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Polyquinolines Containing Fluorene and Anthrone Cardo Units: Synthesis and Properties

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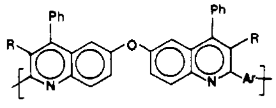
ABSTRACT: A series of polyquinolines with one or two "cardo" fluorenyl and/or 10-anthronyl units in the polymer main chain was synthesized from the appropriate cardo bis(*o*-aminobenzophenones) or bisacetyls. All the polyquinolines show good solubility in chlorinated hydrocarbons and excellent thermal stability (T_d = 500–540 °C in air, TGA). The glass transition temperatures (T_g) of these polyquinolines ranged from 300 to 420 °C. Polyquinolines containing one cardo group and a 4,4′-biphenyl linkage per repeat unit show better mechanical properties than the more flexible analogues containing a cardo group and a 4,4′-diphenyl ether linkage per repeat unit or two cardo groups per repeat unit. None of the polyquinolines show any crystalline transition temperatures (T_m or T_c).

Introduction

Thermally stable polymers containing a rigid backbone as a result of totally aromatic or heteroaromatic repeat units generally exhibit high softening temperatures (T_g) and poor solubilities. Pendent phenyl groups enhance the solubility of this type of polymer.[1] Thermally stable flexible linkages such as ether, sulfide, sulfone, and carbonyl lower the softening temperature and increase the solubility; however, this structural modification results in lowering the end-use temperature to a softening temperature that is well below the decomposition temperature of the polymer.

Phenylated polyquinolines 1 and 2, for example, containing 2,6- and 3,6-quinoline units along the polymer backbone have been prepared[2,3] by the polycondensation of bis(*o*-aminobenzophenone) with bis(ketomethylene) monomers in a polymerization media consisting of *m*-cresol and di-*m*-cresyl phosphate.[4]



1

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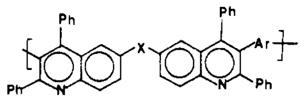

2

X = O or nil

Flexible polyquinolines containing the ether linkage 1 are soluble in chlorinated hydrocarbons and exhibit very high decomposition temperatures (T_d = 500–600 °C in air, TGA). Most of the polyquinolines exhibit detectable crystalline transition temperatures (T_m) above 450 °C even though they are virtually amorphous (<20% crystalline), thus limiting their end-use temperature to the relatively low glass transition temperature (250–350 °C).

Introduction of pendent loops along the polymer backbone has been shown[5] to impart greater solubility and enhanced rigidity as well as better mechanical and thermal properties to the resulting "cardo" polymer. The loops are perpendicular to the chain direction and, depending on the structural symmetry, can produce either an ordered structure or a chain which approximates an atactic arrangement. Furthermore, certain "cardo" polymers have been crystallized from solution or by annealing. Therefore, in order to synthesize and study the properties of thermally stable polyquinolines that possess high glass transition temperatures yet good solubility such that they can be readily processed from solution, we have incorporated cardo groups into polyquinolines.

Results and Discussion

Monomer Synthesis. In order to introduce cardo groups into the polyquinoline framework, bisacetyl and bis(*o*-aminobenzophenone) monomers containing cardo fluorene and anthrone groups were synthesized. The synthesis of the fluorene-containing cardo bisacetyl 7 was accomplished in two ways. One approach, which utilized the formation of a ketone by the reaction of an acid chloride and a tin compound,[6] is outlined in Scheme I.

The acid chloride 6 was synthesized from 9-fluorenone (3) according to the known procedure.[7] Treatment of either the acid chloride 6 with dimethylcadmium or the reaction of the carboxylic acid 5 with methyllithium afforded a low yield (≃25%) of the product ketone 7, whereas the reaction of the acid chloride 6 with tetramethyltin, catalyzed by palladium, resulted in a high yield (≃90%) of the desired compound 7. Another approach, utilizing the acid-catalyzed ring closure of an intermediate carbinol 12, is shown in Scheme II. Biphenyl-2-carboxylic acid (8), prepared by the base-assisted ring opening of 9-fluorenone (3)[8] was converted to the methyl ester by treatment with diazomethane. The protected ketone 11 underwent clean transmetalation with *n*-butyllithium at −78 °C. Its reaction with methyl ester 9 gave carbinol 12, which underwent facile ring closure upon treatment with glacial acetic acid saturated with hydrogen chloride to yield the cardo bisacetyl monomer 7. The synthetic route showed in Scheme II, with an overall yield of ≃67%, is far more convenient and superior to that showed in Sheme I, with an overall yield of ≃24%.

Since the cardo anthrone group has been reported[5] to be more thermally stable than the fluorene group and impart greater solubility, the anthrone-containing bisacetyl monomer 21 was synthesized (Scheme III).

o-Benzoylbenzoic acid (13) was reduced with zinc and ammonium hydroxide[9] to yield *o*-benzylbenzoic acid (14), which was converted to the methyl ester 15. Addition of *p*-tolylmagnesium bromide (16) to the ester 15 resulted in the formation of the carbinol 17, which underwent facile ring closure upon treatment with poly(phosphoric acid) to give the anthracene derivative 18. Aqueous sodium dichromate oxidation of 18 gave the acid 19. Treatment of the acid 19 with phosphorus pentachloride gave the acid chloride 20, which with tetramethyltin in presence of palladium catalyst[6] gave the anthrone-containing bisacetyl monomer 21.

Preparation of the fluorene-based bis(*o*-aminobenzophenone) monomer 9,9-bis(4-amino-3-benzoylphenyl)fluorene (25) was accomplished starting with the reported acid-catalyzed condensation reaction of aniline and fluoren-9-one (3)[10] (Scheme IV). Oxidation[11] of 9,9-bis(4-aminophenyl)fluorene (22) provided a moderate yield of the desired 9,9-bis(4-nitrophenyl)fluorene (23). Conversion of 23 to 9,9-bis[5-(3-phenyl-2,1-benzisoxazolyl)]-

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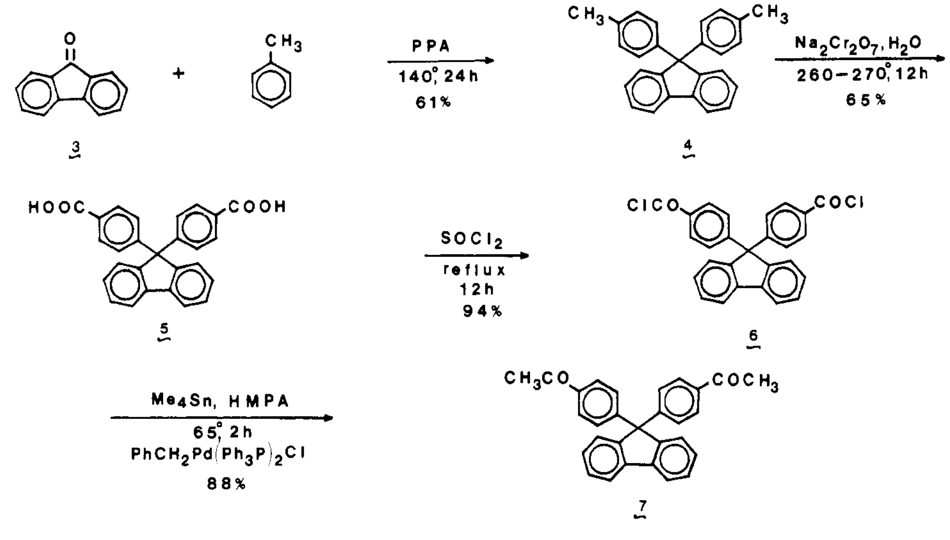
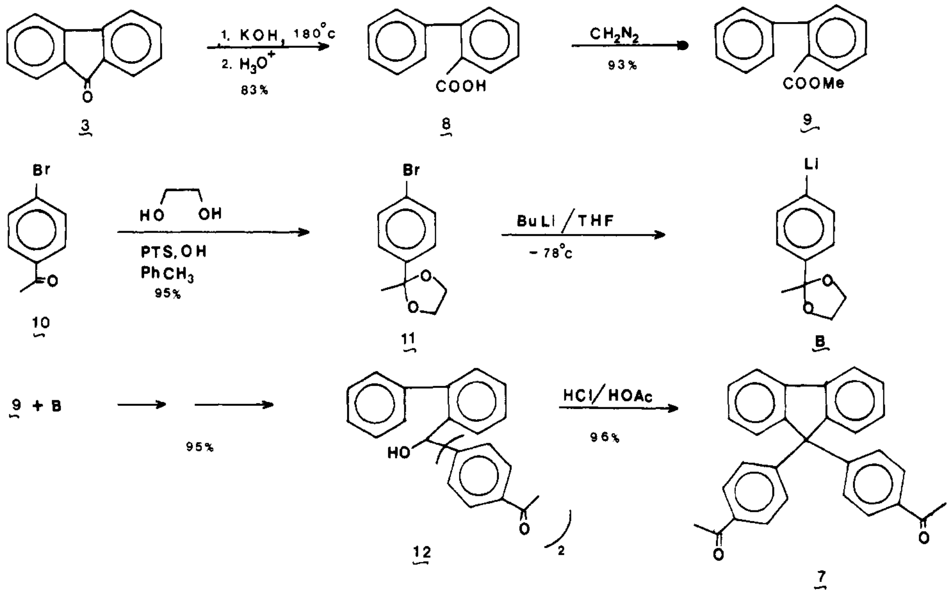
Scheme I
Synthesis of 9,9-Bis(4-acetylphenyl)fluorene



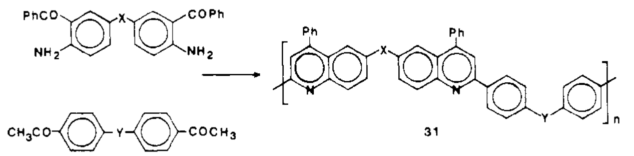
Scheme II
Synthesis of 9,9-Bis(4-acetylphenyl)fluorene



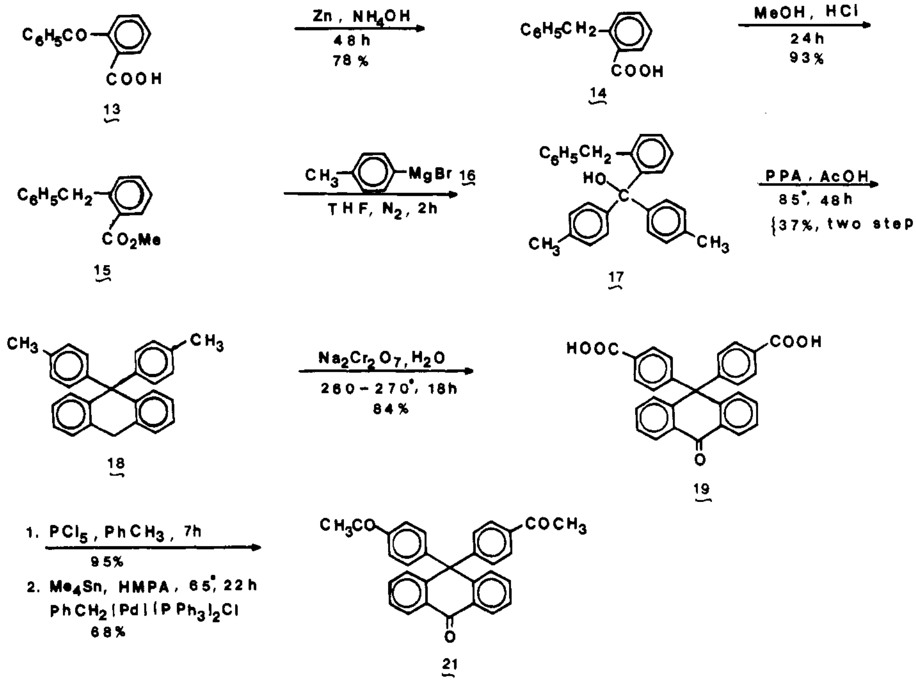
fluorene (24) was effected by the sodium hydroxide assisted reaction of phenylacetonitrile[12] with 23 in a refluxing THF–methanol mixture. Hydrogenation of the fluorene-based bis(anthranil) 24 over a 5% palladium-on-carbon catalyst[2] in THF afforded an almost quantitative yield of the desired monomer 25.

Preparation of 9,9-bis(4-amino-3-benzoylphenyl)-10-anthrone (30) was carried out in a reaction sequence very similar to that for 25 (Scheme V), despite the presence of the possibly reactive 10-anthronyl carbonyl functionality in the cardo group. Initially, aniline was condensed with 9,10-anthroquinone (26) in refluxing aniline to give a moderate yield of the known 9,9-bis(4-aminophenyl)-10-anthrone (27).[10,13] Again the desired cardo framework was constructed at the outset. A transformation of the amino groups in 27 to nitro groups was effected by *m*-chloroperbenzoic acid[14] to generate 9,9-bis(4-nitrophenyl)-10-anthrone (28). A milder amine oxidant was necessary to avoid a Baeyer–Villager oxidation[15] of the anthrone carbonyl to the lactone. The dinitro compound 28 was subjected to the sodium hydroxide generated anion of phenylacetonitrile[12] to form 9,9-bis[5-(3-phenyl-2,1-benzisoxazolyl)]-10-anthrone (29), which was isolated in a suitably pure crystalline form for subsequent reaction. When potassium hydroxide replaced the sodium base, very little of the desired bis(anthranil) product was isolated. Hydrogenation[2] of 29 again provided a quantitative isolated yield of the bis(*o*-amino ketone) monomer 30.

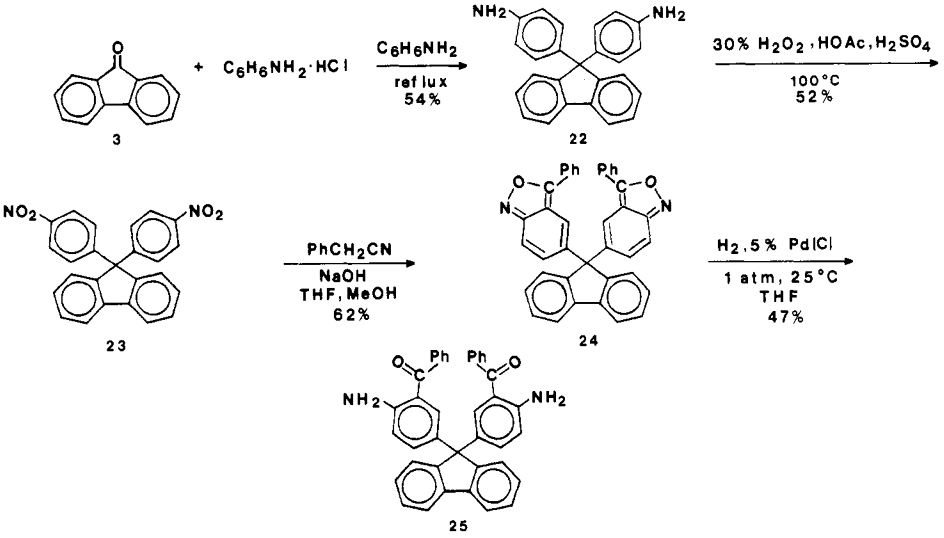
Polymer Synthesis. Cardo polyquinolines 31 (Table I) were prepared by the reaction of an equimolar mixture of the appropriate bis(*o*-aminobenzophenone) with the bisacetyl monomer in a mixture of *m*-cresol and di-*m*-cresyl phosphate[4] at 135–140 °C for a period of 24–48 h, under a static nitrogen atmosphere. Most of the cardo polyquinolines show good solubility in *sym*-tetrachloroethane (TCE) and chloroform, with a few showing good solubility only in *m*-cresol. Tough, transparent films could be cast



Scheme III
Synthesis of 9,9-Bis(4-acetylphenyl)-10-anthrone



Scheme IV
Synthesis of 9,9-Bis(4-amino-3-benzoylphenyl)fluorene (25) via 24



from 10–15% (w/v) solutions (*sym*-tetrachloroethane, TCE) with the exception of **31i** and **31l**.

The difluorene-containing polymer **31a** is soluble in chloroform, but upon prolonged standing (≃48 h) at ambient temperature, precipitation occurred. The precipitated polymer, which was an opaque brittle film, could be redissolved in chloroform. The DSC thermogram of the precipitated polymer showed neither crystalline transition temperatures (T_c or T_m) nor a decrease in the magnitude of the change in heat capacity at T_g.

Small structural changes showed large effects on the solubility of cardo polyquinolines and appeared to depend on the location of the cardo group in the repeat unit. For example, if the fluorenyl group was present only in the bis(*o*-aminobenzophenone) moiety (X) and not in the 4,4′-biphenyl unit of the diacetyl monomer (Y = nil, **31i**), solubility of only 5–10% (w/v) in refluxing *m*-cresol was observed. The polymer containing the reversed placement of the cardo group (X = nil, Y = fluorenyl, **31e**) showed good solubility in chloroform for a comparable molecular weight sample (as indicated by their intrinsic viscosities). Similar parallel solubility behavior was exhibited by the more flexible cardo polyquinolines **31h** and **31l** containing the cardo anthronyl and ether linkages. However, the polymers containing the cardo fluorene and ether linkages, **31f** and **31j**, did not exhibit these characteristic solubility properties, being completely soluble in chloroform and *sym*-tetrachloroethane (TCE).

An indication that films of the polyquinolines **31b,d,i–l** did not order upon casting from *sym*-tetrachloroethane solutions was shown by the fact that they did not show birefringence in polarized light when placed between crossed polarizer and analyzer.[16] This behavior can be attributed to the highly amorphous nature of the cardo polymers and unfortunately may also indicate the very low tendency of these bulky polymer systems to order from solutions of *sym*-tetrachloroethane (TCE).

Thermal Analyses. The glass transition temperatures

Scheme V
Synthesis of 9,9-Bis(4-amino-3-benzoylphenyl)-10-anthrone (**30**) from **29**

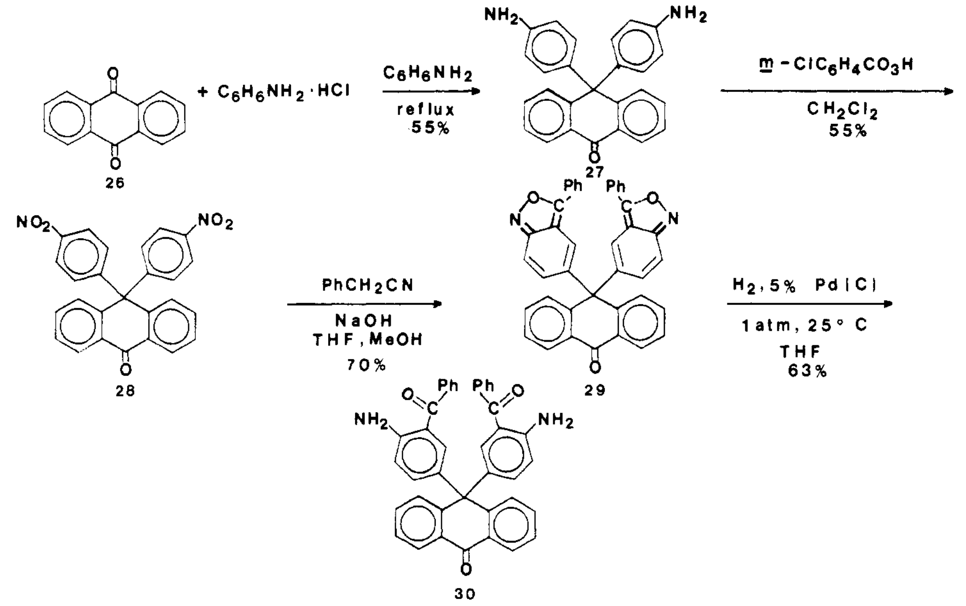
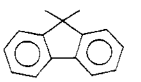
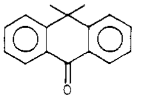


Table I
Properties of Polyquinolines 31 Containing Cardo Units

	polyquinoline		solubility					
	X	Y	$CHCl_3$	TCE	[η], dL/g	T_g, °C	T_d, °C	$10^{-10}E'$(25 °C), dyn/cm²
31a	 i	i	+	+	0.58[a]	390	580	2.1
31b	i	 ii	+	+	0.70[b]	385	530	2.2
31c	ii	i	+	+	1.30[b]	405	540	2.6
31d	ii	ii	+	+	0.53[b]	390	520	1.5
31e	nil	i	+	+	2.50[a]	420	570	1.3
31f	O	i	+	+	1.70[a]	310	570	2.6
31g	nil	ii	−	+	1.44[b]	417	560	1.9
31h	O	ii	+	+	0.87[b]	340	580	1.8
31i	i	nil	−	−[d]	1.95[c]	380	580	1.8
31j	i	O	+	+	0.56[c]	315	575	2.5
31k	ii	nil	+	+	0.69[a]	350	530	2.2
31l	ii	O	−	+[e]	0.97[c]	320	535	

[a] $CHCl_3$. [b] $CHCl_2CHCl_2$. [c] *m*-Cresol. [d] Hot *m*-cresol. [e] Hot TCE.

(T_g) of polyquinolines **31** (Table I) were determined by differential scanning calorimetry, using pressed powder samples. These values are in close agreement with the glass transition temperatures determined by the maximum in the loss modulus (E''_{max}, Rheovibron). The glass transition temperatures of the various cardo polyquinolines ranged from 310 to 420 °C.

Most of the cardo polyquinolines, with the exception of those containing flexible ether linkages, exhibit T_g's comparable to or greater than the high T_g's exhibited by the rodlike polyquinolines (X = Y = nil, T_g = 365 °C).[17] An enhancement in the glass transition temperatures of around 40–70 °C was observed when an ether linkage in polyquinoline **31** (X = Y = O, T_g = 266 °C) was replaced by either fluorenyl or anthronyl groups. Additional increases in T_g of around 45–95 °C resulted from substituting a cardo group for the remaining ether functionality. The ability of the cardo units to introduce stiffness into polyquinolines is evident from the retention of high glass transition temperatures upon successive replacement of biphenyl units in **31** (X = Y = nil) with fluorenyl or 10-anthronyl groups.

The glass transition temperatures of the cardo polymers containing one pendent loop per repeat unit are dependent not only on the stiffness of the linkages along the main chain but also on their relative location in the repeat unit. For example, in the cardo polymers containing biphenyl linkages, interchanging the positions of fluorenyl or 10-anthronyl groups with the biphenyl linkage results in an increase in T_g of 40–70 °C. This pattern is not evident for the more flexible polymers containing the ether linkage.

It appears that the T_g's of the cardo polyquinolines are not dependent on subtle polarity changes resulting from the replacement of a fluorenyl group with a more polar anthronyl unit. Also, all the dicardo polyquinolines **31a–d** tend to exhibit high and similar glass transition temperatures.

None of the cardo polymers showed any crystallinity (T_c

or T_m) when pressed powder samples were subjected to either gradual heating or annealing (DSC) or when films were analyzed by dynamic thermomechanical measurements. Thermal analyses and solubility data appear to indicate that the cardo polymers, which are highly amorphous, exhibit little or no tendency to crystallize either by annealing or from solution.

Dynamic thermomechanical analysis (Rheovibron) of all cardo polyquinolines, except **31e** and **31g**, showed similar behavior. The storage modulus (E') remained fairly constant up to T_g and a significant loss occurred at T_g. The magnitude of the loss of storage modulus, from $\simeq 10^{10}$ dyn/cm^2 at room temperature to 10^8–10^7 dyn/cm^2 above T_g, coupled with their solubility indicates the amorphous nature of these polymers.[18] Polyquinolines **31e** and **31g** showed a smaller loss in the storage modulus, from 10^{10} dyn/cm^2 at room temperature to 10^9 dyn/cm^2 above T_g. The greater chain stiffness brought about by the incorporation of cardo units in the biphenyl portion of the unit (Y) resulted in better mechanical properties above T_g.

All the cardo polyquinolines showed excellent thermal stability both in air and in a nitrogen atmosphere (Table I). Thermogravimetric analysis (TGA) of these polymers showed the onset of decomposition to occur between 500 and 540 °C in air and around 520–580 °C, with only 20–25% weight loss at 800 °C in a nitrogen atmosphere. These decomposition temperatures (T_d) are consistent with those reported for polyquinolines.[19] Typically, the decomposition temperatures for the anthronyl-containing polyquinolines are 30–50 °C lower than those containing the fluorenyl group.

Experimental Section

The following monomers required for the synthesis of the various polyquinolines were prepared by known methods: 4,4′-diamino-3,3′-dibenzoyldiphenyl ether,[2] 4,4′-diacetylbiphenyl,[20] 4,4′-diacetyldiphenyl ether.[21,22]

9,9-Bis(4-tolyl)fluorene (4). The following procedure is a modification of that described.[7] A mixture of 700 g of super poly(phosphoric acid) (PPA) (prepared from 583 g of PPA and 117 g of phosphorus pentoxide),[23] 86 g (0.20 mol) of 9-fluorenone, and 200 mL (1.87 mol) of toluene was stirred at 140 °C for 24 h and then cooled to 80 °C. The resulting highly viscous dark brown reaction mixture was slowly poured into 2.5 L of water, stirred for 1.5 h, cooled to room temperature, and extracted three times with 600-mL portions of benzene. The combined benzene extracts were washed with water and dried ($CaCl_2$). Removal of the solvent under reduced pressure resulted in a yellow solid which was recrystallized from glacial acetic acid to yield 41.5 g (61.0%) of a pale yellow solid, mp 156–160 °C. A small portion of the crude product was subjected to dry column chromatography over neutral alumina. Benzene elution resulted in a white solid, which was recrystallized from ethanol to yield white crystals, mp 169–170 °C (lit.[7] mp 164–165 °C).

9,9-Bis(4-carboxyphenyl)fluorene (5). The following procedure is a modification of that described.[7] Into a stirring 1-L autoclave were charged 24 g (0.069 mol) of crude 9,9-bis(4-tolyl)fluorene (mp 156–160 °C), 42 g (0.12 mol) of sodium dichromate monohydrate, and 360 mL of water. The oxidation was carried out at 260–270 °C for 12 h. The reaction mixture was allowed to cool to room temperature, made slightly alkaline (pH $\simeq$8) with 10% sodium hydroxide, and filtered. The green solid residue was washed with three 50-mL portions of cold water. The combined filtrate and washings were extracted twice with 100-mL portions of benzene, and the benzene layers were discarded. The aqueous layer was boiled with decolorizing carbon and filtered. The hot filtrate was acidified with 1:1 hydrochloric acid–water, boiled for a few minutes, allowed to cool to room temperature, and filtered. The residue was washed with cold water until the washings were colorless and neutral. The resulting white solid was dried at 100 °C to yield 18 g (65%) of product, mp 345–348 °C (lit.[7] mp 346–348 °C).

Acid Chloride of 9,9-Bis(4-carboxyphenyl)fluorene (6). Treatment of 9,9-bis(4-carboxyphenyl)fluorene with thionyl chloride as described[7] yielded the corresponding acid chloride, mp 163–167 °C (lit.[7] mp 155–157 °C).

9,9-Bis(4-acetylphenyl)fluorene (7). Procedure 1. A cold solution of 6.7 g (4.0 mL, 0.070 mol) of methyl bromide in 12 mL of ether was added dropwise to a mixture of 0.81 g (0.33 mol) of magnesium in 7 mL of ether under nitrogen. After the addition was complete, the reaction mixture was heated at reflux for 15 min and subsequently cooled in an ice bath. To this solution of Grignard reagent was added 3.31 g (0.0180 mol) of cadmium chloride over a period of 5 min. The reaction mixture was stirred for 15 min at room temperature and heated at reflux for 1 h. Ether was slowly removed by distillation and 12 mL of benzene was added. The distillation was continued until 4–6 mL of benzene distilled over. Another 12 mL of benzene was added and the reaction mixture was refluxed for 5 min. Heating was discontinued and a warm solution of 4.0 g (9.2 mmol) of the acid chloride of 9,9-bis(4-carboxyphenyl)fluorene in 20 mL of benzene was added slowly, at the end of which the mixture was refluxed for 1 h. The reaction mixture was cooled in an ice bath and 20 mL of cold water was added slowly, followed by 100 mL of 10% sulfuric acid. The mixture was stirred for 15 min and allowed to settle, and the organic layer was separated. The aqueous layer was extracted twice with 50-mL portions of benzene. The combined benzene extracts were washed sequentially with cold water, 5% sodium carbonate, cold water, and brine and then dried ($MgSO_4$). Removal of the solvent under reduced pressure resulted in a pale yellow oil, which was subjected to dry column chromatography over neutral alumina. Elution with 1:1 hexane–ethyl acetate resulted in an off-white solid which was recrystallized from benzene to yield 0.90 g (25%) of white crystals: mp 206–207 °C; IR (KBr) 1680 (s, C=O), 1600, 1450, 1400, 1350, 1270, 830, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 6 H, $COCH_3$), 7 (m, 16 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 197.3 (>C=O), 150.6, 149.6, 140.1, 135.7, 128.4, 128.1, 125.9, 120.4, (aromatic), 65.5 (tertiary carbon), 26.4 (CH_3). Anal. Calcd for $C_{29}H_{22}O_2$: C, 86.54; H, 5.51. Found: C, 86.78; H, 5.46.

Procedure 2. A mixture of 1.0 g (22 mmol) of **6**, 31 mg (6.2 mmol) of bis(triphenylphosphine)benzylpalladium(II) chloride, 0.70 mL (50 mmol) of tetramethyltin, and 2.5 mL of HMPA was stirred in a tightly stoppered 25-mL round-bottom flask at 65 °C for 2 h. The reaction mixture, which had turned black at the end of 2 h, was poured into 25 mL of water, stirred for 15 min, and extracted with three 50-mL portions of benzene. The combined benzene extracts were washed sequentially with water, 5% potassium carbonate, and brine, dried (K_2CO_3), and concentrated (100 mL). Slow addition of this black, clear solution to 100 mL of hexane resulted in a black precipitate, which was removed by filtration. Removal of the solvent from the filtrate resulted in 0.30 g (88%) of a pale yellow solid, mp 200–204 °C, which was recrystallized from carbon tetrachloride to yield 0.79 g (77%) of white crystals, mp 205–206 °C, identical in all respects with the compound obtained by procedure 1.

Procedure 3. An ethereal solution of methyllithium (50 mL, 1.6 M, 0.08 mol) was added dropwise under nitrogen to a stirred solution of 3.0 g (7.4 mmol) of 9,9-bis(4-carboxyphenyl)fluorene in 30 mL of THF. Once the addition was complete, 80 mL of saturated ammonium chloride was added to destroy the excess methyllithium. The organic layer was separated and the aqueous layer was extracted once with 100 mL of chloroform. The combined chloroform extracts and the organic portion were evaporated to dryness under reduced pressure. The residue was redissolved in 100 mL of chloroform and washed twice with 30-mL portions of 5% sodium hydroxide solution, followed by brine, and dried ($MgSO_4$). Removal of the solvent under reduced pressure resulted in a pale yellow solid which was recrystallized from benzene to yield 0.80 g (27%) of white crystals, mp 200–204 °C, which were identical with the product obtained by procedure 1.

Procedure 4. A solution of 4.0 g (9.5 mmol) of the carbinol **12** in 140 mL of glacial acetic acid was saturated with gaseous hydrogen chloride, and the resulting clear yellow solution was heated at reflux for 20 h. The reaction mixture was poured into 600 mL of water and extracted with chloroform (2 × 200 mL). The combined chloroform extracts were washed with water (2 × 100 mL), 5% potassium carbonate (1 × 100 mL), and brine (1

× 100 mL) and then dried (K_2CO_3). The removal of the solvent gave 3.5 g (91%) of an off-white solid, mp 190–193 °C, identical in every respect with the product obtained by procedure 1. This product was further purified by subjecting it to medium-pressure liquid chromatography (SiO_2). Elution with the mixed solvent 98:2 $CHCl_3$–EtOAc gave a white solid which was recrystallized from benzene to yield 2.8 g (73%) of white crystals, mp 206–207 °C.

Biphenyl-2-carboxylic Acid (8). Treatment of 9-fluorenone with potassium hydroxide at 180 °C according to the described procedure[8] gave biphenyl-2-carboxylic acid, mp 112–114 °C (lit.[8] mp 113.5–114.5 °C).

2-(Carbomethoxy)biphenyl (9). Diazomethane (prepared from 35 g (0.34 mol) of *N*-nitrosomethylurea)[24] in 340 mL of ether was added in small portions to an ice-cold solution of 50 g (0.25 mol) of biphenyl-2-carboxylic acid in 250 mL of ether. The reaction mixture was stirred for 2 h at 0 °C and 1 h at room temperature. The resulting clear, water white, ethereal solution was washed successively with 10% sodium hydroxide, water, and brine and dried (K_2CO_3). Removal of the solvent gave an oil, which was distilled under reduced pressure to give 40 g (93%) of the ester, bp 116–118 °C (2–3 mm) [lit.[25] bp 308 °C (760 mm)].

2-Methyl-2-(4-bromophenyl)-1,3-dioxolane (11). Treatment of 4-bromoacetophenone with ethylene glycol in the presence of *p*-toluenesulfonic acid as described[26] gave the desired compounds, mp 46–47 °C (lit.[26] mp 44–45 °C).

Bis(4-acetylphenyl)biphenyl-2-ylcarbinol (12). To a solution of 4.8 g (0.020 mol) of bromo dioxolane 11 in 80 mL of THF at −78 °C was added, dropwise, 12.2 mL (0.0200 mol) of a 1.65 M hexane solution of *n*-butyllithium under a nitrogen atmosphere. After the addition was complete, the reaction mixture was stirred for an additional hour at −78 °C. A solution of 2.1 g (0.010 mol) of 2-(carbomethoxy)biphenyl in 20 mL of THF was added dropwise to the above lithio dioxolane at −78 °C. The reaction mixture was allowed to reach room temperature overnight, quenched with 10 mL of water, poured into 300 mL of 5% hydrochloric acid, and stirred at room temperature for 3 h. Volatiles were removed by rotary evaporation to yield an off-white solid, which was collected by suction filtration and washed thoroughly with water and subjected to dry column chromatography (SiO_2/ether) to yield 4.0 g (95%) of a white solid: mp 72–77 °C; IR (KBr) 3540 (OH), 1680 (C=O), 1610, 1270 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.6–7.7 (m, 17 H, aromatic), 3.0 (s, 1 H, OH, undergoes D_2O exchange), 2.4 (s, 6 H, $COCH_3$).

***o*-Benzylbenzoic Acid (14).** Reduction of *o*-benzoylbenzoic acid with zinc and ammonium hydroxide as described[9] resulted in *o*-benzylbenzoic acid, mp 117–118 °C (lit.[9] mp 118 °C).

Methyl *o*-Benzylbenzoate (15). A mixture of 110 g (0.480 mol) of *o*-benzylbenzoic acid and 500 mL of absolute methanol saturated with hydrogen chloride was heated at reflux for 24 h. The reaction mixture upon cooling produced a two-phase system. The methanol layer was separated from the oily phase, concentrated under reduced pressure, and extracted twice with 200-mL portions of benzene. The combined benzene extracts and the oily layer were further diluted with 500 mL of benzene, washed successively with water, 5% aqueous sodium hydroxide, and water, and dried (K_2CO_3). Removal of the solvent and distillation of the resulting pale yellow oil under reduced pressure yielded 109 g (93%) of a clear water white liquid, bp 141–143 °C (2 mm) [lit.[9] bp 320 °C (760 mm)].

(*o*-Benzylphenyl)bis(*p*-tolyl)carbinol (17). A solution of 43 g (0.19 mol) of methyl *o*-benzylbenzoate (16) in 100 mL of THF was added dropwise, under a nitrogen atmosphere, to Grignard reagent 17 (prepared from 15.8 g (0.650 mol) of magnesium and 111 g (0.650 mol) of *p*-bromotoluene in 480 mL of THF at 0 °C. The reaction mixture was heated at reflux for 2 h, cooled to room temperature, poured into 800 mL of 10% aqueous hydrochloric acid, stirred for 30 min, and cooled in an ice bath. The THF layer was separated and the aqueous layer was extracted with benzene (2 × 200 mL). The combined benzene and THF layers were washed successively with water, 10% sodium hydroxide, and water and dried (K_2CO_3). Removal of the solvent under reduced pressure gave a pale yellow highly viscous oil. The solution of this viscous oil in 100 mL of benzene, upon standing at room temperature overnight, gave 26 g (36%) of white crystals: mp 94–98 °C: IR (KBr) 3560, 3480 (br, OH), 3020, 1610, 1460, 1330, 1170, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.8–7.3 (m, 17 H, aromatic), 3.8 (s, 2 H, CH_2), 2.8 (s, 1 H, OH, undergoes D_2O exchange), 2.2 (s, 6 H, CH_3). Anal. Calcd for $C_{28}H_{26}O$: C, 88.85; H, 6.92. Found: C, 88.79; H, 6.96.

9,9-Bis(*p*-tolyl)-9,10-dihydroanthracene (18). Procedure 1. A mixture of 100 g of poly(phosphoric acid), 200 mL of glacial acetic acid, and 20 g (0.053 mol) of carbinol **17** was stirred at 85–90 °C for 24 h. The reaction mixture was poured into 2.5 L of water, stirred for 15 min, and extracted three times with 300-mL of portions of benzene. The combined benzene extracts were washed twice with 10% sodium hydroxide, followed by water, and dried (K_2CO_3). Removal of the solvent gave a yellow solid, which was subjected to dry column chromatography over silica gel. Elution with benzene gave an off-white solid which was recrystallized from glacial acetic acid to yield 13.2 g (69.0%) of white crystals: mp 173.5–174.5 °C; ^1H NMR ($CDCl_3$) δ 2.2 (s, 6 H, CH_3), 3.5 (s, 2 H, CH_2), 6.5–7.1 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 144.6, 141.7, 137.2, 135.2, 130.0, 129.1, 127.8, 125.7, 125.1 (aromatic), 59.7 (tertiary carbon), 36.4 (CH_2), 20.8 (CH_3). Anal. Calcd for $C_{28}H_{24}$: C, 93.24; H, 6.71. Found: C, 92.97; H, 6.53.

Procedure 2. The procedure was the same as that described in procedure 1 with the following exception. The crude carbinol 18 obtained from the previously described Grignard reaction was employed. Thus, treatment of the highly viscous pale yellow oil (obtained by the Grignard reaction of 43 g (0.19 mol) of ester as described previously) with 2500 g of poly(phosphoric acid) and 400 mL of glacial acetic acid at 80–90 °C for 24 h gave 25.2 g (36.7%) of 17, mp 171–173 °C.

9,9-Bis(4-carboxyphenyl)-10-anthrone (19). The procedure was the same as that described for 4 with the following exception. The molar ratio of 19 to sodium dichromate employed was 1:4.81. Thus, oxidation of 10 g (0.027 mol) of **18** with 39 g (0.13 mol) of sodium dichromate monohydrate in 400 mL of water at 260–270 °C for 18 h gave 10.5 g (84.0%) of white solid, mp 310–314 °C (lit.[27] mp 303–304 °C), which was recrystallized from aqueous ethanol: IR (KBr) 3500–2800 (br, OH), 1700 (s, C=O), 1600, 1400, 1310, 1010, 920, 730 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 12.8 (br, 1 H, COOH, undergoes exchange with D_2O), 6.8–8.0 (m, 12 H); ^{13}C NMR (Me_2SO-d_6) δ 182.6 (C=O), 166.4 (COOH), 150.0, 147.4, 133.3, 130.8, 130.2, 129.4, 129.0, 127.5, 126.5 (aromatic), 57.5 (tertiary carbon). Anal. Calcd for $C_{28}H_{18}O_5$: C, 77.41; H, 4.18. Found: C, 76.88; H, 4.14.

Acid Chloride of 9,9-Bis(4-carboxyphenyl)-10-anthrone (20). A mixture of 2.80 g (64.5 mmol) of acid **19**, 3.0 g (0.014 mol) of phosphorus pentachloride, and 30 mL of toluene was heated at reflux for 17 h. Toluene and phosphorus oxychloride were removed under reduced pressure. The residue was refluxed with 100 mL of petroleum ether (bp 60–100 °C) for 10 min, allowed to cool to room temperature, and filtered to yield 2.85 g (95.0%) of an off-white solid, mp 186–191 °C. A small portion of this acid chloride was washed with hot petroleum ether (bp 60–100 °C) to yield an off-white solid: mp 199–202 °C; IR (KBr) 3080, 1785 (s, C=O), 1750, 1680, 1600, 1220, 1190, 980, 875, 750 cm^{-1}.

9,9-Bis(4-acetylphenyl)-10-anthrone (21). A mixture of 9.0 g (0.019 mol) of the acid chloride **20**, 25 mL of HMPA, 0.248 g (0.500 mmol) of bis(triphenylphosphine)benzylpalladium(II) chloride, and 8.13 g (6.30 mL, 0.0450 mol) of tetramethyltin was stirred at 65 °C for 24 h. The reaction mixture was poured into 250 mL of water, stirred for 10 min, and extracted three times with 300-mL portions of benzene. The combined benzene extracts were washed successively with water, 5% sodium hydroxide, and water and dried (K_2CO_3). Removal of the solvent gave an off-white solid, which was subjected to dry column chromatography over alumina (F-20, Alcoa). Elution first with chloroform removed less polar impurities. Ethyl acetate elution gave the required product, which was recrystallized from a mixture of ethanol and water to yield 4.65 g (68.5%) of white crystals: mp 245–246 °C; IR (KBr) 3080, 3020, (C–H), 1680, 1660 (C=O), 1600, 1460, 1410, 1320, 1270, 1190, 1020, 960, 930, 830, 760, 720, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.4 (s, 6 H), 6.8–8.2 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 196.6 ($COCH_3$), 183.0 (>C=O), 150.4, 147.3, 135.3, 132.6, 131.7, 130.0, 129.8, 127.8, 127.4, 127.2 (aromatic), 58.0 (tertiary carbon), 26.4 (CH_3). Anal. Calcd for $C_{30}H_{22}O_3$: C, 83.70; H, 5.15. Found: C, 84.15; H, 5.13.

9,9-Bis(4-aminophenyl)fluorene (22).[10] A mixture of 73.0 g (0.405 mol) of fluoren-9-one (3), 222 g (1.71 mol) of aniline hydrochloride, and 420 g (344 mL, 4.51 mol) of aniline was refluxed for 5 h with stirring. The warm reaction mixture was precipitated into 2 L of a 10% potassium hydroxide solution. After this mixture was boiled for 10 min, the red aqueous layer was decanted. This same procedure was followed with two 2-L portions of water. The remaining reddish white solid was collected by suction filtration. Crystallization of the impure diamine from 1.75 L of benzene provided 59 g (37%) of off-white **22**, mp 233.0–234.5 °C. A second crop of **22**, weighing 24 g (17%), was obtained, mp 233.0–234.5 °C, thus giving a total yield of 83 g (54%) of the diamine (lit.[10] mp 235–236 °C).

9,9-Bis(4-nitrophenyl)fluorene (23). To a solution of 31.6 g (0.0907 mol) of **22** dissolved in 1083 mL of glacial acetic acid at 25 °C was added dropwise 225 mL of 30% hydrogen peroxide over 15 min. The mixture was heated on an oil bath at 105 °C with stirring. In two 1-h intervals, additional portions of 100 and 40 mL of 30% hydrogen peroxide were added with continued heating at 105 °C for 2.5 h. The reaction mixture was allowed to cool overnight. Collection of the precipitated solid gave 22.2 g (60.0%) of the impure yellow dinitro compound, mp 252.5–253.5 °C. Crystallization from methyl Cellosolve, with the aid of decolorizing charcoal, yielded 14 g (38%) of a yellow crystalline solid **23**, mp 259.5–260.5 °C. A second crop provided an additional 4.0 g (11%) of **24** for a combined yield of 15 g (52%): IR (KBr) 3060–3020, 1610, 1595, 1515, 1355 (NO_2), 750, 690 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 149.3, 145.8, 144.3, 137.6, 126.4, 126.1, 123.5, 121.5, 118.6 (aromatic), 64.1 (tertiary carbon). Anal. Calcd for $C_{25}H_{16}N_2O_4$: C, 73.52; H, 3.95; N, 6.86. Found: C, 73.29; H, 3.75; N, 6.74.

9,9-Bis[5-(3-phenyl-2,1-benzisoxazolyl)]fluorene (24). To an ice-cooled mixture of 70.0 mL of tetrahydrofuran, 17.5 mL of methanol, and 7.2 g (0.18 mol) of sodium hydroxide was added 7.9 mL (7.8 g, 0.067 mol) of phenylacetonitrile. After 5 min of stirring, 7.00 g (0.0171 mol) of **23** was added and the mixture was refluxed for 3 h. An additional 10 mL of methanol was added, with continued heating for 13 h, and the mixture was cooled to 25 °C. Collection of the light brown solid by suction filtration, followed by washing with 100 mL of water and 400 mL of methanol and air-drying, afforded 5.9 g (62%) of a light beige solid **24**, mp 261.0–262.5 °C. This material was suitably pure for subsequent hydrogenation: IR (KBr) 3080, 1650 (>C=N), 1560, 1530, 1450, 755, 690 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 164.1, 156.9, 148.8, 146.4, 140.1, 132.2, 129.9, 129.0, 128.2, 127.9, 127.8, 126.1, 125.5, 120.6, 117.7, 115.8, 114.0 (aromatic), 65.0 (tertiary carbon); mass spectrum, *m/e* 552 (parent peak). Anal. Calcd for $C_{39}H_{24}N_2O_2$: C, 84.76; H, 4.38; N, 5.07. Found: C, 84.22; H, 4.68; N, 4.92.

9,9-Bis(4-amino-3-benzoylphenyl)fluorene (25). A suspension of 3.50 g (6.33 mmol) of **24**, 0.408 g of 5% palladium-on-carbon, 1.4 mL of triethylamine, and 42 mL of tetrahydrofuran was subjected to a hydrogen atmosphere at ambient temperature and atmospheric pressure until hydrogen uptake ceased. Gravity filtration of the reaction mixture, followed by removal of the solvent, gave 3.3 g (94%) of a bright yellow solid, mp 226.0–227.5 °C. Crystallization from carbon tetrachloride and the ethanol provided, after drying at 105 °C (0.075 mm), 1.6 g (47%) of bright yellow cubic crystals **25**: mp 230.0–230.5 °C; IR (KBr) 3490 (NH_2), 3465 (NH_2), 3355 (NH_2), 3080, 3040, 1640 (>C=O), 1600, 1580, 1255, 750, 700 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 198.1 (>C=O), 150.8, 149.1, 139.5, 139.1, 133.7, 133.5, 132, 130.8, 128.9, 127.5, 127.2, 125.2, 119.9, 117.4, 116.7 (aromatic), 63.1 (CH_2); mass spectrum, *m/e* 556 (parent peak). Anal. Calcd for $C_{39}H_{28}N_2O_2$: C, 84.15; H, 5.07; N, 5.03. Found: C, 83.98; H, 5.24; N, 5.01.

9,9-Bis(4-aminophenyl)-10-anthrone (27).[10,13] To a homogeneous mixture of 39 g (0.19 mol) of 9,10-anthraquinone (**26**) and 114 g (0.88 mol) of aniline hydrochloride, prepared by vigorously shaking the two components in a 500-mL three-necked flask, was added 187 mL (238 g, 2.45 mol) of aniline. Heating this mixture at reflux for 5 h followed by cooling to ambient temperature gave a gummy crystalline mass. This material was transferred to a Büchner funnel and washed with a 1:1 ethanol–water mixture until color was absent from the washings. The resulting solid residue was placed in 1 L of ethanol, and the heterogeneous mixture was heated for 10 min. Metallic brown crystals were collected by suction filtration. The impure diamine was twice crystallized from 200 mL of nitrobenzene, yielding 17 g (55%) of a light greenish tinted powder, **27**, mp 302–305 °C (lit.[13] mp 303–304 °C).

9,9-Bis(4-nitrophenyl)-10-anthrone (28). To a stirred suspension of 23 g (0.13 mol) of *m*-chloroperbenzoic acid and 140 mL of dichloromethane was added 7.0 g (0.019 mol) of **27**. Following the brief exotherm, the mixture was refluxed for 11 h and then cooled at 25 °C for 24 h. Suction filtration of the reaction mixture removed a large portion of the precipitated *m*-chlorobenzoic acid. The remaining acid was extracted with a potassium carbonate solution until the extracts became colorless. Removal of solvent yielded 7.6 g (94%) of a light yellow solid. Chromatography of the crude material on a column of silica gel (eluted with benzene) provided 4.5 g (55%) of a light green yellow solid, **28**: mp 265–267 °C; IR (KBr) 3110, 3080, 3050, 1660 (>C=O), 1600, 1515, 1345 (NO_2), 750, 700 cm^{-1}: ^{13}C NMR ($CDCl_3$) δ 183.0 (>C=O), 152.2, 146.7, 146.3, 133.3, 131.9, 130.7, 129.9, 128.3, 127.9, 123.4 (aromatic), 58.1 (tertiary carbon); mass spectrum, *m/e* 436 (parent peak). Anal. Calcd for $C_{26}H_{16}N_2O_5$: C, 71.55; H, 3.70; N, 6.42. Found: C, 71.26; H, 3.68; N, 6.41.

9,9-Bis[5-(3-phenyl-2,1-benzisoxazoylyl)]-10-anthrone (29). To a solution of 4.8 g (0.12 mol) of sodium hydroxide in 24 mL of methanol and 80 mL of tetrahydrofuran, cooled to 0 °C (ice bath), was added 5.1 mL (5.2 g, 0.044 mol) of phenylacetonitrile. After 3 min had elapsed 4.8 g (0.011 mol) of **28** was also added. The reaction mixture was heated to and kept at a reflux for 18.5 h; then 70 mL of methanol was added and the mixture was allowed to cool for 7 h. Collection of the precipitate by suction filtration, followed by washing with methanol, gave 6.1 g (96%) of a beige crystalline powder, mp 264–265 °C. Crystallization of this solid from benzene afforded 4.5 g (70%) of light beige crystalline **29**: mp 265–266 °C; IR (KBr) 3060, 1660 (>C=O), 1630 (>C=N), 1590, 744, 690 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 183.5 (>C=O), 164.7, 156.4, 145.9, 141.1, 133.1, 132.7, 130.1, 129.7, 129.0, 127.9, 127.6, 126.1, 120.9, 115.4, 113.5 (aromatic), and 58.1 (tertiary carbon); mass spectrum, *m/e* 580 (parent peak). Anal. Calcd for $C_{40}H_{24}N_2O_3$: C, 82.74; H, 4.17; N, 4.82. Found: C, 82.48; H, 4.08; N, 4.79.

9,9-Bis(4-amino-3-benzoylphenyl)-10-anthrone (30). A mixture of 0.21 g of 5% palladium-on-carbon, 1.94 g (3.34 mmol) of **29**, 0.7 mL of triethylamine, and 22 mL of tetrahydrofuran was degassed (water aspirator) and the mixture was exposed to a hydrogen atmosphere until gas uptake ceased. Gravity filtration of the reaction mixture, followed by solvent removal, gave 2.22 g of a bright yellow crystalline solid. The product was crystallized twice from dichloromethane and dried at 105 °C (0.5 mm) to yield 1.24 g (63%) of bright yellow crystals of **31**: mp 288.0–289.5 °C; IR (KBr) 3480 (NH_2), 3420 (NH_2), 3360 (NH_2), 3320 (NH_2), 3060, 3030, 1650 (anthronyl >C=O), 1625 (benzophenone >C=O), 1250, 750, 700 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 198.2 (benzoyl >C=O), 184.2 (anthronyl >C=O), 149.2, 148.7, 139.8, 135.5, 135.2, 132.7, 132.2, 130.7, 129.6, 128.7, 127.7, 127.4, 126.9, 116.8, 116.7 (aromatic), 56.5 (tertiary carbon); mass spectrum, *m/e* 584 (parent peak). Anal. Calcd for $C_{40}H_{28}N_2O_3$: C, 82.17; H, 4.83; N, 4.79. Found: C, 82.64; H, 4.70; N, 4.72.

Polymerizations

Poly[2,2′-(*p*,*p*′-oxydiphenylene)-6,6′-(9,9-fluorenyl)bis(4-phenylquinoline)] (31j). A general procedure for the preparation of cardo polyquinolines is illustrated for the polymerization of amino ketone **12** and 4,4′-diacetyldiphenyl ether.

A mixture of 1.0000 g (1.7960 mmol) of 9,9-bis(4-amino-3-benzoylphenyl)fluorene (**25**), 0.4567 g (1.796 mmol) of 4,4′-diacetyldiphenyl ether, 4 mL of *m*-cresol, and 12 g (44 mmol) of di-*m*-cresyl phosphate was heated at 135–140 °C, with mechanical stirring, for 24 h. Precipitation of this amber-colored reaction mixture into 250 mL of a 10% triethylamine–90% ethanol solvent system provided a fibrous off-white material.

After the polymer was collected by filtration and chopped as a suspension in the amine–alcohol mixture in a Waring blender, the polymer was collected and dried by suction filtration. The polymer was reprecipitated from chloroform into the ethanolamine solution, chopped again in the blender, and filtered. Extracting the polymer for 24 h with the ethanolamine solution, followed by drying for 24 h at 105 °C (0.5 mm), afforded 1.22 g (92%) of **31j** (elemental analysis in Table II).

Films of polyquinoline **31j** were obtained by uniformly spreading *sym*-tetrachloroethane solutions containing 10–20% (w/v) polymer onto glass plates with a doctor's knife and allowing

Table II
Elemental Analyses of "Cardo" Polyquinolines 31

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

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

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

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

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References and Notes

(1) Noren, G. K.; Stille, J. K. *J. Polym. Sci., Part D* **1971**, *5*, 385.
(2) Norris, S. O.; Stille, J. K. *Macromolecules* **1976**, *9*, 496.
(3) Beever, W. H.; Stille, J. K. *Macromolecules* **1979**, *12*, 1033.
(4) Beever, W. H.; Stille, J. K. *J. Polym. Sci., Polym. Symp.* **1978**, *No. 65*, 41.
(5) Korshak, V. V.; Vinogradova, S. V.; Vygodski, Y. S. *J. Macromol. Sci., Rev. Macromol. Chem.* **1974**, *C11*, 45.
(6) Milstein, D.; Stille, J. K. *J. Org. Chem.* **1979**, *44*, 1613.
(7) Vinogradova, S. V.; Reimigh, G.; Tur, D. R.; Ulkrikh, G.; Suprun, A. P.; Vointseva, I. J. *Izv. Akad. Nauk, Ser. Khim.* **1975**, *1*, 191.
(8) Graebe, C.; Rateanu, A. S. *Justus Liebigs Ann. Chem.* **1894**, *279*, 257.
(9) Barnett, E. B.; Cook, J. E.; Niton, I. G. *J. Chem. Soc.* **1927**, 508.
(10) Khar'kov, S. N.; Chegolya, A. S.; Baranov, A. N. *Volokna Sint. Polim.* **1970**, 19.
(11) Holmes, R. R.; Bayer, R. P. *J. Am. Chem. Soc.* **1960**, *82*, 3456.
(12) Davis, R. B.; Pizzini, L. C. *J. Org. Chem.* **1960**, *25*, 1884.
(13) Etienne, A.; Arcos, J. C. *Bull. Soc. Chim. Fr.* **1951**, 727.
(14) Nunno, L. D.; Florio, S.; Todesco, P. E. *J. Chem. Soc. C* **1970**, 1433.
(15) Hassall, C. H. *Org. React.* **1957**, *9*, 73.
(16) Billmeyer, F. W., Jr. "Textbook of Polymer Science", 2nd ed.; Wiley: New York, 1971; p 178.
(17) Sybert, P. D.; Beever, W. H.; Stille, J. K. *Macromolecules* **1981**, *14*, 493.
(18) Koo, G. P. *Plast. Eng.* **1974**, *30*, 33.
(19) Wrasidlo, W.; Norris, S. O.; Wolfe, T. F.; Katto, T.; Stille, J. K. *Macromolecules* **1976**, *9*, 512.
(20) Tani, H.; Toda, F.; Matsumuja, K. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 391.
(21) Jones, M. E. B.; Thorton, D. A.; Webb, R. F. *Makromol. Chem.* **1961**, *49*, 62.
(22) Shamis, E. M.; Dashevskii, M. M. *J. Org. Chem. USSR (Engl. Transl.)* **1967**, *3*, 1055.
(23) Bailey, D. M.; Degrazia, C. G. *J. Med. Chem.* **1973**, *16*, 151.
(24) Vogel, A. I. "Textbook of Practical Organic Chemistry", 4th ed.; Longmans: London, 1978, p 289.
(25) "Dictionary of Organic Compounds"; Oxford University Press: New York, 1934; Vol. 1, p 650.
(26) Neville, R. G. *J. Org. Chem.* **1959**, *24*, 111.
(27) Vinogradova, S. V.; Salazkin, S. N.; Beridge, L. A.; Pavlova, T. S.; Korshak, V. V. USSR Patent 318564; *Chem. Abstr.* **1972**, *76*, 46003.

Synthesis and Properties of Rigid-Rod Polyquinolines

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

Introduction

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

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