of 8 was added to the solution. An additional 10 ml of m-cresol was used to assure complete transfer of the monomer. The solution was stirred under a static nitrogen atmosphere and

was heated at 130 °C for 120 h. The solution was precipitated into 95% ethanol, and the resulting precipitate was extracted with ethanol in a Soxhlet extractor for 24 h. The polymer was dried at 100 °C under reduced pressure to afford 1.8 g (90%) of 11: $[\eta] = 1.3$ dl/g (sulfuric acid). The polymer was soluble only in strong acids.

Polymer Properties. The viscosity measurements of the polymers were determined in chloroform, m-cresol, or sulfuric acid at 25 °C. The intrinsic viscosity for each polymer was obtained from plots of η_{inh} vs. c and η_{red} vs. c.

The number average molecular weight (M_n) determinations summarized in Table III were determined on chloroform solutions of fractionated samples of polymer 10a. Fractionation was carried out at 25 °C by the dropwise addition of ethanol to a solution of 3.4 g of 10a in 340 ml of vigorously stirred chloroform until the solution became slightly turbid. Addition of 1-2 ml of chloroform afforded a clear solution which was cooled to 0 °C then kept at that temperature for 12-14 h. The solution was decanted from the polymer film which had formed on the bottom of the flask. The film was dissolved in chloroform and was reprecipitated into ethanol to afford 100-250 mg of fractionated 10a. The decanted chloroform solution was treated with ethanol as described above to afford the next fraction.

The data obtained from Mechrolab High Speed Membrane Osmometer that was used for the M_n calculations are given in Table XVI. Analysis by gel permeation chromatography (chloroform solvent) was performed by Waters Associates, Milford, Mass.

Thermogravimetric analyses (TGA) were conducted on film samples of the polymers using a Du Pont 900 and 950 Thermal Analyzer at a heating rate of 5°/min in both air and nitrogen atmospheres (Table VI). Isothermal aging curves (Figure 6) were obtained in a circulating air atmosphere at temperatures of 300 and 371 °C for 100 h each.

X-ray diffraction patterns were carried out by Dr. Norman Baenziger, University of Iowa, on powder, film, and fiber samples using a Debye-Shearer Powder Camera with Cu K α radiation.

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Glass Transition of Polyquinoline

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ABSTRACT: The glass transition interval of a polyquinoline ($T_g = 251$ °C and $T_m = 483$ °C) has been studied by calorimetric, dilatometric, and dynamic mechanical techniques. The behavior of this polymer in the T_g interval has been quantitatively examined as a function of thermal history. Specifically it was of interest to determine (1) the effects of annealing temperatures at constant heating and cooling rates, (2) the effect of cooling rates at constant annealing temperatures, (3) the effect of heating rates at constant cooling rates, and (4) the effect of annealing time at constant annealing temperature and heating rate. The data show that widely different nonequilibrium structures result as a consequence of variable formation histories. Overlapping the normal second-order T_g , there are heat absorptions which exhibit distinct first-order character in addition to residual hysteresis effects (i.e., time-dependent configurational rearrangements).

In the course of studies relating to the thermal behavior of fully aromatic polymers² we have investigated the glass transition interval of polyquinolines, a new class of aromatic-heterocyclic polymers which has recently been synthesized.³⁻⁵ Like numerous other aromatic polymers, certain of the polyquinolines are largely amorphous solids in that no long-range periodicity is observed by x-ray techniques and they exhibit viscoelastic properties typical of amorphous materials.⁶ Because of their high stiffness energies, polyquinolines show glass transition intervals at relatively high temperatures. Depending on chemical repeat unit structures, high molecular weight polyquinolines show T_{g} 's ranging from 250 to 400 °C. It is also possible to synthesize symmetrical and unsymmetrical geometric isomers for a given polymer with the symmetrical structure always exhibiting the higher T_g . The introduction of flexibilizing groups into the chains produces a pronounced lowering, while incorporation of fused rings causes a substantial increase in $T_{\rm g}$. All these observations suggest that intramolecular effects seem to dominate the thermal behavior of these polymers. Unlike many other aromatic-heterocyclic polymers, polyquinolines can be synthesized into single isomers and in that sense they exhibit configurational regularity. Therefore, at least on a "local level", say up to 20 Å, these polymers are capable of spacial ordering. However, attempts to crystallize polyquinolines, i.e., produce regular conformation either from the melt or from solution to a high degree have failed to date.

DSC of six different polyquinolines resulted in complex scans in the T_g interval showing in addition to discontinuities of C_p , minima just below T_g , followed by overlapping single and at times multiple maxima in the form of relatively sharp endothermic peaks. It was the main objective of this study to examine these peaks with respect to formation histories (i.e., quenching, annealing) and it was hoped that a quantitative analysis of the results would offer explanation to the nature of these thermal processes.

Experimental Section

The polyquinoline used in this study, poly[2,2'-(oxydi-p-phenylene)-4,4'-(oxydi-p-phenylene)diquinoline], had the following repeat structure:



The material had an intrinsic viscosity of 0.44 in chloroform (for complete characterization see ref 4 and 5). Films were cast from chloroform solutions and dried under reduced pressure at 100 °C for 4 h. Most experiments reported here were made on a Du Pont Thermal Analyser Model 990. For DSC measurements a heat transfer analysis was performed according to a method described by Strella and Ehrhardt.⁷ Accordingly, the heating rate dependence of the glass transitions is a result of: (a) a time lag in the sample, (b) a time lag in the heat path through the sample, and (c) free volume effects. The instrument error involved because of time lag to the sample was estimated from a plot of maximum rate of melting vs. heating rate for a 0.03-mg sample of indium. The maximum error over a 100 °C/min heating rate range was 8.5 °C. An estimate of the combined temperature error due to machine and sample can be obtained from the following equation:⁸

$$\Delta \Theta \sim \beta \frac{l_{\rm sc}^2}{2k_{\rm sc}} + \frac{4l_{\rm s}^2}{\pi^2 k_{\rm s}}$$

where β = heating rate; l_{sc} = sample chamber thickness; l_s = sample thickness; k_{sc} = thermal diffusivity of sample chamber; k_s = thermal diffusivity of sample. The first term in brackets which is the time interval by which the sample chamber surface lags the heated surface