Synthesis and Thermal Properties of Aromatic Polymers Containing 3,6-Quinoline Units in the Main Chain

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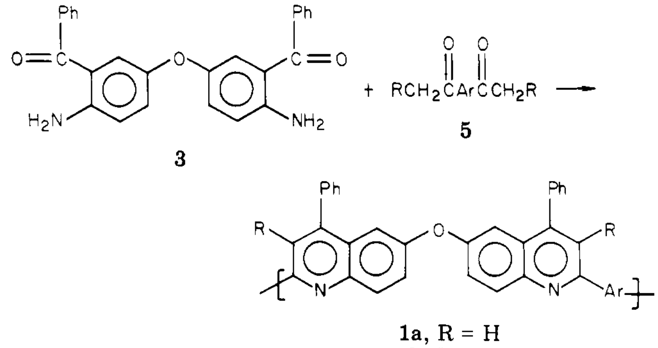
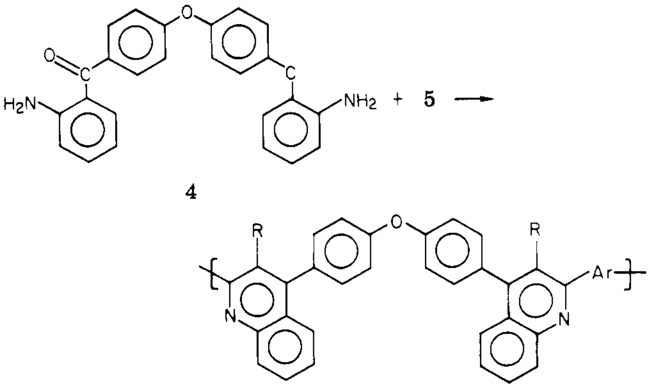
ABSTRACT: The condensation of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether and 4,4′-diamino-3,3′-dibenzoylbiphenyl with a series of bis(phenacyl) monomers in *m*-cresol-di-*m*-cresyl phosphate afforded high molecular weight polyquinolines with varying degrees of flexibility in the polymer main chain. The more flexible polymers exhibited good solubilities in chloroform or *sym*-tetrachloroethane and had glass transition temperatures (T_g) ranging from 255 to 325 °C. The less flexible polymers were soluble in acidic solvents such as *m*-cresol or sulfuric acid and exhibited T_g's ranging from 305–390 °C and crystalline transition temperatures ranging from 475–530 °C. Although initially the polymers were X-ray amorphous (<20%), approximately 30–50% crystallinity could be induced either by precipitation from solution or by annealing above the T_g.

Polyquinolines **1** containing 2,6-quinoline units in the main chain and polyquinolines **2** containing 2,4-quinoline units have been prepared[1,2] by condensation of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**3**) and 4,4′-bis(2-aminobenzoyl)diphenyl ether (**4**), respectively, with various diacetyl and bis(phenylacetyl) aromatic monomers (**5**). The polymerization reaction can be carried out most effectively by using a mixture of *m*-cresol and di-*m*-cresyl phosphate.[3]



1a, R = H
b, R = Ph



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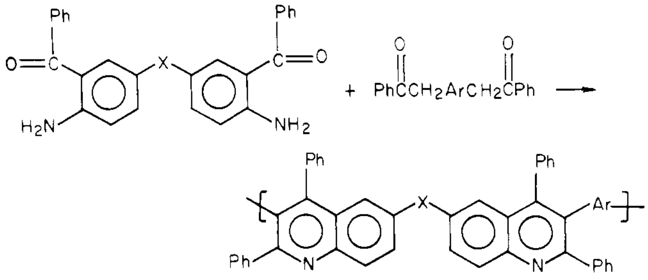
Polyquinolines **1** and **2** are readily soluble in common organic solvents such as chloroform, *sym*-tetrachloroethane and *m*-cresol. In addition, the polymers exhibit excellent thermal stability (TGA) with polymer decomposition temperatures ranging from 520–545 °C in air and from 545–575 °C in nitrogen. A film of polymer **1a** (Ar = 4,4′-$C_6H_4OC_6H_4$) retained fingernail creaseability up to 11 days at 300 °C and up to 6 months at 250 °C in air.[3,4]

Most of the polyquinolines have high crystalline transition temperatures (T_m) but a low degree of crystallinity (<20%).[5,6] Thus the effective use temperature of the polymers is restricted to the glass transition temperature (T_g) which is considerably lower than the decomposition temperature (T_d). This difference is as much as 260 °C for polymer **1a** (Ar = 4,4′-$C_6H_4OC_6H_4$). Increasing the crystallinity of the polymers could raise their use temperatures up to their crystalline transition temperatures, affording polymers with ultimate use temperatures considerably higher than the amorphous materials.

Attempts to increase the crystallinity of polymer **1a** (Ar = 4,4′-$C_6H_4OC_6H_4$) by annealing films above T_g afforded a threefold increase in the storage modulus, but the films remained essentially X-ray amorphous. Thus, the increase in modulus was attributed to an ordering of the amorphous material and not to an increase in crystallinity.[5]

In an effort to prepare polyquinolines which would have good solubilities and show the ability to crystallize by annealing above T_g, polymers containing 3,6-quinoline units in the main chain were synthesized. These polymers can be prepared by the condensation of bis *o*-amino ketones with bis(phenacyl) monomers in place of the bis(phenylacetyl) monomers (**5**). Thus, the synthesis of a number of new bis(phenacyl) monomers was accomplished.



Results and Discussion

Monomer Syntheses. The synthesis of the new bis(phenacyl) monomer, 4,4′-bis(phenacyl)biphenyl (**6**), was carried out by two methods. One involved a Friedel–Crafts reaction of an intermediate diacid chloride with benzene (Figure 1).

The synthesis of 4,4′-diacetylbiphenyl (**7**) was accomplished by treatment of biphenyl with acetyl chloride.[7] The reaction of **7** with sulfur and morpholine gave the intermediate bis(thioacetmorpholide) (**8**), which upon basic hydrolysis followed by acidification afforded a 74% yield of 4,4′-biphenylylbis(acetic acid) (**9**).[8] Bis(acid chloride) **10** was then obtained by treatment of **9** with phosphorus pentachloride. The Friedel–Crafts reaction of **10** with benzene afforded a quantitative yield of crude 4,4′-bis(phenacyl)biphenyl (**6**). Crude **6** exhibited an infrared band at 1695 cm^{-1} characteristic of a phenyl ketone, but purification of the product to monomer grade purity could not be accomplished.

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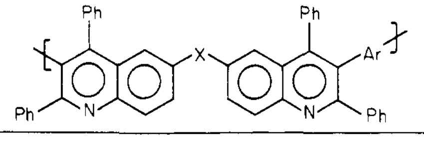
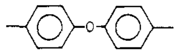
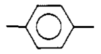
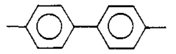
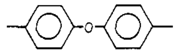
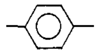
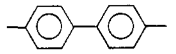
Table I
Properties of Phenylated Polyquinolines



poly-mer	X	Ar	solubility[a]	[η] (solvent), dL/g	T_g, °C		T_c, °C	T_m, °C	TGA[c]		
					DSC	E''_{max}			air	N_2	% wt loss at 800 °C (N_2)
14a	0		$CHCl_3$	1.2 ($CHCl_3$)	255	250			530	575	30
14b	0		$CHCl_3$	0.7 ($CHCl_3$)	312	310			535	570	28
14c	0		TCE[b]	3.6 (*m*-cresol)	325	335			530	550	28
15a	nil		*m*-cresol	0.8 (*m*-cresol)	305	310	415	475	575	580	30
15b	nil		H_2SO_4	0.5 (H_2SO_4)	370		437	550	570	575	25
15c	nil		*m*-cresol	2.4 (*m*-cresol)	390	420		530	570	585	25

[a] Solubility defined as the ability to dissolve 10% by weight of polymer. [b] *sym*-Tetrachloroethane. [c] Onset of decomposition.

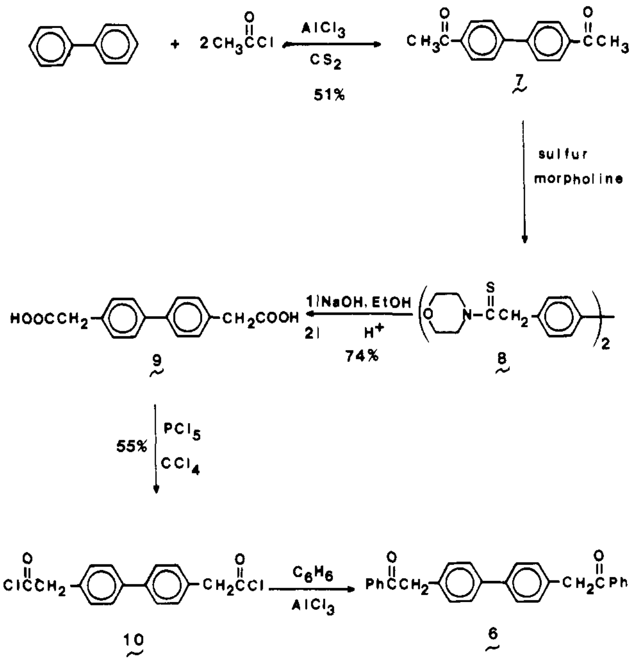


Figure 1. Synthesis of 4,4'-bis(phenacyl)biphenyl (6) from 4,4'-biphenylylbis(acetyl chloride) (10).

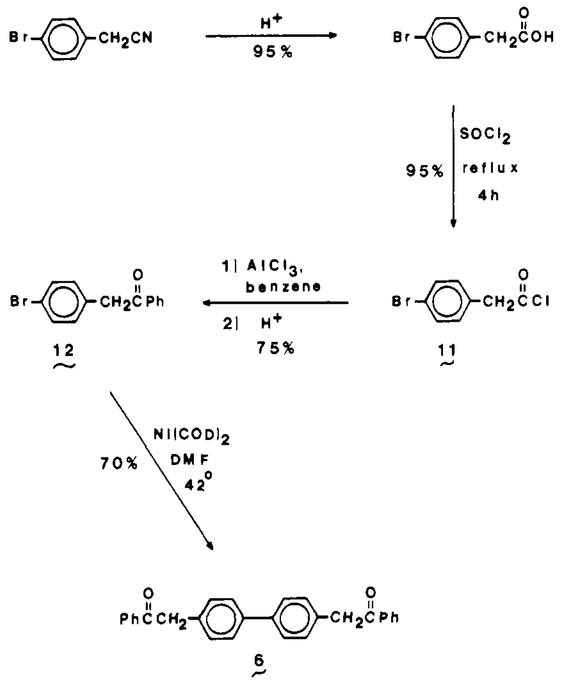


Figure 2. Synthesis of 4,4'-bis(phenacyl)biphenyl (6) from α-(*p*-bromophenyl)acetophenone (12).

A better synthetic procedure for the preparation of 6 involved a nickel-promoted coupling of aryl halides (Figure 2). Hydrolysis of *p*-bromophenylacetonitrile[9] gave the acid which was converted to *p*-bromophenylacetyl chloride (11), isolated (distilled) as a pink oil.[10] Treatment of 11 with benzene and aluminum chloride afforded α-(*p*-bromophenyl)acetophenone (12).[11] The desired monomer 6 was then obtained in a 70% yield by the 1,5-bis(cyclooctadiene)nickel(0)-promoted coupling of 12.

The synthesis of the other bis(phenacyl) monomer, 4,4'-bis(phenacyl)diphenyl ether (13), was accomplished as outlined in Figure 3. Di-*p*-tolyl ether (14) was prepared by a copper-catalyzed nucleophilic displacement reaction between *p*-cresol and *p*-bromotoluene.[12] Free-radical bromination of 14 afforded α-bromo-*p*-tolyl ether (15),[13] which was then treated with 2-lithio-2-phenyl-1,3-dithiane[14] to afford the bis(dithiane) 16. Oxidation of 16 with *N*-bromosuccinimide in a 97% acetone–water solution afforded 4,4'-diphenacyldiphenyl ether (13) in a 10% yield.

Polymer Synthesis. Polymers containing 3,6-quinoline units in the main chain were prepared by the condensation of bis(phenacyl) monomers 6 and 13 and 1,4-bis(phenacyl)benzene with two *o*-amino ketone monomers, 4,4'-diamino-3,3'-dibenzoyldiphenyl ether and 4,4'-diamino-3,3'-dibenzoylbiphenyl,[15] in a *m*-cresol–di-*m*-cresyl phosphate medium at 130–135 °C for 24–48 h (Table I).

Polymers 14 showed improved solubilities over the analogous polyquinolines with the 2,2'-catenation[1] being readily soluble in chloroform or *sym*-tetrachloroethane

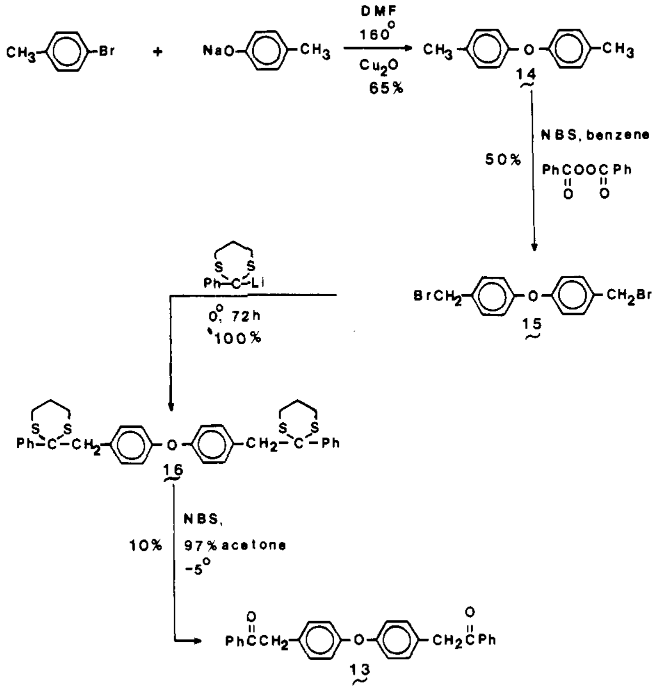


Figure 3. Synthesis of 4,4′-bis(phenacyl)diphenyl ether (13).

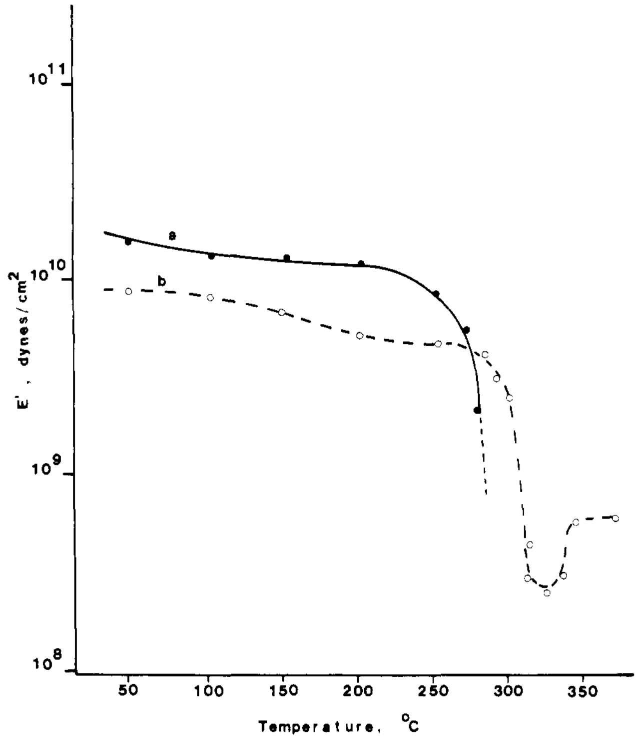


Figure 4. Dynamic storage modulus as a function of temperature for: (a) 14a and (b) 15a.

(TCE). Tough, transparent films of **14a–c** could be cast from 10–15% by weight solutions of the polymers in chloroform, TCE, or *m*-cresol. When preparation of a 10–15% by weight solution of **14c** in chloroform was attempted, the polymer initially went into solution but then slowly precipitated. The solvent was allowed to evaporate slowly, and the resultant thick opaque film was analyzed for crystallinity. From X-ray analysis, the film was estimated to be approximately 50% crystalline, exhibiting very light diffuse halos due to amorphous regions at 9.0 and 4.9 Å and numerous sharp diffraction lines due to crystalline regions, the most intense of which were at 11.4, 8.7, 5.0, 4.5, and 4.0 Å. Thus, polymer **14c** could be crystallized to a moderately high degree from a chloroform solution.

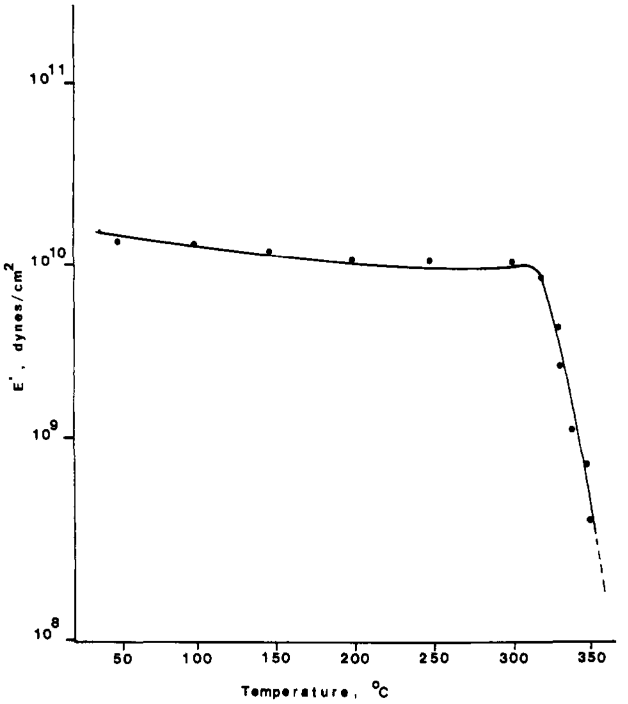


Figure 5. Dynamic storage modulus as a function of temperature for 14b.

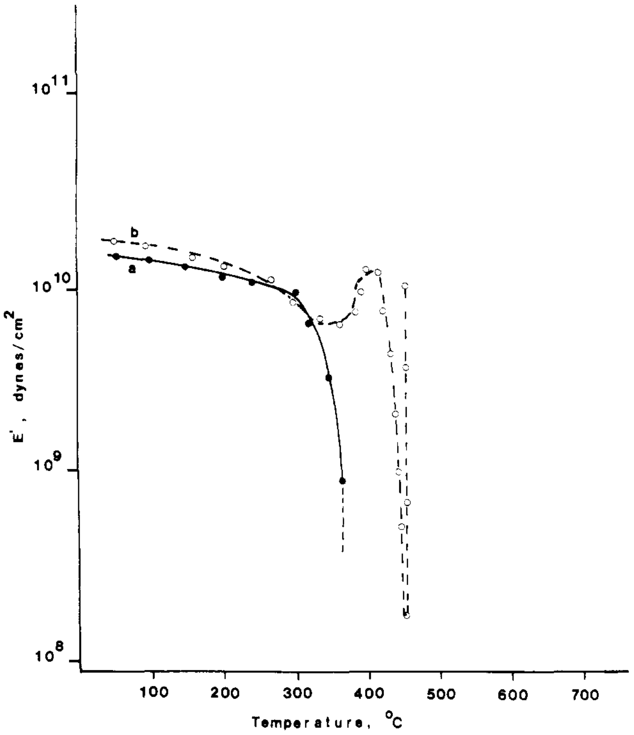


Figure 6. Dynamic storage modulus as a function of temperature for (a) 14c and (b) 15c.

Polymers **15a,c** exhibited good solubilities in *m*-cresol, whereas **15b** exhibited only limited solubility in concentrated sulfuric acid. Films of **15a,c** could be cast from 10% wt solutions of the polymers in *m*-cresol. A film of **15b** could not be obtained due to the polymer's poor solubility.

Thermal Analyses. Pressed powder and film samples of polyquinolines **14** and **15** were analyzed by differential scanning calorimetry (DSC) and by dynamic thermomechanical analysis to obtain information on thermal transitions that occur in the polymers (Table I and Figures 4–6). The glass transition temperatures (T_g) ranged from

255 to 390 °C, with polymers **15** having T_g's 50–65 °C higher than the more flexible polymers **14**. The values of the T_g's [as loss $E''_{\max}$] determined by thermomechanical analysis of films on a Rheovibron Model DDV-II-C were in close agreement with the values obtained by DSC.

Polymers **15** exhibited crystalline transition temperatures (T_m) ranging from 475–530 °C, whereas polymers **14** did not exhibit crystalline transitions. This difference in crystallinity of the polymers apparently is due, at least to some extent, to the variation in the rigidity of the polymer chains, since rigid polymers generally exhibit a higher degree of crystallinity than flexible polymers.[16] The difference in the amount of crystallinity is apparently small though, since both polymers **14** and **15** are essentially amorphous (~15% or less crystallinity by X-ray).

In addition to high crystalline transition temperatures, polymers **15a,b** showed crystallization temperatures (T_c) of 415 and 437 °C. This temperature should occur at a value approximately two-thirds between the T_g and T_m. The value obtained for polymer **15a** was exactly two-thirds between its T_g and T_m, whereas the value for polymer **15b** was only one-third between its T_g and T_m. When polymers **15a** and **15b** were annealed at their respective T_c's for 1 h and then slowly cooled and the DSC scan was run again, the magnitude of the T_g had decreased, and the exotherm corresponding to the T_c was no longer observed. The continued presence of the T_g indicates that the polymers still have amorphous regions which did not crystallize on annealing.

Dynamic thermomechanical analysis showed that polymer **15a** exhibited only a small loss of modulus at its T_g (Figure 4), indicative of the presence of a considerable amount of crystallinity in the polymer. This crystallinity was most likely induced during the measurement of curve b, since the crystallinity of **15a** was initially very low (~15%).

Curve b of Figure 6 was obtained from polymer **15c** by running the scan as usual up to 440 °C and then annealing the polymer at this temperature. Within 15 min, the storage modulus increased from 2.6×10^8 to 1.1×10^{10} dyn/cm^2, which was close to the value that the polymer had at room temperature (1.7×10^{10} dyn/cm^2). This increase in modulus can be attributed to either an increase in crystallinity or an introduction of cross-links into the polymer. Although X-ray analysis was not conducted on the annealed film of **15c**, a powder sample of **15c** exhibited an increase in crystallinity from nearly zero to approximately 30%, after being annealed at 485 °C for 1.5 h. Consequently, the increase in modulus for **15c** may be attributed, at least to some extent, to an increase in crystallinity.

As expected, the polyquinolines synthesized in this work showed outstanding thermal stability both in inert atmospheres as well as in air (Table I). Thermogravimetric analysis (TGA) of polymers **14** and **15** showed the onset of decomposition in air at 530–570 °C and in nitrogen at 550–585 °C with only 25–30% weight loss at 800 °C under nitrogen. In general, polymers **14** having oxygen links between the quinoline rings showed 35–45 °C lower decomposition temperatures than polymers **15** in air.

Experimental Section

4,4′-Diamino-3,3′-dibenzoyldiphenyl Ether (16). Catalytic hydrogenation of the bis(benzisoxazole) formed from 4,4′-dinitrodiphenyl ether and benzyl cyanide gave **16**, which was recrystallized from methanol to afford yellow needles, mp 158.5–160 °C (lit.[1] mp 157.5–158.5 °C).

1,4-Bis(phenacyl)benzene (17). Acetylation of benzene was effected with 1,4-bis(phenacyl) chloride and aluminum chloride.[17] Recrystallization from chloroform followed by benzene afforded white crystals, mp 207.5–208.5 °C (lit.[17] mp 203–205 °C).

4,4′-Diacetylbiphenyl (7). To a solution of 75 g (0.49 mol) of biphenyl in 420 mL of dry carbon disulfide was added 196 g (1.47 mole) of aluminum chloride. To the stirred mixture was slowly added, over 1 h, 154 g (1.96 mol) of acetyl chloride, and the resultant mixture was heated to the reflux temperature and maintained for 11 h. The carbon disulfide was removed, and the oily residue was poured onto a mixture of ice and hydrochloric acid to afford a yellow precipitate which was collected by filtration. The precipitate was then washed with water and with boiling ethanol. Recrystallization from benzene–methanol (2:1) gave 60 g (50%) of white platelets, mp 195–196 °C (lit.[7] mp 190–191 °C).

4,4′-Biphenylylbis(acetyl chloride) (10). A total of 30.8 g (148 mmol) of phosphorus pentachloride was added to 450 mL of dry carbon tetrachloride, and the mixture was vigorously stirred for 15 min. To this slurry was slowly added 20.0 g (74.0 mmol) of 4,4′-biphenylylbis(acetic acid),[8] and the mixture was heated, with stirring, at the reflux temperature for 24 h. The resultant dark brown solution was filtered hot, protected from moisture, and cooled overnight in a refrigerator. The crude product was collected by filtration, washed well with cold, dry carbon tetrachloride, and recrystallized from dry carbon tetrachloride to afford 12 g (55%) of off-white needles: mp 108.5–110 °C; IR (KBr) 1800 cm^{-1}.

4,4′-Bis(phenacyl)biphenyl (6). From 4,4′-Biphenylylbis(acetyl chloride) (10). To an ice-cooled, stirred mixture of 2.0 g (6.5 mmol) of **10** in 20 mL of dry benzene was slowly added 2.2 g (16 mmol) of anhydrous aluminum chloride. The resultant brown mixture was stirred in an ice bath for an additional 10 min then heated up to 50 °C and maintained at this temperature for 24 h to give a dark brown mixture. This was poured onto a mixture of 20 mL of concentrated hydrochloric acid and ice, affording initially a yellow precipitate which became a pink emulsion with continued stirring. The water layer was separated, and the emulsion was broken by filtration to afford 2.5 g (100%) of pink solid, mp 252–256 °C, which could not be suitably purified: IR (KBr) 1695 cm^{-1} (PhC=O).

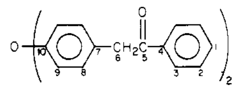
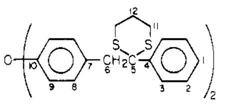
4,4′-Bis(phenacyl)biphenyl (6). From α-(*p*-Bromophenyl)acetophenone (12). To a slurry of 11.9 g (43.2 mmol) of bis(1,5-cyclooctadiene)nickel(0)[18] in 300 mL of dry deoxygenated *N*,*N*-dimethylformamide (stirred over barium oxide, allowed to reflux over calcium hydride for 1 h, followed by distillation from calcium hydride over reduced pressure, and then thoroughly degassed with argon) was added under an argon atmosphere 11.9 g (43.2 mmol) of α-(*p*-bromophenyl)acetophenone.[11] The resultant green mixture was stirred under a static argon atmosphere for 60 h at 42 °C to afford a gray mixture. The mixture was poured into 300 mL of a 2% hydrochloric acid solution and filtered to afford a white crystalline product. The filtrate was extracted with methylene chloride until the extract was colorless, and the methylene chloride was then removed on a rotoevaporator to afford additional white crystals. The crude product was washed thoroughly with water to afford 6.0 g (72%) of white crystals, mp 258–260 °C. Extractive recrystallization from toluene afforded white needles: mp 260–261 °C; IR (KBr) 1695 cm^{-1} (PhC=O). Anal. Calcd for $C_{28}H_{22}O_2$: C, 86.13; H, 5.68. Found: C, 86.12; H, 5.90.

Di-*p*-tolyl Ether (14). The reaction of *p*-cresol with *p*-bromotoluene gave **14**.[12] Purification by column chromatography (SiO_2, toluene) followed by recrystallization from ethanol (charcoal) afforded white needles: mp 49.5–50 °C (lit.[12] mp 50 °C); ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3 H, CH_3), 6.6–7.1 (m, 4 H, aromatic).

α-Bromo-*p*-tolyl Ether (15). Bromination of **14** with *N*-bromosuccinimide in benzene afforded **15**.[13] Extractive recrystallization from hexane gave white crystals: mp 93–95 °C (lit.[13] mp 98 °C); ^{1}H NMR ($CDCl_3$) δ 4.4 (s, 2 H, CH_2), 6.7–7.3 (m, 4 H, aromatic).

Bis(1,3-propane dithioketal) of 4,4′-Bis(phenacyl)diphenyl Ether (16). To a stirred solution of 24.3 g (124 mmol) of 2-phenyl-1,3-dithiane[14] in 240 mL of dry tetrahydrofuran at −26 °C was added under nitrogen 7.90 g (124 mmol) of *n*-butyllithium (76.5 mL of a 1.62 M solution in hexane) at a rate of 5 mL/min. The dark yellow solution was stirred at −26 °C for 1.5 h and then cooled to −78 °C. To this solution, 22 g (62 mmol) of **15** in 190 mL of dry tetrahydrofuran was quickly added. The resultant

Table II
Carbon-13 Data for 13 and 16

carbon no.				
	calcd[a]	obsd	calcd[a]	obsd
1	132.2	132.9	132.2	131.5
2	128.0	128.3	128.0	126.5
3	128.1	128.4	128.1	127.8
4	137.1	136.2	137.1	139.9
5		197.2	58.2	59.5
6	51.6	44.5	49.1	50.4
7	129.2	129.0	129.2	128.6
8	129.7	130.5	129.7	128.9
9	113.5	118.8	113.5	117.1
10	156.5	155.7	156.5	155.5
11			21.7	24.8
12			36.6	27.2

[a] Chemical shift values calculated on the basis of the additivity of the chemical shift parameters based on monosubstituted benzenes as outlined in ref 19.

light-yellow solution was stirred for an additional 2 h at -78 °C, allowed to slowly warm to 0 °C, and maintained at this temperature for 72 h. The pale-yellow solution was then poured into 1.5 L of water and extracted with 2 L of chloroform, and the chloroform layer was washed with water, 10% aqueous potassium hydroxide, and then water again. Drying the chloroform layer with potassium carbonate followed by removal of the chloroform under reduced pressure afforded 37.6 g (>100%) of yellow crystals. The crude product was used without purification for the next step. An analytical sample was obtained by extractive recrystallization from acetone, affording off-white crystals: mp 148–150 °C; IR (KBr) 3080 (aromatic), 2970, 2920 (aliphatic), 1510, 1245 (COC), 710 cm^{-1} (CS); ^{1}H NMR (CDCl$_3$) δ 1.65–2.1 (m, 2 H), 2.35–2.8 (m, 4 H), 3.16 (s, 2 H), 6.5 (s, 4 H), 7.0–7.3 (m, 3 H), 7.48–7.7 (m, 2 H). See Table II for ^{13}C NMR data. Anal. Calcd for $C_{34}H_{34}S_4O$: C, 69.58; H, 5.84; S, 21.85. Found: C, 69.59; H, 5.79; S, 21.36.

4,4′-Diphenacyldiphenyl Ether (13). To a stirred solution of 142 g (797 mmol) of *N*-bromosuccinimide in 1.9 L of a 97% solution of acetone in water at -5 °C was added, during 1 h, 26.0 g (44.3 mmol) of **16** in 1.5 L of reagent acetone. The red solution was stirred for 3 h at -5 °C to afford a pale yellow solution which was poured into a solution of 195 g of sodium sulfite in 4 L of water. The acetone was removed under reduced pressure from the resultant yellow solution, and the white precipitate which formed was collected by filtration. The precipitate was added to 4 L of toluene, and the toluene was heated to the reflux temperature and then allowed to cool to room temperature. The toluene layer was separated from any undissolved precipitate by filtration and was removed under reduced pressure to afford a yellow oil which crystallized on standing. The yellow crystals were dissolved in 1 L of chloroform, and the chloroform layer was washed with a 10% aqueous sodium bicarbonate solution followed by water. After drying the chloroform layer with magnesium sulfate, the chloroform was removed under reduced pressure to afford 9 g (50%) of yellow crystals. Initial purification by column chromatography (SiO$_2$, toluene followed by chloroform) followed by further purification on a medium pressure liquid chromatograph (SiO$_2$, methylene chloride) and one recrystallization from toluene afforded 0.8 g (10%) of white crystals: mp 127–128 °C; IR (KBr) 1690 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ 4.2 (s, 2 H), 6.7–7.5 (m, 7 H), 7.7–7.95 (m, 2 H). See Table II for ^{13}C NMR data. Anal. Calcd for $C_{28}H_{22}O_3$: C, 82.74; H, 5.45. Found: C, 82.53; H, 5.47.

Polymerizations. The synthesis of poly[3,3′-(*p*,*p*′-biphenylene)-6,6′-oxybis(2,4-diphenylquinoline)] (**14c**) is given below as a general procedure for the polymerization reaction affording the remaining polymers.

To a resin flask was added 1.0460 g (2.5610 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether, 1.0000 g (2.5610 mmol) of 4,4′-bis(phenacyl)biphenyl, 17 g (62 mmol) of di-*m*-cresyl phosphate, and 6 mL of fresh *m*-cresol. The resin flask was purged with nitrogen, and the solution was stirred for 48 h under a static nitrogen atmosphere at 135 °C. The polymer was isolated by precipitating the dark red polymerization solution into a stirring solution of 400 mL of ethanol and 30 mL of triethylamine to afford a white fibrous precipitate. The polymer was collected by filtration, chopped in a blender, and dissolved in 50 mL of chloroform. The chloroform solution was slowly poured into a solution of 1 L of ethanol and 50 mL of triethylamine that was being stirred, and the resultant precipitate was chopped in a blender and collected by filtration. After the polymer was continuously extracted with a solution of ethanol–triethylamine for 4 days, the polymer was filtered and dried under reduced pressure at 110 °C for 24 h to afford 1.6 g (84%) of cream fibrous polymer (Table III, elemental analyses).

Table III
Elemental Analyses of Polyquinolines

polymer	calcd, % C	calcd, % H	calcd, % N	found, % C	found, % H	found, % N
14a	87.31	4.61	3.77	86.28	4.54	3.72
14b	88.59	4.65	4.31	87.33	4.87	4.20
14c	89.22	4.71	3.85	88.48	4.74	3.64
15a	89.23	4.71	3.85	88.38	4.62	3.77
15b	90.82	4.76	4.41	89.82	4.78	4.31
15c	91.23	4.82	3.94	89.87	4.86	3.72

Films of **14c** and **15a,c** were obtained by the following procedure. A 10% by weight solution of the polymer in *m*-cresol was smoothed onto a glass plate with a doctor's knife, and the polymer coated glass plate was put into a dust-free chamber at room temperature for 12 h. The plate was then placed into a vacuum oven at 100 °C for 6–8 h, after which time the film was slowly peeled from the glass plate.

Clear flexible films of **14a** and **14b** were obtained by smoothing a 10–15% by weight solution of the polymer in *sym*-tetrachloroethane onto a glass plate with a doctor's knife and allowing the solvent to slowly evaporate.

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

Thermal analyses were conducted using a DuPont 990 differential thermal analyzer equipped with a differential scanning calorimeter (DSC) cell base module II and a 950 thermalgravimetric analyzer (TGA). The DSC analyses were obtained on pressed powder samples at a heating rate of 10 °C/min under a flowing nitrogen atmosphere. Either powder or pressed powder samples were used for TGA analyses. The analyses were conducted at a heating rate of 5 °C/min in both flowing air and flowing nitrogen atmospheres.

Dynamic thermomechanical analyses were determined as follows, using a Rheovibron (Model DDV-II-C). Film samples were cut into narrow strips 3 cm in length and 0.3 cm in width. Runs were made at a frequency of 35 Hz at an approximate heating rate of 10 °C/min in a flowing nitrogen atmosphere. The dynamic moduli of the films were then calculated by using the following equation:

$$|E^*| = \frac{2}{(A)(\mathrm{DF} - K)} \frac{L}{S} \times 10^9 \ \mathrm{dyn/cm^2}$$

where A is a constant given by the instrument manual,[20] DF is the value of the dynamic force dial when measuring tan δ, L is the length of the sample in cm, S is the cross-sectional area in cm^2, and K is an error constant due to the modulus of electricity and displacement of the stress gauge. This value was experimentally determined for polyquinolines and found to be 1, independent of temperature. Values of the storage modulus (E') and the loss modulus (E'') were then obtained from the following equations:

$$E' = |E^*| \cos \delta \text{ and } E'' = |E^*| \sin \delta$$

X-ray diffraction patterns were carried out by Dr. J. B. Lando, Department of Macromolecular Science, Case Western Reserve University, on powder and film samples, using a Satton Powder Camera with Cu Kα radiation. Pictures were taken on flat film, so an accurate determination of crystallinity was not possible.

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Synthesis and Ion Binding Properties of Epoxy Polymers with Diazacrown Ethers

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ABSTRACT: The synthesis of polymers obtained by polycondensation of two macrocyclic diamines [21] and [22] (1,4,10-trioxa-7,13-diazacyclopentadecane and 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane) with the diglycidic ether of 2,2-bis(4-hydroxyphenyl)propane (Epikote 815) is described. The polymers strongly chelate with cations, and their efficiency and selectivities in binding cations are compared with those of their monomeric analogues by using data obtained from water–chloroform extraction measurements. The stability constants for the polymeric complexes are comparable to those of the analogues whatever the ratio of complexation, indicating that the polymeric structure has no influence on the structure of the complexes. With all of the cations studied (alkali, alkaline earth, and Cu^{2+}, Cd^{2+}, and Pb^{2+}), the stoichiometry 1:1 was observed in chloroform. With alkali and alkaline earth cations, the selectivity is governed by the respective size of the cations and of the internal cavity of the cycles. With Cu^{2+}, Cd^{2+}, and Pb^{2+} cations, higher stabilities are obtained with the larger cycle. Experiments with mixtures of cations indicate that complexation properties are additive. The stability constants obtained with picrate and perchlorate anions are very comparable, showing that both anions lead to complexes with comparable binding energies. These results, in addition to results obtained by UV spectroscopy, are interpreted in terms of interactions of the anions with the protons of the hydroxylic groups present near the cycles. Aging experiments with oxygen and carbon dioxide indicate that the binding properties are not affected by the aging of the polymers.

Since the discovery by Pedersen[1,2] and Lehn[3] that synthetic macrocycles can form stable complexes with cations, relatively little has been published concerning the synthesis and the study of polymers containing such macrocyclic ligands. Most of these works concern the preparation and study of cross-linked resins[4-6] or membranes.[7,8] The only published investigation of linear soluble polymers or copolymers was by Smid et al.,[9] who synthesized and studied various poly(vinylcrown ethers).

In a previous article, we reported the synthesis of some polymers obtained by polycondensation of diazacrown ethers.[10] In this paper, the synthesis and binding properties of one type of these polymers are discussed. They are obtained by the polycondensation of a diepoxy monomer with the cyclic diamines 1,4,10-trioxa-7,13-diazacyclopentadecane (diamine [21]H) or 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (diamine [22]H). Their ion binding properties are studied by extration equilibria obtained in a water–chloroform system and compared to those of the monomeric analogues which have recently been studied.[11]

Experimental Section

Reagents and Solvents. All of the solvents used are purified and distilled by classical methods. The diamines [21]H and [22]H (Kryptofix 21- and 22-Merck) are purified as previously reported.[11] The diglycidic ether of 2,2-bis(4-hydroxyphenyl)propane (Epikote 815 from Shell Chimie) is purified by dissolution in chloroform, filtration, and precipitation in heptane. The soluble part is recovered after evaporation and drying. The content of the epoxide groups, determined by HCl in dioxan,[12] is found to be 8.74% compared with the theoretical value of 9.40%. Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.12; H, 7.06; O, 18.82; Cl, 0. Found: C, 73.53; H, 7.02; O, 18.88; Cl, 0.53.

Polymerizations. The polycondensations of the diamines [21]H or [22]H with the diepoxy leading to the polymers P-[21]EpiDPP or P[22]EpiDPP are carried out as described below.

Purified Epikote 815 (4.8 mmol) with 5 mL of tetrahydrofuran are placed in a 100-mL flask equipped with a magnetic stirrer, a drying tube, and a nitrogen inlet. [21]H (4.8 mmol) dissolved in 15 mL of dry methanol is added to the flask. The mixture is heated under reflux for 72 h. The polymer is recovered by evaporation of the solvents in a rotary evaporator. It is then dissolved in 10 mL of chloroform, precipitated in 1 L of dry methanol, and dried under low pressure at 40°C for 1 week. The

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