13th ed, American Public Health Association, Washington, D.C., 1971: (a) p 57; (b) p 334.
(24) R. G. Schweiger, *Kolloid-Z.*, **196,** 47 (1964).
(25) R. A. Morton and W. T. Earlam, *J. Chem. Soc.*, 159 (1941).
(26) R. Möhlau, *Chem. Ber.*, **46,** 443 (1913).
(27) E. A. Biryuk, V. A. Mazarenko, and R. V. Ravitskaya, *Zh. Anal. Khim.*, **23,** 1975 (1968); *J. Anal. Chem. USSR (Engl. Transl.)*, p 1577).
(28) D. A. Rees, *Biochem. J.* **126,** 257 (1972).
(29) R. Kohn, I. Furda, A. Haug, and O. Smidsrφd, *Acta Chem. Scand.*, **22,** 3098 (1968).

The Synthesis and Solution Properties of Aromatic Polymers Containing 2,4-Quinoline Units in the Main Chain[1]

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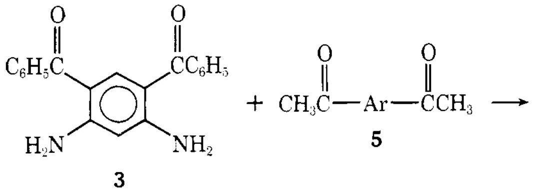
ABSTRACT: The acid-catalyzed polycondensation of 4,4′-bis(2-aminobenzoyl)diphenyl ether with diacetyl or diphenacetyl aromatic compounds afforded polymers containing quinoline groups linked by a variety of aromatic units. The polymers were soluble in phenolic and chlorinated hydrocarbon solvents, and tough, flexible films could be cast from these solutions. Poly[2,2′-(oxydi-*p*-phenylene)-4,4′-(oxydi-*p*-phenylene)diquinoline] showed no weight loss at 300 °C in air after 100 h and a TGA break in air at 510 °C. The polymer could be extruded from the melt at 430 °C through large bore capillaries. These extrudates could be drawn at temperatures above the glass transition temperatures of 251 °C with the resulting material showing an increase in crystallinity by x-ray diffraction. The Mark–Houwink equation for the polymer in chloroform at 20 °C was determined from viscometry and membrane osmometry to be $[\eta] = 5.5 \times 10^{-3}(\bar{M}_n)^{0.44}$. The polymerization followed second-order kinetics and attained number-average molecular weights greater than 25 000 within 15 h of reaction.

The Friedländer quinoline synthesis[2,3] has been utilized under a variety of base- and acid-catalyzed conditions to afford aromatic heterocyclic polymers.[4–6] High molecular weight phenylated polyanthrazolines (**1**) and polyisoanthrazolines (**2**) were prepared[6] by the reaction of 4,6-dibenzoyl-1,3-phenylenediamine (**3**) and 2,5-dibenzoyl-1,4-phenylenediamine (**4**), respectively, with diacetyl aromatic monomers (**5**). These polymers were partially soluble in a number of organic solvents and clear films could be cast from trifluoroacetic acid solutions. The greater solubility of these polymers when compared with the nonphenylated polyanthrazolines[4] was attributed to phenyl substitution on the polymer backbone. In general, polymers **1** which have pseudo-meta catenation due to the 1,9-anthrazoline moiety were found to be more soluble than polymers **2** which have a pseudo-para catenation due to the 1,6-anthrazoline moiety.[6]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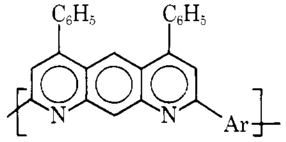
$$+ \ CH_3\overset{\overset{O}{\|}}{C}—Ar—\overset{\overset{O}{\|}}{C}CH_3 \longrightarrow$$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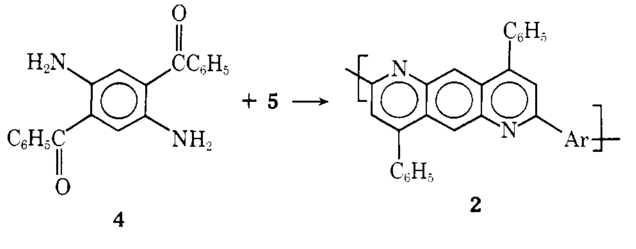
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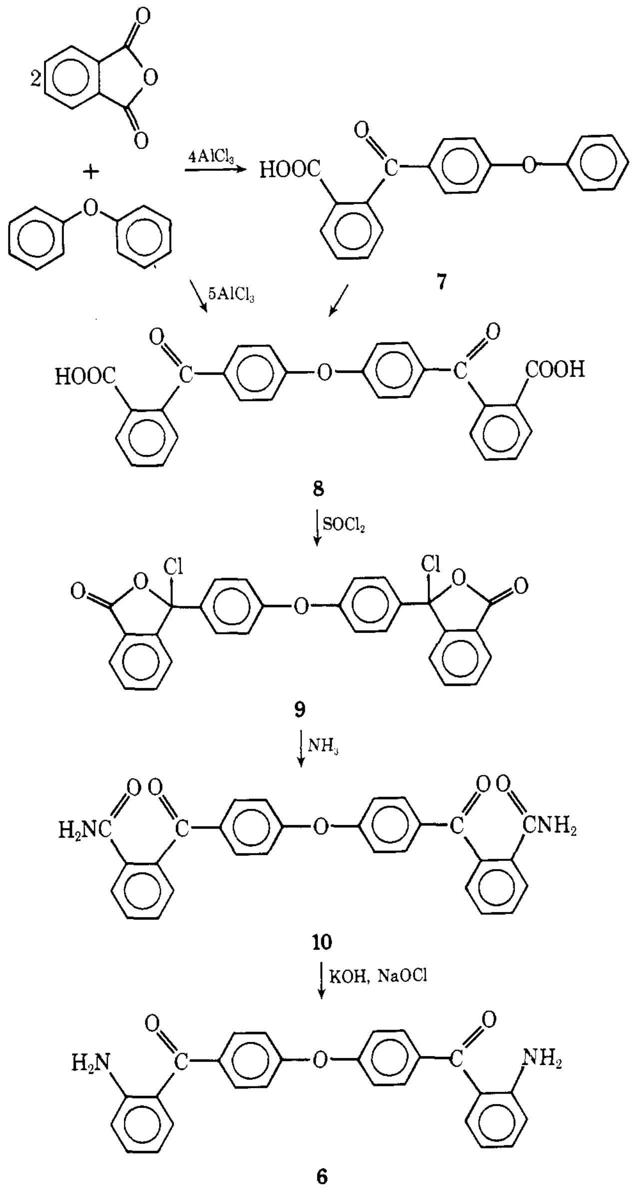
Since the thermal transitions of the polyanthrazolines (**1**) and the polyisoanthrazolines (**2**) are all above 360 °C,[7] with decomposition temperatures near 500 °C,[6] processing of these polymers by compression molding or melt extrusion techniques would cause degradation of the polymer chain. The processing temperature for these polymers which affords a low enough melt viscosity is generally 150 °C above T_g. Therefore, a method of decreasing the glass transition temperature to a value to allow fabrication was desirable. In general, an increase in the number of flexibilizing groups per repeating unit in a series of polyquinoxalines led to decreasing glass transition temperatures.[8] Thus, an effort to prepare aromatic polymers via the Friedländer synthesis which were processable by both solution and melt methods by the introduction of an increased number of meta and flexible units was undertaken. Monomers were necessary, therefore, in which the two *o*-aminoketo functionalities were positioned on different rings with the result that the polymer would contain a quinoline rather than an anthrazoline nucleus.

Discussion

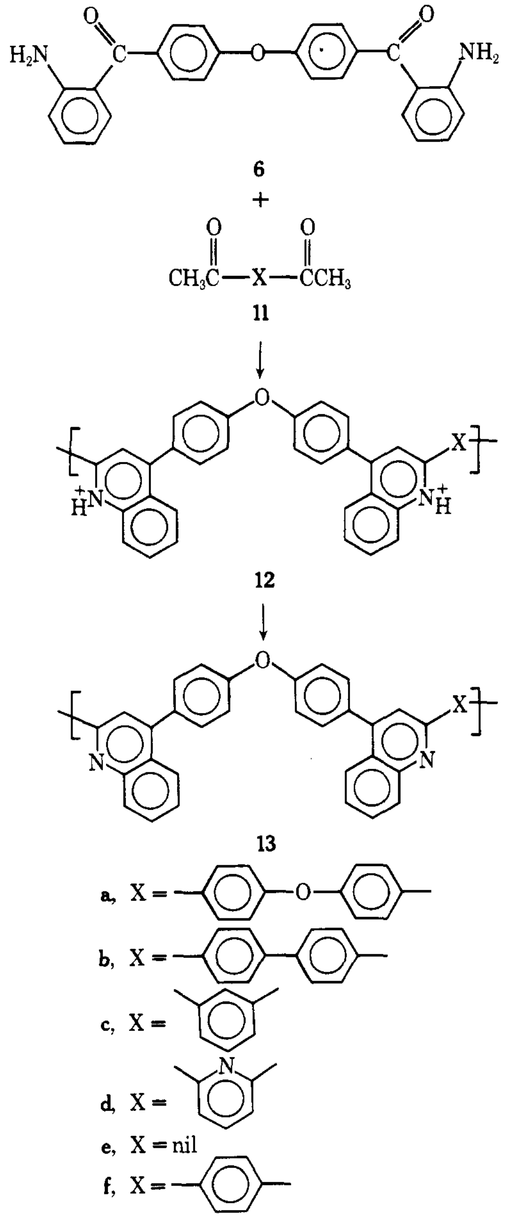
Monomer Synthesis. The polyquinoline-forming monomer, 4,4′-bis(2-aminobenzoyl)diphenyl ether (**6**), was synthesized as outlined in Scheme I. The Friedel-Crafts reaction of 2 mol of phthalic anhydride with 1 mol of diphenyl ether afforded either the monoadduct **7** or the diadduct **8** depending on the amount of aluminum chloride and solvent used. Five moles of aluminum chloride in a concentrated solution favored the formation of **8**. The monoadduct **7** was allowed to react further with 2 mol of phthalic anhydride to afford the diadduct 4,4′-bis(2-carboxybenzoyl)diphenyl ether (**8**) in 67% yield. The reaction of thionyl chloride with *o*-benzoylbenzoic acids has been reported to give pseudoacid chlorides.[9,10] Thus, the reaction of **8** with refluxing thionyl chloride gave the bis(pseudoacid chloride) **9**. Treatment of a cold, *N*-methyl-2-pyrrolidinone solution of **9** with anhydrous ammonia gas afforded 4,4′-bis(2-carbamylbenzoyl)diphenyl ether (**10**).

The Hofmann rearrangement of the bis(ketoamide) **10** was

Scheme I



Scheme II



carried out in aqueous potassium hydroxide with the addition of sodium hypochlorite. The yield of monomer-grade **6** was substantially reduced by the numerous recrystallizations which were necessary to obtain monomer free of acid and amide impurities. However, column chromatography was found to be very effective in the removal of these impurities from **6**. Infrared, mass spectral, elemental, and ^{13}C NMR analyses were entirely consistent with the assigned structure for **6**.

Polymerizations (Scheme II). In order to determine the optimum conditions for the acid-catalyzed Friedländer polymerization, polycondensations of **6** with 4,4′-diacetyldiphenyl ether (**11a**) were carried out in a variety of solvent–catalyst systems (Table I). Since the protonated polyquinoline **12** is the species formed in an acid-catalyzed system, high molecular weight polymer can only be obtained if **12** is soluble in the medium until the reaction is complete. Precipitation of the yellow polymer **12** prior to 18 h of reaction resulted in polymers with inherent viscosities in *m*-cresol of less than the maximum value of 0.66 dl/g.

The solvent system found to be most effective was prepared by the reaction of *m*-cresol with phosphorus pentoxide to afford a *m*-cresol solution of cresyl phosphate esters. The polymerization mixture remained homogeneous throughout the reaction and high molecular weight polyquinoline was obtained. Although the exact nature of the active catalyst species is not clear, it is believed that solubility of the growing polymer is aided by a low degree of protonization due to the relatively low concentration of acidic species.

The reaction of *m*-cresol with polyphosphoric acid (PPA) also provided an effective solvent system for high molecular weight polymers. The solvent system is highly acidic and highly protonated polyquinoline (**12**) is formed. Since **12** was not soluble in *m*-cresol alone, the polymer precipitated within 4–5 h from solvent systems in which the proportion of *m*-cresol to PPA was high (i.e., 7:1 or 8:1). Polymer did not precipitate from 3:1 *m*-cresol:PPA mixtures until after 27 h of reaction and molecular weights comparable to the polymers formed in *m*-cresol/phosphorus pentoxide were obtained. Increasing the PPA concentration to 1:1 or failure to allow the PPA and *m*-cresol to react to form a homogeneous mixture resulted in low molecular weight polymer. Polymerizations in PPA alone also afforded dark polymers of low molecular weight even though the polymer was soluble throughout the reaction. Thus, in the latter two systems in which the concentration of

Table I
Polymerizations of 6 with 11a to give Polyquinoline 13a

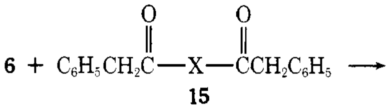
Run No.	Solvent/catalyst[a]	Wt % monomer	Heating, °C/h	Polymer color	η_{inh}[b]
1	MC/P_2O_5	7.5	125/20	White	0.66
2	MC/P_2O_5	7.5	100/11, 135/30	White	0.56
3	MC/PPA (3:1)	7.5	125–130/63[d]	White	0.60–0.62
4	MC/PPA (3:1)[c]	7.5	95/9, 170/5, 195/24	Tan	0.24
5	MC/PPA (3:1)	7.5	110/10, 160/7, 195/55	White	0.57
6	MC/PPA (8:1)	3	120/4,[e] 180/18	Gray	0.2
7	MC/PPA (7:1)	7.5	140/19[e]	Tan	0.47
8	MC/PPA (1:1)[c]	7.5	90/3, 120/6, 155/18, 190/45	Brown	0.2
9	PPA	4	120/3, 155/13	Brown	0.2
10	Sulfolane/H_3PO_4	10	100–130/5,[f] 130/16, 170/24	Yellow	0.38

[a] PPA = polyphosphoric acid, MC = *m*-cresol. [b] Determined in *m*-cresol at 25.0 °C, C = 0.500 g/dl. [c] MC/PPA mixture was not premixed to homogeneity. [d] Precipitation occurred after 24 h. [e] Precipitation occurred after 4 h. [f] Precipitation occurred after 5 h.

acidic catalyst species was highest, the attainable molecular weight may be limited by side reactions such as acetyl trimerization.[11] In the early stages of the polymerization when the concentration of acetyl groups is high, this side reaction would lead to stoichiometric depletion of acetyl groups and thus lower the possible molecular weight. The polymerization of **6** with **11a** was also carried out in sulfolane with phosphoric acid added as the catalyst. However, precipitation of the protonated polymer **12a** occurred within 5 h of reaction affording only moderate molecular weight polymer **13a.**

The polymerizations in *m*-cresol with either phosphorus pentoxide or PPA could be effectively carried out at 125–130 °C. The higher temperatures of 170 or 195 °C which were used in polymerizations during early stages of this work afforded polymers of lower molecular weight that were darker in color than those prepared at 125–130 °C.

Polymerizations were also carried out in *m*-cresol/PPA in which the aromatic moiety in monomer 11 was varied. This afforded polyquinolines **13b** and **13c** with *p,p*′-biphenylene and *m*-phenylene linkages in the main chain in addition to polymer **13a.** Polymers **14** with *p,p*′-biphenylene and *p*-phenylene linkages and with pendant phenyl groups in the 3 and 3′ positions were prepared by the reaction of **6** with **15b** and **15f,** respectively. Attempts were also made to prepare polyquinolines from the reaction of **6** with 2,6-diacetylpyridine (**11d**) and 2,3-butanedione (**11e**). It is believed that 2,6-diacetylpyridine complexes with the acidic solvent and thus does not react in the normal fashion. The reaction of **11e** with **6** did not occur below 90 °C and monomer was lost when heated



$$6 + C_6H_5CH_2\overset{\overset{\displaystyle O}{\|}}{C}—X—\overset{\overset{\displaystyle O}{\|}}{C}CH_2C_6H_5 \longrightarrow$$

15

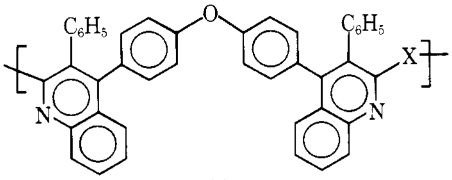


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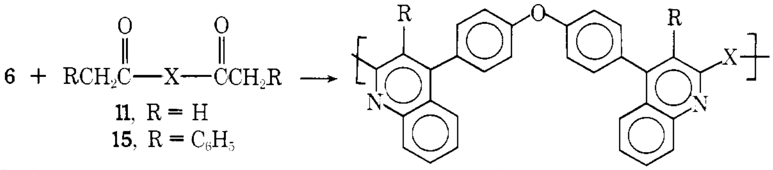
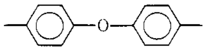
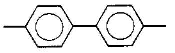
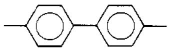
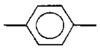
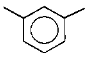
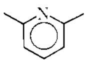
Table II
Polymerizations of Monomer 6 with Various Diacetyl Monomers 11 and Diphenacetyl Monomers 15



	R	Conditions,[a] °C/h	$[\eta]$[b]	Solubility	
				$CHCl_3$	*m*-Cresol
	H	125/50, 130/13	0.62	S	S
	H	110/5,[c] 120/12, 150/24	0.38	S	S
	C_6H_5	110/10, 140/72	0.57	I	S
	C_6H_5	125/42, 145/16	0.26	I	S
	H	100/16, 130/45	0.36	S	S
	H	100/18, 135/48	0.08	S	S
Nil	H	25/20, 50/20, 50–100/12, 120/16	No polymer		

[a] 7.5% monomer concentration in 3/1 *m*-cresol/PPA. [b] Intrinsic viscosities in *m*-cresol at 25 °C. [c] Precipitation of polymer occurred.

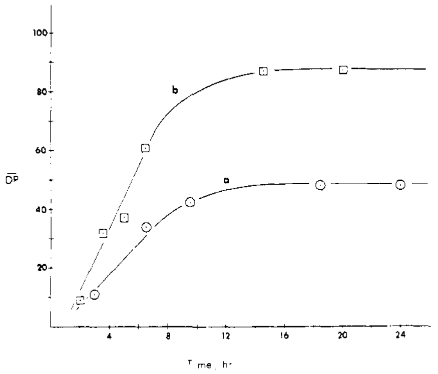


Figure 1. Kinetics of the Friedländer polymerization: (a) *m*-cresol/PPA; (b) *m*-cresol/phosphorus pentoxide.

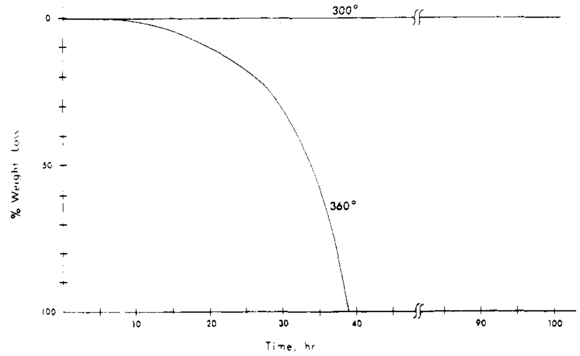


Figure 2. Isothermal aging of polyquinoline **13a**.

Table III
Solution Properties of Polyquinoline 13a

$[\eta]^a$	$(\pi/c)_{c\to 0}{}^b$	$\overline{M}_n{}^c$	$\overline{DP}{}^d$	A_2,^{e} (cm^3 mol)/g^2
0.73	0.21	78 900	266	7.0×10^{-7}
0.63	0.32	48 900	166	4.1×10^{-7}
0.51	0.47	35 300	120	8.0×10^{-7}

[a] In chloroform at 25 °C. [b] Osmotic pressure (π) measured with c ranging from 1.0 to 9.12 g/l. [c] $\overline{M}_n = RT/(\pi/c)_{c\to 0}$. [d] $\overline{DP} = 2(\overline{M}_n/M_0)$ where M_0 = 590.65 for **13a**. [e] Second virial coefficient, $A_2 = (1/RT)/(\mathrm{d}(\pi/c)/\mathrm{d}c)$.

above its boiling point. Sealed tube conditions are necessary for this reaction. Polymerization conditions and properties of the resultant polymers are listed in Table II.

Kinetics of the Friedländer Polymerization. The polymerizations of **6** with **11a** in both *m*-cresol/phosphorus pentoxide and *m*-cresol/polyphosphoric acid to give polyquinoline **13a** were employed in the kinetic studies. This step-growth polymerization should follow second-order kinetics and obey the expression $\overline{DP} = C_0K't + 1$ where $\overline{DP}$ is the average degree of polymerization, C_0 is the initial concentration of functional groups of one type (i.e., either acetyl or *o*-amino ketone) in mole/kilogram of solvent, t is time, and K' is the rate constant. The rate constant K' includes the concentration of the catalyst which is assumed to be constant within each polymerization run. It should be noted, however, that since the nature of the active catalyst species is not certain, care must be taken in comparing numerical values of K' for different solvent–catalyst systems.

A plot of $\overline{DP}$ vs. time should yield a straight line with a slope of C_0K' and an intercept of 1. The average degree of polymerization was obtained by using the Mark–Houwink equation $[\eta] = K(\overline{M}_n)^a$ and $\overline{DP} = 2(\overline{M}_n/M_0)$ where M_0 is the molecular weight of a repeating unit. The constants $K = 5.5 \times 10^{-3}$ and $a = 0.44$ for the Mark–Houwink equation were determined from number-average molecular weights ($\overline{M}_n$) (determined by osmotic pressure measurements on fractionated samples of **13a** in chloroform) and intrinsic viscosities ($[\eta]$) (chloroform). This allowed the kinetic data to be taken from intrinsic viscosity measurements (Figure 1).

A least-squares analysis was applied to the initial three data points of the *m*-cresol/PPA polymerization (curve a) and the initial four points of the *m*-cresol/phosphorus pentoxide polymerization (curve b). From a linear dependence of $\overline{DP}$ vs. time in the early stages of reaction, second-order rate constants were obtained for the Friedländer polymerization. The value of K' for the polymerization in *m*-cresol/PPA was found to be 5.6×10^{-3} kg/(mol s), with a value of 1.1×10^{-2} kg/(mol s) for the reaction in *m*-cresol/phosphorus pentoxide. Recalling that the value of K' includes the concentration of the catalyst species, the two polymerizations could be compared with respect to rate per mole of phosphorus added. Since the amount of phosphorus in both polymerizations was equal, either the phosphorus pentoxide system was inherently faster or more of the active catalyst species were being formed than in the polyphosphoric acid system. The reason for the termination of the reaction in *m*-cresol/PPA at a $\overline{DP}$ of approximately 48 could be due to small amounts of impurities in the monomers or the occurrence of side reactions in the more highly acidic system. The negative intercepts in Figure 1 were due to the slower rate of reaction in the first hour when the actual temperature was below the specified reaction temperature.

Solution Properties of 13a. Dilute solution properties of fractionated samples of polymer **13a** in chloroform were determined by high-speed membrane osmometry and by dilution viscometry. Table III lists the number-average molecular weights which were determined for the three fractionated samples. From these data the Mark–Houwink relationship was calculated to be $[\eta] = 5.5 \times 10^{-3}[\overline{M}_n]^{0.44}$. The low exponent a value of 0.44 (a = 0.5 for a random coil in a theta solvent) indicated a low degree of polymer–solvent interaction with minimal chain extension. This behavior is similar to that observed with phenylated polyphenylenes and is consistent with the formation of metastable aggregates with configurations resembling randomly branched molecules.[12] The low value of the second virial coefficient, A_2, is also consistent with these observations (Table III). A significant amount of scatter was obtained in the osmotic pressure measurements for the intermediate molecular weight sample ($[\eta]$ = 0.63) and this must be considered the reason that the value of A_2 for this sample does not correspond more closely with the other two values. *m*-Cresol was found to be a better solvent for the polymer than was chloroform as evidenced by the higher intrinsic viscosity for a given sample of **13a** (e.g., 0.62 vs. 0.44). Polymer **13a** was soluble to the extent of 15–20 wt % in chloroform, *m*-cresol, and highly acidic solvents. Tough, flexible films of polymer **13a** were formed from concentrated chloroform or *m*-cresol solutions.

The phenylated polyquinolines **14b** and **14f** show interesting solubility behavior in chloroform. Polymer **14b** was completely soluble in chloroform directly after precipitation from the polymerization solvent. When a chloroform solution of the polymer was then precipitated into Skelly B a chloroform-insoluble fraction (10–15%) was formed. The entire sample became chloroform insoluble after two additional reprecipitations. The polymer could then be dissolved completely in *m*-cresol and precipitated into Skelly B, and the polymer was again soluble in chloroform. Polyquinoline **14f**

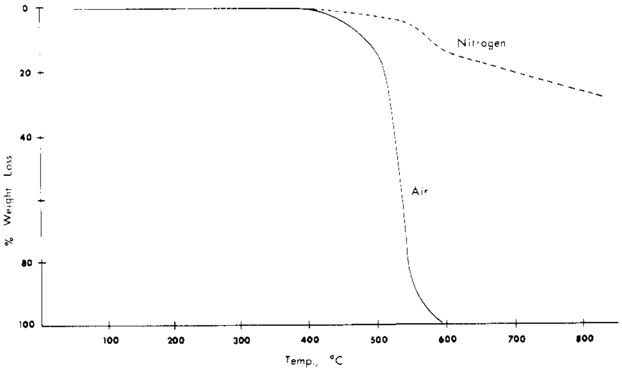


Figure 3. Thermogravimetric analysis of polyquinoline **13a**.

showed similar solubility behavior. It is believed that the insolubility occurred as a result of the formation of metastable aggregates in chloroform solution which were chloroform insoluble after precipitation. The degree of crystallinity was low since the precipitated polymer was shown to be essentially amorphous by x-ray diffraction. *m*-Cresol was a sufficiently good solvent to dissociate the polymer aggregates thus regenerating the chloroform-soluble material. This behavior is in direct contrast to the effect of pendant phenyl groups on other aromatic polymers,[13,14] in which the pendant phenyl groups impart greater solubility. The greater tendency of **14b** and **14f** to form polymer aggregates when compared to the nonphenylated polymers **13** is believed to be due to the restriction in rotation in the polymer chain caused by three adjacent aromatic units on the quinoline ring.

Thermal Analysis. The heating-rate independent glass transition temperature of **13a** was found to be 251 °C with a crystalline transition at 480 °C.[7,15] Since the decomposition temperature of **13a** was above 510 °C, extrusion through a large bore capillary at 430 °C to afford a fiber with a diameter of 1 mm was possible. Stability of the material toward cross-linking under the extrusion conditions was indicated by retention of chloroform solubility. Due to a high melt viscosity, extrusion of fibers of finer denier was not possible. This fiber was then drawn at 270–280 °C under mild tension. The X-ray diffraction patterns of the stretched and unstretched polymer fibers showed an increase in crystallinity after drawing.

When a thin film of polymer **13a** was heated at 300 °C in circulating air for 100 h no weight loss was observed. However, when films were heated to 360 °C in air, 10% weight loss occurred after 21 h and decomposition was complete after 39 h (Figure 2). Thermogravimetric analysis at a heating rate of 5 °C/min of polyquinoline **13a** showed a break in air at 510 °C and 25% weight loss in nitrogen at 800 °C (Figure 3).

Experimental Section

4-(2-Carboxybenzoyl)diphenyl Ether (7). The reaction of 29.6 g (0.200 mol) of phthalic anhydride, 17.0 g (0.100 mol) of diphenyl ether, and 53.3 g (0.400 mol) of anhydrous powdered aluminum chloride in 270 ml of 1,1,2,2-tetrachloroethane and 60 ml of nitrobenzene afforded a 75% yield of **7** as white needles: mp 161–163 °C (lit.[16] mp 163.5 °C).

Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 76.35; H, 4.53.

4,4′-Bis(2-carboxybenzoyl)diphenyl Ether (8). Method a. The diacid **8** was prepared by the published procedure[17] with several modifications. To an ice-cooled mixture of 186 g (1.26 mol) of phthalic anhydride, 102 g of diphenyl ether (0.600 mol), 650 ml of 1,1,2,2-tetrachloroethane, and 85 ml of nitrobenzene was added 400 g (3.00 mol) of powdered anhydrous aluminum chloride over a 1.5-h period. Under a slow stream of nitrogen the red mixture was allowed to warm to room temperature with vigorous stirring. Additional tetrachloroethane (100 ml) was added after 12 h due to difficulty in effectively stirring the viscous mixture. After 24 h, the dark red mixture was poured into 2 l. of ice-water containing 500 ml of concentrated hydrochloric acid. The resulting precipitate was dissolved in 5% sodium hydroxide and the organic layer was allowed to separate on standing. The aqueous layer was decanted and acidified with 6 N hydrochloric acid to give a white precipitate. The product was recrystallized from aqueous acetic acid with the addition of activated charcoal to give 212 g (77%) of **8** as white needles: mp 263–267 °C (lit.[17] mp 265 °C); ir (KBr) 1715 and 1675 (C═O) and 1245 cm^{-1} (COC).

Anal. Calcd for $C_{28}H_{18}O_7$: C, 72.10; H, 3.89. Found: C, 72.30; H, 3.84.

Method b. To a mixture of 13.5 g (92.0 mmol) of phthalic anhydride, 200 ml of 1,1,2,2-tetrachloroethane, and 30.6 g (230 mmol) of anhydrous aluminum chloride was added 15.0 g (46.0 mmol) of **7** in 60 ml of tetrachloroethane. The solution was stirred for 17 h at room temperature and then an additional 24 h at 50 °C. The product was then hydrolyzed and purified as described in method a to give 14 g (67%) of **8**: mp 259–262 °C.

Pseudo-4,4′-bis(2-chloroformylbenzoyl)diphenyl Ether (9). To 39 g (84 mmol) of **8** was added 90 ml of thionyl chloride. After 18 h of reflux the pale orange solution was concentrated on a rotary evaporator which was fitted with a calcium chloride drying tube. Dry benzene (4 × 30 ml) was added and removed by distillation under reduced pressure in order to ensure complete removal of the thionyl chloride. Benzene (100 ml) was added to give an orange solution which was frozen and then freeze-dried under reduced pressure to afford a pale orange solid: mp 122–133 °C; ir (KBr) 1800 (lactone C═O), 1715 (carboxyl C═O), 1670 (ketone C═O), and 1250 cm^{-1} (COC). The absorptions at 1715 and 1670 cm^{-1} indicated some hydrolysis during ir analysis: mol wt calcd 502; mass spectrum (70 eV) *m/e* (rel intensity) 469 (2) [(P + 2) − ^{35}Cl], 467 (5), 432 (22), 301 (32), 188 (61), 167 (39), 37 (49), 35 (100). **9** was used for the subsequent reaction without further purification.

4,4′-Bis(2-carbamylbenzoyl)diphenyl Ether (10). The bis(pseudoacid chloride) **9** which was prepared from 39 g (84 mmol) of **8** was dissolved in 250 ml of cold, freshly distilled, *N*-methyl-2-pyrrolidinone. Ammonia gas was bubbled through the solution while cooling in an ice bath such that the temperature was maintained at 25 °C for 15 min. The ammonia gas was then bubbled through the stirred solution for an additional hour while the temperature was maintained at 0–5 °C. The mixture was allowed to stand for 6 h and then poured into 2 l. of water containing 20 g of sodium chloride. The resultant tan precipitate solidified to a hard mass upon cooling. The product was pulverized, washed with water and with ethanol, and allowed to air dry to give 32.5 g (85%) of **10**: mp 195–200 °C (slow decomposition at temperatures >100 °C); ir (KBr) 1700 (broad C═O) and 1245 cm^{-1} (COC). Due to the lack of suitable recrystallization solvent **10** was used in the following preparation without further purification.

4,4′-Bis(2-aminobenzoyl)diphenyl Ether (6). To a cooled solution of 42 g (740 mmol) of potassium hydroxide in 510 ml of water was added 32 g (69 mmol) of **10** to give a white slurry. Sodium hypochlorite (224 ml, 155 mmol, 5.25% aqueous solution) was added dropwise over a 25-min period while maintaining the temperature between 5 and 10 °C. The mixture was stirred for 10 min at 5 °C and then heated on a steam bath to 85 °C over a 15-min period. Precipitation of the bright yellow product occurred when the temperature reached 80 °C. The mixture was heated for an additional hour at 80–90 °C and was cooled and filtered to give 25 g (89%) of **6** as a yellow powder: mp 142–144 °C. Column chromatography on silica gel gave solutions of pure monomer near the solvent front by elution with chloroform. Recrystallization from methanol/2% benzene afforded yellow hexagonal prisms: mp 146–147.5 °C; ir (KBr) 3415, 3340 (NH_2), 1620 (*o*-amino C═O) and 1245 cm^{-1} (COC); mass spectrum (70 eV), m/e (rel intensity) 408 (7), 407 (23), 406 (18), 120 (23), 28 (100); see Table IV for ^{13}C NMR data.

Anal. Calcd for $C_{26}H_{20}N_2O_3$: C, 76.46; H, 4.93; N, 6.86. Found: C, 76.42; H, 5.06; N, 6.84.

4,4′-Diacetyldiphenyl ether (11a) was synthesized by the acetylation of diphenyl ether with acetyl chloride and aluminum chloride in carbon disulfide[18,19] and was recrystallized from ethanol to give colorless hexagonal platelets: mp 101.5–102.5 °C (lit.[19] mp 102–103 °C). See Table IV for ^{13}C NMR data.

4,4′-Diacetylbiphenyl (11b) was prepared by the acetylation of biphenyl[20] and was recrystallized from benzene and methanol to give colorless platelets: mp 191–192 °C (lit.[20] mp 189–191 °C).

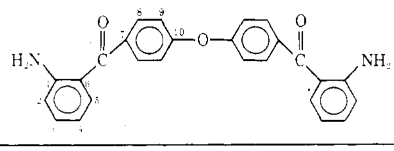
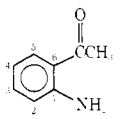
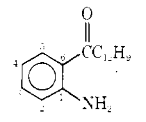
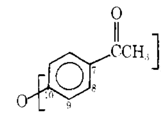
***m*-Diacetylbenzene (11c)** was purified by distillation under reduced pressure prior to use: mp 31–32 °C (lit.[21] mp 31–32 °C).

2,6-Diacetylpyridine (11d) was purified by recrystallization from isooctane to give white needles: mp 81–82.5 °C (lit.[22] mp 79 °C).

2,3-Butanedione (11e) was distilled at atmospheric pressure prior to use: bp 86–87 °C (lit.[23] bp 89–90 °C).

1,4-Diphenacetylbenzene (15f) was prepared by hydrolysis of the product of the reaction between benzylmagnesium chloride and

Table IV
^{13}C-NMR Chemical Shifts for 4,4′-Bis(2-aminobenzoyl)diphenyl Ether (6) and Related Compounds

C	 Obsd (Calcd^a)	Off-Res^b	 Obsd^c	 11a Obsd^c	 Obsd^c
C=O	197.5	s	200.7	198.6	196.4
1	150.8 (148.2)	s	150.8	150.9	
2	115.4 (115.2)	d	115.4	115.5	
3	134.1 (133.0)	d	134.4	134.4	
4	117.1 (118.5)	d	117.3	117.1	
5	131.6^d (131.1)	d	132.1	134.2	
6	118.1 (124.6)	s	118.0	118.2	
7	135.4 (132.2)	s			133.1
8	131.6^d (131.2)	d			130.8
9	118.3 (113.9)	d			118.7
10	158.9 (163.6)	s			160.2

^{a} Based on tabulated ^{13}C substituent effects on benzene.[26] ^{b} Off-resonance decoupling experiment, s = singlet, d = doublet. ^{c} Calculated shifts are the same as corresponding carbons in column 1. ^{d} Overlapping resonance.

terephthalonitrile and recrystallized from ethyl acetate:[24] mp 179–180 °C (lit.[24] mp 179–180 °C).

1,4-Diphenacetylbiphenyl (15b) was prepared by a procedure analogous to the preparation of **15f** starting from 4,4′-dicyanobiphenyl and recrystallization from methylene chloride:[25] mp 235–236 °C (lit.[25] mp 225.5–226.5 °C).

4-(2-Aminobenzoyl)biphenyl (16) was prepared as a spectroscopic model for **6** in a manner analogous to the synthesis of **6**. The monoadduct of the Friedel–Crafts reaction of phthalic anhydride with biphenyl was converted to the ketoamide via the pseudoacid chloride, with subsequent rearrangement to the ketoamine **16**: mp 146–147 °C; ir (KBr) 3485 and 3350 (NH) and 1622 cm^{-1} (*o*-amino C=O); mass spectrum (70 eV) *m/e* (rel intensity) 273 (80), 272 (100), 196 (31), 152 (60), 120 (36), 92 (35); see Table IV for ^{13}C NMR data.

Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.46; H, 5.71; N, 4.96.

2,4-Diphenylquinoline (17) was prepared from *o*-aminobenzophenone and acetophenone with an acid catalyst:[6] mp 112 °C (lit.[27] mp 114 °C); mass spectrum (70 eV) *m/e* (rel intensity) 281 (100), 202 (55), 176 (45), 127 (15), 77 (30); see Table V for ^{13}C NMR data.

Anal. Calcd for $C_{21}H_{15}N$: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.55; H, 5.40; N, 4.95.

4,4′-Bis(2-phenyl-4-quinolyl)diphenyl Ether (18). To 20 ml of *m*-cresol was added 9.12 g of polyphosphoric acid and the mixture was heated under a nitrogen atmosphere for 1 h at 150 °C to give a clear solution. The solvent was cooled to 90 °C and 1.00 g (2.45 mmol) of **6**, 1.76 g (14.7 mmol) of acetophenone, and 8 ml of *m*-cresol were added. After 30 h at 120 °C the solution was allowed to cool and was poured into 350 ml of ethanol containing 50 ml of triethylamine. Addition of 250 ml of water caused the formation of a white precipitate. The white solid was filtered, washed with water and hot methanol, and dried to afford 1.40 g (99%) of **18**. The model compound was dissolved in chloroform and precipitated into methanol: mp 193–197 °C; ir (KBr) 1600, 1495, 1245 cm^{-1} (COC); Calcd mol wt 576, mass spectrum (70 eV) *m/e* (rel intensity) 576 ± 1 (100), 280 (43), 267 (23), 202 (8); see Table V for ^{13}C NMR data.

Anal. Calcd for $C_{42}H_{28}N_2O$: C, 87.47; H, 4.89; N, 4.86. Found: C, 86.37; H, 4.79; N, 4.81.

Polymerizations. Typical polymerizations were carried out as follows.

In *m*-Cresol/Polyphosphoris Acid. A mixture of 17.2 g of PPA and 30 ml of *m*-cresol was stirred under a nitrogen atmosphere for 30 min at 80 °C and for 1 h at 100 °C after which time the solution was colorless and homogeneous. The solvent was then allowed to cool to room temperature and 3.4330 g (8.4047 mmol) of **6** and 2.1372 g (8.4047 mmol) of **11a** were added all at once from a beaker. The beaker was rinsed into the reaction flask with an additional 21 ml of *m*-cresol to ensure complete transfer of the monomers and to afford a 7.5 wt % solution of the monomers in 3/1 *m*-cresol/PPA. The solution was then heated at 125–130 °C for 63 h under a static nitrogen atmosphere. After 27 h at 125 °C a small amount of yellow precipitate had formed which remained for the duration of the reaction.

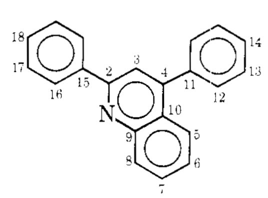
The reaction mixture was allowed to cool and then was poured into 1 l. of ethanol containing 50 ml of triethylamine to give a white fibrous material. The polymer was filtered, washed with ethanol, dissolved in 750 ml of chloroform, and precipitated into 2 l. of Skelly B. The polymer was filtered and dried for 5 h at 110 °C under reduced pressure to give 4.73 g (95.3%) of **13a**: ir (film) 3060 (aromatic CH), 1597 (aromatic CC), and 1245 cm^{-1} (COC); no carbonyl absorption was detectible, [η] in *m*-cresol at 25.0 °C, 0.62 dl/g; see Table V for ^{13}C NMR data. The elemental analysis is given in Table VI.

In *m*-Cresol/Phosphorus Pentoxide. To 8.5 g of phosphorus pentoxide in a flask cooled in an ice bath was added 20 ml of *m*-cresol under a nitrogen atmosphere. The mixture was stirred for 3 h at 110 °C to afford a clear homogeneous solution. After allowing the solvent to cool to room temperature 2.0423 g (5.0000 mmol) of **6** and 1.2714 g (5.0000 mmol) of **11a** were added and rinsed into the flask with an additional 15 ml of *m*-cresol. The amber solution was stirred at 100 °C for 11 h and then at 135 °C for 30 h.

After allowing the reaction mixture to cool, the product was obtained as a fibrous off-white material by pouring the mixture into 70 ml of ethanol and 50 ml of triethylamine. After stirring the mixture for 3 h, the polymer was filtered, washed with ethanol, dissolved in chloroform, and precipitated into Skelly B. The polymer was dried under reduced pressure for 12 h at room temperature and then for 3 h at 110 °C to give 2.9 g (98%) of **13a**: [η] in *m*-cresol at 25.0 °C, 0.66 dl/g.

In Sulfolane/Phosphoric Acid. To 0.8169 g (2.000 mmol) of **6** and 0.5086 g (2.000 mmol) of **11a** was added 17 ml of freshly distilled sulfolane. The mixture was stirred to effect solution and then 8 drops of 85% phosphoric acid was added under a stream of nitrogen. The yellow solution was then heated between 110 and 130 °C for 5 h. At this time a yellow precipitate began to form. The reaction mixture was heated at 130 °C for an additional 16 h and then at 170 °C for 24 h; however, the yellow precipitate remained. The mixture was allowed to cool and then poured into 500 ml of 95% ethanol to give a yellow

Table V
^{13}C-NMR Chemical Shifts for Polymer 13a and Related Compounds



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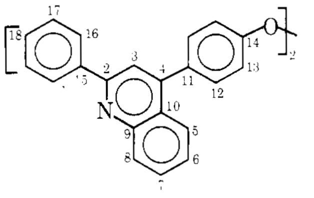
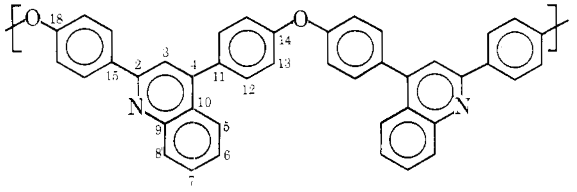


18



13a

	Obsd (Calcd[a])		
C	**17**	**18**	**13a**
2	157.8 (164.6)	157.2 (164.6)	157.4 (164.6)
3	119.3 (119.5)	119.3 (119.5)	119.2[c] (119.5)
4	149.1 (149.9)	148.3 (149.9)	148.4 (149.9)
5	129.3 (129.2)	129.3 (129.2)	129.2 (129.2)
6	126.3 (127.0)	126.4 (127.0)	126.3 (127.0)
7	129.5 (129.9)	129.5 (129.9)	129.7 (129.9)
8	130.1 (130.3)	130.2 (130.3)	130.2 (130.3)
9	148.8 (149.9)	148.8 (149.9)	148.9) (149.9)
10	125.7 (126.6)	125.7 (126.6)	125.7 (126.6)
11	138.3 (141.6)	133.6 (133.9)	133.7 (133.9)
12	128.3 (127.4)	131.2 (128.4)	131.2 (128.4)
13	128.5 (128.9)	119.1 (114.5)	119.2[c] (114.5)
14	125.5[b] (127.3)	156.8 (158.7)	156.2 (158.7)
15	139.6 (141.6)	139.6 (141.6)	135.0 (133.9)
16	127.5 (127.4)	127.5 (127.4)	
17	128.8 (128.9)	128.8 (128.9)	
18	125.5[b] (127.3)	125.4 (127.3)	158.3 (158.7)

[a] See ref 24. [b] Overlapping resonances. [c] Overlapping resonances.

Table VI
Elemental Analyses of Polyquinolines

	Calcd, %			Found, %		
Polymer	C	H	N	C	H	N
13a	85.40	4.44	4.74	85.30	4.56	4.72
13b	87.78	4.56	4.88	86.78	4.62	4.64
13c	86.72	4.45	5.62	85.98	4.49	5.43
14b	89.23	4.71	3.85	88.14	4.77	3.62
14f	88.59	4.65	4.30	85.50	4.74	4.19

Table VII
Kinetic Data for the Friedländer Polymerization

Sample No.	Reaction time, h	$[\eta]$[b]	$\overline{M}_n \times 10^{-4}$ [c]	$\overline{DP}$[d]
m-Cresol/PPA[a]				
1	3	0.19	0.31	11
2	6.5	0.32	1.02	35
3	9.5	0.35	1.26	42
4	18.5	0.37	1.43	48
5	24.5	0.36	1.34	46
Bulk	48	0.36	1.34	46
m-Cresol/P_2O_5[e]				
1	2	0.18	0.29	10
2	3.5	0.31	0.94	32
3	5	0.33	1.10	37
4	6.5	0.41	1.80	61
5	14.5	0.48	2.57	87
6	20	0.48	2.57	87
Bulk	38	0.48	2.57	87

[a] C_0 = [acetyl functions] = [*o*-aminoketone functions] = 0.244 mol/kg of solvent; reaction temperature = 130 °C. [b] Intrinsic viscosity in chloroform at 25.0 °C. [c] Calculated from the Mark–Houwink equation, $[\eta] = 5.5 \times 10^{-3} \times M_n^{0.44}$. [d] Calculated from M_n given that $\overline{DP} = 2M_n/M_0$ where M_0 = 590.65 for polymer **13a**. [e] C_0 = 0.26 mol/kg of solvent; T = 127 °C.

powder. The polymer was washed with dilute aqueous sodium hydroxide, water, and ethanol to afford 1.1 g (94%) of **13a** as a light yellow powder: $[\eta]$ in *m*-cresol at 25.0 °C; 0.38 dl/g.

Additional polymerizations were carried out with other diacetyl monomers in *m*-cresol and polyphosphoric acid by similar procedures and are listed in Table III. Elemental analyses are given in Table VI.

Polymerization Kinetics in *m*-Cresol/PPA. Polymer **13a** was prepared as described previously using 23.000 g (56.309 mmol) of **6** and 14.3188 g (56.309 mmol) of **11a** in a premixed solution of 115 g of PPA and 345 g of *m*-cresol with the following modifications. A thermometer was immersed in the polymerization mixture and the reaction flask was placed in an oil bath at 130 °C immediately after addition of the monomers; however, the internal temperature did not equilibrate at 130 ± 3 °C until after 1 h of reaction time. Samples (8 ml each) were removed with a pipet at specified intervals (Table VII) and were precipitated into 300 ml of ethanol and 50 ml of triethylamine. The samples were then washed with ethanol and dried at 110 °C under reduced pressure (0.5 Torr) for a minimum of 6 h. Intrinsic viscosities were measured in chloroform from extrapolation of inherent and relative viscosities at zero concentration. The data are presented in Table VII and plotted in Figure 1, curve a.

Polymerization Kinetics in *m*-Cresol/Phosphorus Pentoxide. Polymer **13a** was prepared as described for polymerizations in *m*-cresol/phosphorus pentoxide using 20.4230 g (50.000 mmol) of **6** and 12.7145 g (50.000 mmol) of **11a** in a premixed solution of 84 g of phosphorus pentoxide in 300 g of *m*-cresol. The flask was placed in an oil bath preheated to 125 °C immediately after addition of the monomers. Stabilization of the internal temperature at 127 ± 3 °C occurred after 1 h of reaction time. Samples (2 ml each) were removed at specified intervals (Table VII) and were precipitated into 150 ml of ethanol and 20 ml of triethylamine. The samples were washed and dried as described in the previous section. The intrinsic viscosities were measured in chloroform. The data are presented in Table VII and plotted in Figure 1, curve b.

Polymer Fractionation. Fractionation of polymer **13a** was carried out by the addition of methanol to the onset of turbidity over a 1-h period to a rapidly stirred solution of 1.0 g of the polymer in 750 ml of chloroform. Upon heating from room temperature to the reflux temperature chloroform (15 ml) was added to afford a clear solution. The solution was cooled to 25 °C over a 2-h period with stirring and then maintained at 25.0 ± 0.05 °C for 18 h. The supernatant liquid (sol phase) was then carefully decanted leaving a thin gel phase on the bottom of the flask. The precipitated polymer was then dissolved in chloroform and reprecipitated into Skelly B. The polymer was filtered and dried to give 0.05 g of a white powder (Sample no. 1). This procedure was repeated twice more by adding methanol to the sol phase allowing very slight turbidity at the reflux stage to give sample no. 2 and 3, weighing 0.36 and 0.20 g, respectively. Sample no. 4 (lowest molecular weight) was obtained by concentrating the sol phase and precipitating the remaining polymer into Skelly B.

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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References and Notes

(1) Taken in part from the Ph.D. thesis of J. F. Wolfe, University of Iowa, December 1975.

(2) P. Friedländer, *Ber.*, **15**, 2572 (1882).
(3) E. A. Fehnel, *J. Org. Chem.*, **31**, 2899 (1966); *J. Heterocycl. Chem.*, **4**, 565 (1967).
(4) W. Bracke, *Macromolecules*, **2**, 286 (1969).
(5) J. K. Stille, E. F. Johnson, J. Wolfe, M. F. Winegardner, and S. Wratten, *Am. Chem. Soc., Div. Org. Coat. Plast. Chem. Pap.*, **33**, 127 (1973).
(6) Y. Imai, E. F. Johnson, T. Katto, M. Kurihara, and J. K. Stille, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 2233 (1975).
(7) W. Wrasidlo, S. O., Norris, J. F. Wolfe, T. Katto, and J. K. Stille, *Macromolecules*, **9**, 512 (1976).
(8) W. Wrasidlo, *J. Polym. Sci., Part A-2*, **9**, 1603 (1971).
(9) M. Ueda, M. Ohkura, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 719 (1974).
(10) M. V. Bhatt, K. M. Kamath, and M. Ravindranathan, *J. Chem. Soc. C*, 1772 (1971).
(11) V. V. Korshak, A. L. Rusanov, T. G. Iremashvili, L. K. Plieva, and T. V. Lekae, *Makromol. Chem.*, **176**, 1233 (1975).
(12) G. C. Berry, J. L. Work, and J. K. Stille, *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(13) P. M. Hergenrother, *J. Macromol. Sci., Rev. Macromol. Chem.*, **6**, 1 (1971).
(14) G. K. Noren and J. K. Stille, *J. Polym. Sci., Part D*, **5**, 385 (1971).
(15) W. Wrasidlo and J. K. Stille, *Macromolecules*, **9**, 505 (1976).
(16) H. Kipper, *Ber.*, **38**, 2492 (1905).
(17) R. L. Broadhead and Y. S. Rao, U.S. Patent 3,592,341, July 1971.
(18) E. M. Shamis and M. M. Dashevskii, *J. Org. Chem. USSR (Engl. Transl.)*, **3**, 1005 (1967).
(19) M. E. B. Jones, D. A. Thornton, and R. F. Webb, *Makromol. Chem.*, **49**, 62 (1961).
(20) H. Tani, F. Toda, and K. Matsumiya, *Bull. Chem. Soc. Jpn.*, **36**, 391 (1963).
(21) P. Ruggli and E. Gassenmeier, *Helv. Chim. Acta*, **22**, 496 (1939).
(22) R. Lukes and M. Pergál, *Chem. Listy*, **52**, 68 (1958); *Chem. Abstr.*, **52**, 1634e (1958).
(23) C. Dufraisse and H. Moureu, *Bull. Soc. Chim. Fr.*, **41**, 1370 (1927).
(24) M. A. Ogliaruso and E. I. Becker, *J. Org. Chem.*, **30**, 3354 (1965).
(25) M. A. Ogliaruso, L. A. Shadoff, and E. I. Becker, *J. Org. Chem.*, **28**, 2725 (1963).
(26) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, p 81.
(27) W. Borsche and F. Sinn, *Justus Liebigs Ann. Chem.*, **538**, 283 (1939).

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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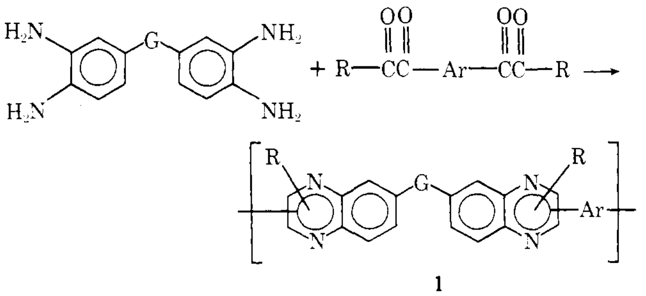
ABSTRACT: The condensation of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether with a series of diacetyl and bis(phenylacetyl) aromatic monomers afforded a series of new high molecular weight polyquinolines. The polymers were prepared in solvents consisting of a premixed solution of *m*-cresol and either polyphosphoric 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.



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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 crys-