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Syntheses of Polyquinolines Containing Diphenylphosphine Ligands as Heterogeneous Supports for Homogeneous Catalysts

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ABSTRACT: Polyquinolines containing diphenylphosphine ligands attached to an incorporated phenanthrene ring were prepared by the polymerization of the appropriate molar ratios of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether, 4,4′-diacetyldiphenyl ether, and 3,6-diacetyl-9-(diphenylphosphino)phenanthrene or by the phosphination of the polyquinoline containing 9,10-dichlorophenanthrene units in the backbone with alkali diphenylphosphide. Hydroformylation reactions were carried out in the presence of these polyquinoline-supported catalysts.

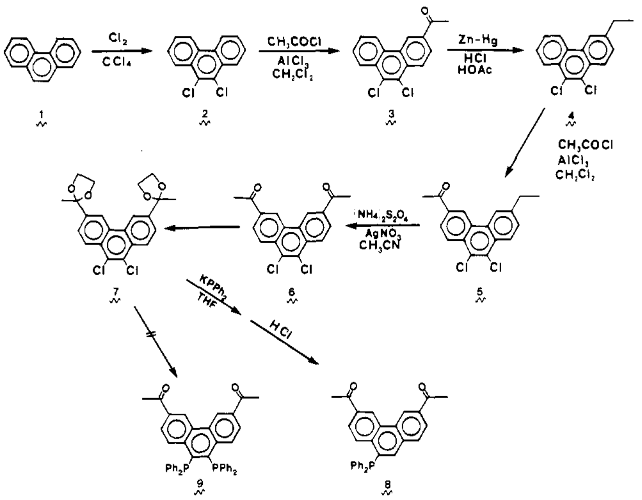
Introduction

Although homogeneous catalytic reactions generally require lower reaction temperatures than the corresponding heterogeneous catalytic reactions, there are still a number of homogeneously catalyzed reactions that are performed at relatively high temperatures. For example, a Fischer–Tropsch reaction has been carried out at 150–270 °C in the presence of iron, cobalt, ruthenium, and osmium homogeneous catalysts.[1-3] Homologations of methanol and acetic acid take place with cobalt catalysis at 200–220 °C,[4-9] and the water-gas shift reaction requires a wide range of temperatures.[10,11]

There are a number of advantages to be gained by attaching a homogeneous catalyst to an insoluble support, probably the most important of which are a simplification of the process and catalyst recovery.[12] Although cross-linked polystyrene, because of its availability, is the most commonly used polymer support for homogeneous catalysts, it is mechanically and thermally unstable.[13] Further, polystyrene has poor chemical stability and will not endure a number of catalytic processes, such as oxidation or photochemical reactions. Thus, it was desirable to develop a heterogeneous polymer support that possessed greater thermal stability.

Polyquinoline was selected as a thermally stable support for some homogeneous catalysts because of its excellent thermal stability, good chemical stability, solubility in certain common organic solvents, and ability to undergo certain cross-linking reactions.[14] Furthermore, the polymerization reaction and the latitude available in the monomer synthesis promised to allow the preparation of monomers bearing the desired ligands, particularly chelating phosphine ligands.

Scheme I



The particular target monomer (**9**) containing chelating phosphine ligands (Scheme I) could not be synthesized. Instead a monomer (**8**) bearing a single phosphine was obtained. In this work we describe the syntheses of polyquinolines containing a diphenylphosphino ligand and some hydroformylation reactions using polyquinoline-supported catalysts.

Results and Discussion

Synthesis of 3,6-Diacetyl-9,10-dichlorophenanthrene (Scheme I). When 9,10-dichlorophenanthrene was prepared according to the literature,[15] the yield of the pure product was only about 20% and was dependent on the quality of the phenanthrene. When technical phenanthrene (content 90%) was used, no precipitate appeared during the chlorination, but a dark solution resulted, from which a product difficult to purify

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Table I
^{1}H NMR Chemical Shifts (δ) in Phenanthrene Derivatives

protons	3,6-dicyano-phenanthrene	3,6-dibromo-phenanthrene	6	7
4, 5	9.02	8.75	8.46	8.75
1, 2, 7, 8	7.8-8.2	7.74-7.76	7.89	7.60-8.35

was obtained. Among the chlorination byproducts was 2,9,10-trichlorophenanthrene.

The acetylation of phenanthrene by the Friedel-Crafts reaction in various solvents such as nitrobenzene, chloroform, and carbon tetrachloride produces a mixture of isomers.[16] Acylation of **2** with acetyl chloride and aluminum chloride in methylene chloride under mild conditions, however, gave a monoacetyl compound. It was necessary to stir the mixture of acetyl chloride and aluminum chloride in methylene chloride for at least 15 min before the addition of dichlorophenanthrene; otherwise, the product was an oil. Direct diacetylation has been attempted by using a large excess of acetylating reagent or from the monoacetyl compounds, but only a mixture of products, including monoacetyl phenanthrene was obtained.

Reduction of 3-acetyl-9,10-dichlorophenanthrene (**3**) to the corresponding ethyl derivative followed by a second acylation was necessary for the clean introduction of the second acetyl group. Oxidation of the ethyl group to the desired acetyl functionality could not be carried out by the same procedure used to oxidize *p*-ethylacetophenone to *p*-diacetylbenzene.[17] The insolubility of **5** in this reaction medium (potassium permanganate in a buffered solution of magnesium oxide in nitric acid and water) accounts for the lack of oxidation. Diacetyl monomer (**6**) was obtained by oxidation of **5** with potassium permanganate in acetic acid or chromic acid in acetic acid-water, both in very low yield.

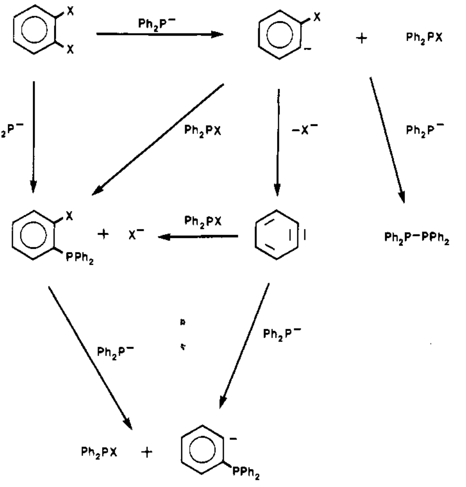
Structure of 3,6-Diacetyl-9,10-dichlorophenanthrene. In the ^{13}C NMR spectrum of **6**, only one peak was observed for each carbonyl or methyl carbon, at 169.57 and 26.91 ppm, respectively. Moreover, there are only seven peaks, corresponding to the seven different aromatic carbons of the phenanthrene nucleus, confirming that a symmetrical structure was obtained.

In the ^{1}H NMR spectra of 3,6-dicyanophenanthrene and 3,6-dibromophenanthrene,[18] the peak assigned to the 4,5 protons is located furthest downfield in the spectrum, and the peaks assigned to the 1,2,7,8 protons are very close to those in the ^{1}H NMR spectrum of **6** (Table I).

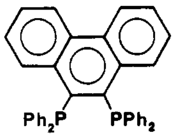
In the ^{1}H NMR spectrum of **7**, there is an AB pattern in the 8.35-7.60 ppm range, and the single peak assigned to the 4,5 protons can still be seen. This rules out not only the 1,8- and 4,5-substituted products but also the 2,7-substituted product. Thus, the structure of the diacetyl compound has been assigned as 3,6-diacetyl-9,10-dichlorophenanthrene.

Phosphination of 3,6-Diacetyl-9,10-dichlorophenanthrene. Although alkali phosphides react readily with alkyl halides to give the desired tertiary phosphines, usually in good yields, the reaction with aromatic halides is more difficult. The substitution of bromides and iodides can be carried out,[19,20] but the substitution of aryl bromides and iodides by phosphines has been demonstrated only with monohalides or in aromatic dihalides in which the halides are not adjacent.[21] Substitution reactions of *o*-dihalo aromatics are much more difficult, particularly with diphenylphosphide. *o*-Phenylenebis(diphenylphosphine) has been synthesized by the reaction of chlorodiphenylphosphine with the *o*-halo Grignard reagent followed by metalation of the *o*-halophosphine with lithium and reaction of the aryllithium again with chlorodiphenylphosphine.[22,23]

Scheme II



The reaction of *o*-dihalo aromatics with alkali diphenylphosphide yields mainly triphenylphosphine, probably as a consequence of benzyne generation[24] (Scheme II). In our hands, the reaction of *o*-dichlorobenzene with sodium or potassium diphenylphosphide gave 6% *o*-phenylenebis(diphenylphosphine) while *o*-diiodobenzene produced 4.8% of the desired product. Although the phosphination of 9,10-dichlorophenanthrene with lithium diphenylphosphide has been reported to yield 9,10-bis(diphenylphosphino)phenanthrene in a 65% yield,[25] this result could not be repeated. We obtained a 5% yield of **10** with a melting point of 200 °C, not 140 °C, as reported.[25]



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Phosphination of **7** with diphenylphosphide in THF produced only **8** in a 3% yield. Although the use of 18-crown-6 did increase the yield in the phosphination of *o*-dihalobenzene, it did not increase the yield of **8** or **9**.

Syntheses of Polyquinoline-Supported Phosphines. The polymerization of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**11**) with 4,4′-diacetyldiphenyl ether (**12**) and **6** was carried out to obtain a polyquinoline (**13**) containing dichlorophenanthrene units. Phosphination of **13** with alkali phosphide was carried out to give the polyquinoline-supported phosphine (Schemes III and IV). A polymer containing monophosphinated phenanthrene units on the polymer was obtained using a twofold excess of phosphinating reagent, while use of a larger excess phosphinating reagent degraded the polymer, yielding a low molecular weight material with a larger phosphorus content than could be accounted for by displacement of all the halogen (Table III, Experimental Section). Polymerization of **11** with **12** and **8** gave a polyquinoline with evenly distributed phosphine ligands (Scheme IV, Table III, Experimental Section).

Table II
Hydroformylation of 1-Pentene[a]

Rh complex	phosphine ligand	conversion, %	ratio[b]
$[Rh(CO)_2Cl]_2$		100	0.76
$[Rh(CO)_2Cl]_2$	PPh_3	99	0.88
$[Rh(CO)_2Cl]_2$	diphos	82.2	0.86
$[Rh(CO)_2Cl]_2$	*o*-phenylenebis(diphenylphosphine)	72.8	1.55
$[Rh(CO)_2Cl]_2$[c]	**10c**	93.7	3.20
$[Rh(COD)_2Cl]_2$[c]	**10c**	100	0.73
$[Rh(CO)_2Cl]_2$	**14c**	100	0.91

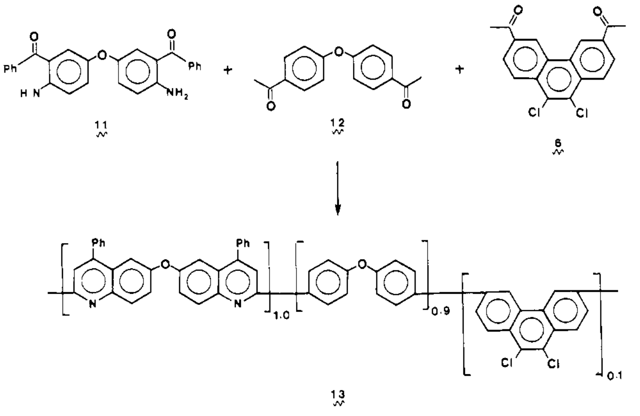
[a] Reaction conditions: 1-pentene, 1.0 mL; benzene, 10 mL; temperature, 100–110 °C; pressure, 600 psi ($[CO]:[H_2] = 1:1$); time, 16–18 h; [Rh], 0.008 mg atom; [P]:[Rh] = 2:1. [b] [*n*-Hexanal]:[2-methylpentanal]. [c] [Rh] = 0.0126 mg atom; [P]:[Rh] = 7:1.

Table III
Polyquinolines with Phosphine as Ligand

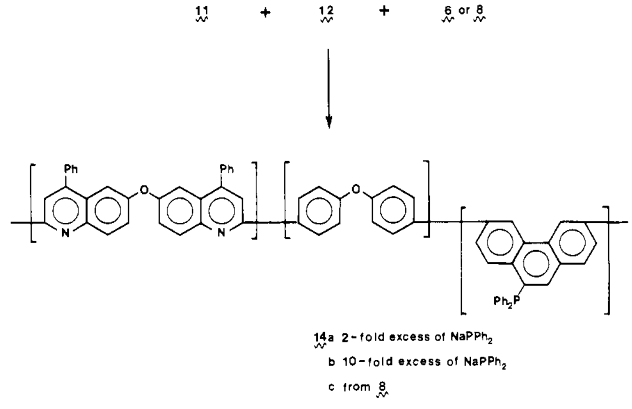
polymer	[η],[a] dL g^{-1}	yield, %	elemental anal.[c] % C	% H	% N	% Cl	% P
13	2.25	94.4	83.35	4.43	4.67	1.15	
			(84.78)	(4.36)	(4.69)	(1.06)	
14a	0.47[b]	93.5	82.18	4.53	4.52		0.28
			(85.31)	(4.38)	(4.51)		(0.64)
14b	0.13[b]	97.6					1.65
			(85.31)	(4.38)	(4.51)		(0.64)
14c	1.74	94.7	85.28	4.55	4.68		0.45
			(85.45)	(4.45)	(4.62)		(0.40)

[a] $CHCl_3$, 25 °C. [b] Inherent viscosity, 0.5%, $CHCl_3$, 25 °C. [c] The values in parentheses are calculated.

Scheme III



Scheme IV



Hydroformylation of 1-pentene was carried out with a rhodium catalyst and added triphenylphosphine or the polymer-bound phosphine ligands (Table II). The ratio of branched to normal isomers was dependent on the phosphine to rhodium ratio, higher ratios of *n*-aldehyde being obtained with higher phosphine to rhodium ratios. These results are consistent with those obtained from the analogous homogeneous hydroformylation with catalysts containing triphenylphosphine ligands.

Experimental Section

^1H NMR spectra were obtained on a Varian EM360 spectrometer, and ^{13}C NMR spectra were obtained on a JEOL FX-100 instrument, both using tetramethylsilane as the internal standard. ^{31}P NMR spectra were obtained on a Nicolet NT-150 instrument, with 85% H_3PO_4 as the external reference. Infrared spectra were taken on a Beckman Acculab 3 spectrophotometer. GLC separations were performed on a Varian 3700 on a 10% SE 30/Chromosorb W (60–80 mesh) 0.25 in. × 20 ft column. Melting points and boiling points are uncorrected. Elemental analyses were determined by Micro-Tech Laboratories, Inc.

9,10-Dichlorophenanthrene (2). Into an ice-cooled stirred suspension of 100 g (0.56 mol) of phenanthrene and 200 mL of carbon tetrachloride was passed dry chlorine through a 6-mm (i.d.) glass tube at a rate of about 200 bubbles per minute. The reaction was monitored by weighing the reaction flask periodically. The reaction mixture became a clear green-yellow solution after about 20 g of chlorine was absorbed. The absorption of chlorine slowed down in the following 1–2 h and then increased again as more and more white crystals appeared. The reaction was stopped after the absorption of about 40 g (0.56 mol) of chlorine. From the slurry, 39 g of crystals was obtained by filtration and washed with carbon tetrachloride. The filtrates were combined and the solvent was distilled under 1 atm. The product was distilled under reduced pressure to give 73.5 g (180–200 °C (0.2 mm)) of crude product. The solid products were combined and recrystallized from carbon tetrachloride three times to afford 30 g (21.7%) of white crystals, mp 160–164 °C (lit.[15] mp 160.5 °C). 2,9,10-Trichlorophenanthrene was a byproduct (mp 141–145 °C (lit.[26] mp 144 °C)).

3-Acetyl-9,10-dichlorophenanthrene (3). To an ice-cooled mixture of 10.0 g (75.0 mmol) of anhydrous aluminum chloride and 60 mL of methylene chloride (dried over molecular sieves) was added dropwise 5.36 mL (5.90 g, 75.0 mmol) of acetyl chloride to give a homogeneous solution. After 15 min of stirring, 6.18 g (25.0 mmol) of **2** was added in portions over 5 min. A green-yellow precipitate appeared 30 min after the addition of **2**. The reaction was allowed to continue overnight at room temperature. The slurry was slowly poured into a mixture of ice and hydrochloric acid to hydrolyze the complex. The water layer was extracted with methylene chloride. The organic layers were combined and washed with water, aqueous sodium bicarbonate, and water again and dried over anhydrous magnesium sulfate. After the removal of solvent, the residue was recrystallized from toluene to give 4.9 g (68.1%) pale crystals: mp 173.5–175.5 °C; ^{1}H NMR (CDCl$_3$) δ 8.8–7.3 (m, 7 H), 2.65 (s, 3 H); IR (KBr) 1670 (C=O). Anal. Calcd for $C_{16}H_{10}Cl_2O$: C, 66.46; H, 3.49. Found: C, 66.02; H, 3.48.

9,10-Dichloro-3-ethylphenanthrene (4). To a stirred mixture of 40 g of zinc dust and 4.0 g of mercury chloride was added a solution of 2 mL of hydrochloric acid and 50 mL of water. After stirring for 5 min, the water layer was decanted. A mixture of 100 mL of concentrated hydrochloric acid, 100 mL of glacial acetic acid, 40 mL of toluene, and 7.23 g (25.0 mmol) of **3** was added to the amalgam. The reaction mixture was heated to reflux with stirring for 4 h. After cooling, the mixture was poured into 500 mL of water. The toluene layer was separated, and the water layer was extracted with ether. The amalgam residue was ground and extracted thoroughly with ether. The ether extracts were combined with the toluene layer and washed, in turn, with water, aqueous sodium bicarbonate solution, and water. The organic layer was dried over anhydrous magnesium sulfate. The solvents were removed by distillation and the residual thick oil was distilled under reduced pressure to give 4.4 g (64.0%) of white product: bp 160–167 °C (0.1 mm); mp 73.5–75.5 °C (ethanol); ^{1}H NMR (CDCl$_3$) δ 8.4–7.1 (m, 7 H), 2.8 (q, 2 H), 1.3 (t, 3 H). Anal. Calcd for $C_{16}H_{12}Cl_2$: C, 69.84; H, 4.40. Found: C, 69.69; H, 4.37.

6-Acetyl-9,10-dichloro-3-ethylphenanthrene (5). To an ice-cooled suspension of 6.0 g (4.50 mmol) of anhydrous aluminum chloride in 40 mL of methylene chloride (dried over molecular sieves) was added dropwise 3.2 mL (3.5 g, 45.0 mmol) of acetyl chloride. After 15 min of stirring, 4.1 g (15 mmol) of **4** was added. A green-yellow solid appeared in a few minutes. The reaction was continued overnight at room temperature. This slurry was hydrolyzed in a mixture of ice and hydrochloric acid. The water layer was extracted with methylene chloride. The organic layers were combined, washed with water, aqueous sodium bicarbonate solution, and water, and dried over anhydrous magnesium sulfate. After the removal of the methylene chloride, the residue was purified by recrystallization from toluene to afford 3.4 g (71.4%) of light yellow crystals: mp 153.5–155.5 °C; ^{1}H NMR (CDCl$_3$) δ 8.8–7.3 (m, 6 H), 2.9 (q, 2 H), 2.65 (s, 3 H), 1.3 (t, 3 H); IR (KBr) 1685 (C=O). Anal. Calcd for $C_{18}H_{14}Cl_2O$: C, 68.15; H, 4.45. Found: C, 68.25; H, 4.46.

3,6-Diacetyl-9,10-dichlorophenanthrene (6). To a suspension of 9.3 g (29.3 mmol) of **5** in 207 mL of acetonitrile was added a solution of 14.7 g (64.5 mmol) of ammonium persulfate in 70 mL of water. The mixture was heated to reflux, and 0.14 g (0.80 mmol) of silver nitrate in a few drops of water was added by pipet. Reflux was continued for 8 h, and then an additional part of the ammonium persulfate was added followed by the addition of silver nitrate as described above. After 8 h of further reflux, the mixture was cooled and the organic layer was separated. Acetonitrile was removed to dryness under reduced pressure. The residue was stirred in chloroform, and the insoluble material was filtered. The filtrate was concentrated and subjected to column chromatography on alumina using chloroform as an eluent. The second band was collected to afford 2.29 g (23.6%) of yellow solid. Further purification was accomplished by recrystallization from toluene three times to give 1.29 g of monomer-grade light yellow needles: mp 203.0–204.0 °C; ^{1}H NMR (CDCl$_3$) δ 8.46 (s, 2 H), 7.89 (s, 4 H), 2.65 (s, 6 H); ^{13}C NMR (CDCl$_3$) 169.57 (CO), 135.09, 131.30, 130.77, 128.55, 126.69, 125.75, 122.48 (carbons in phenanthrene nucleus), 28.91 (CH$_3$); IR (KBr) 1680 (C=O). Anal. Calcd for $C_{18}H_{12}Cl_2O_2$: C, 65.28; H, 3.65. Found: C, 65.17; H, 3.79.

3,6-Bis(2-methyl-1,3-dioxolan-2-yl)-9,10-dichlorophenanthrene (7). A mixture of 3.80 g (11.5 mmol) of **6**, 4.30 g (68.8 mmol) of ethylene glycol, and 0.20 g (1.15 mmol) of *p*-toluenesulfonic acid in 100 mL of toluene was heated to reflux for 24 h. Water generated during the reaction was removed via a Dean–Stark trap. After the removal of toluene, the pale crystals were washed with ethanol thoroughly to give 3.42 g (71.3%) of **7**: mp 191.5–193.5 °C; ^{1}H NMR (CDCl$_3$) δ 8.7 (s, 2 H), 8.4–7.6 (q, 4 H), 4.2–3.7 (m, 8 H), 1.75 (s, 6 H). Anal. Calcd for $C_{22}H_{20}Cl_2O_4$: C, 63.02; H, 4.81. Found: C, 62.82; H, 4.76.

3,6-Diacetyl-9-(diphenylphosphino)phenanthrene (8). To 50 mL of liquid ammonia was added 0.750 g (32.5 mmol) of sodium. After 15 min of stirring, 6.05 g (32.5 mmol) of diphenylphosphine was added dropwise to the dark blue solution followed by the addition of 40 mL of THF. The temperature was allowed to rise gradually to let the ammonia evaporate smoothly. The orange solution was heated to reflux for 30 min to drive off the final traces of ammonia. A solution of 3.40 g (8.10 mmol) of **7** in 75 mL of THF was added slowly to the phosphide at −20 °C. The mixture was warmed and heated to reflux for 2 h; then 10 mL of methanol was added dropwise to the brown mixture to quench the reaction. After an additional 15-min reflux, 50 mL of 2 N hydrochloric acid was added, and the reflux was continued overnight. THF was removed under reduced pressure. Toluene was added to the red oil, and the solution was washed successively with aqueous sodium bicarbonate and water and was then dried over anhydrous sodium sulfate. After the removal of solvent, the yellow oil was subjected to column chromatography on alumina using methylene chloride as an eluent. The second band was collected and recrystallized from methylene chloride/ethanol (1:1) to give 0.17 g (3.0%) of bright yellow crystals: mp 219.5–221.5 °C; ^{1}H NMR (CDCl$_3$) δ 9.5–7.2 (m, aromatic protons), 2.7 (s, 6 H); ^{31}P NMR (CDCl$_3$) −11.1 ppm; mass spectrum, m/z 446. Anal. Calcd for $C_{30}H_{23}O_2P$: C, 80.70; H, 5.19; P, 6.94. Found: C, 81.02; H, 5.29; P, 7.33.

***o*-Bis(diphenylphosphino)benzene.** To 1.76 g (45.0 mmol) of potassium in 20 mL of THF was added 8.38 g (45.0 mmol) of diphenylphosphine at room temperature. The reaction mixture was slowly heated to reflux for 1 h and then cooled to 0 °C. A solution of 2.21 g (15.0 mmol) of *o*-dichlorobenzene and 0.6 g of 18-crown-6 in 30 mL of THF was added. After 15 min of stirring, the ice bath was withdrawn. The reaction was carried out at room temperature for 1 h and then the mixture was heated to reflux for 2 h. The THF was removed under reduced pressure. To the residue were added 150 mL of water and 150 mL of ether. The layers were separated and extracted with 50 mL of ether and 50 mL of water twice, respectively. The combined ether layer was dried over anhydrous magnesium sulfate. The ether was evaporated under reduced pressure, and the residue was dissolved in 10 mL of ethanol and was added to a solution of 3.57 g (15.0 mmol) of nickel chloride hexahydrate in 30 mL of ethanol at the reflux temperature under a nitrogen atmosphere. After stirring for 1 h, the mixture was cooled, and an orange-brown precipitate was filtered. The precipitate was washed with ethanol and then suspended in 20 mL of methylene chloride. To the suspension was added a solution of 1.95 g (30.0 mmol) of potassium cyanide in 20 mL of water. The mixture was stirred at room temperature for 1 h. The organic layer was separated, washed with water, dried over anhydrous magnesium sulfate, and then concentrated to 1–2 mL. Ethanol (2 mL) was added and the solution was stored in the refrigerator overnight. The white crystals obtained were filtered, washed with ethanol, and dried under reduced pressure to give 0.53 g (8.0%) of *o*-bis(diphenylphosphino)benzene: mp 183.5–185.5 °C (lit.[22] mp 185–187 °C).

When the reaction was carried out with *o*-diiodobenzene instead of the chloro analogue, a yield of 4.8% of diphosphine was obtained. Irradiation of the reaction mixture with a tungsten bulb during phosphination did not improve the yield.

9,10-Bis(diphenylphosphino)phenanthrene (10). To 20 mL of liquid ammonia was added 0.46 g (20.0 mmol) of sodium. After 15 min of stirring, 3.72 g (20.0 mmol) of diphenylphosphine was syringed into the dark blue solution followed by the addition of 20 mL of THF. The temperature was allowed to rise gradually to let the ammonia evaporate smoothly. The orange solution was heated to reflux for 30 min to drive off the final traces of ammonia. A solution of 2.47 g (10.0 mmol) of dichlorophenanthrene in 20 mL of THF was added to the phosphide at 0 °C, and the mixture was then heated to reflux for 2 h and then cooled. After the removal of the THF, ether and water were added to the yellow-brown residue. The ether layer was washed with water and then dried over anhydrous magnesium sulfate. After the removal of the ether, methylene chloride (solvent) and ethanol (nonsolvent) were added and the mixture was stored in the refrigerator for 2 days. The yellow crystals (0.44 g) were filtered and recrystallized from toluene/hexane (1:1) to give 0.25 g (4.6%) of light yellow crystals: mp 196–201 °C (lit.[25] mp 140 °C).

To the crude yellow oil was added excess sulfur in toluene. The solution was heated to reflux overnight. The yellow solid was collected by filtration without cooling and washed with hot toluene twice. The product, having the composition of 9,10-bis(diphenylphosphino)phenanthrene monosulfide, was obtained in a yield of 13%: mp 294.5–297.5 °C; ^{31}P NMR (tetrachloroethane) δ 40.3, 39.2, −13.0, −14.0. Anal. Calcd for $C_{38}H_{28}P_2S$: C, 78.87; H, 4.88; P, 10.71; S, 5.54. Found: C, 78.55; H, 4.98; P, 11.59; S, 5.56.

The phosphination was carried out with lithium diphenylphosphide as phosphinating reagent. After reflux for 12 h, the chloride ion released during the reaction was only 38.2%.

General Procedure for the Polymerization. To a resin flask were added 0.8169 g (2.000 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**11**), 0.4577 g (1.800 mmol) of 4,4′-diacetyldiphenyl ether (**12**), 0.2000 mmol of the comonomer (**6** or **8**), 10 g of di-*m*-cresyl phosphate, and 4 g of *m*-cresol.[14] The flask was purged with nitrogen. The polymerization was carried out at 135–140 °C with mechanical stirring for 24 h. An additional portion of *m*-cresol was added when the mixture became too thick for stirring. The yellow-orange viscous solution was precipitated into 200 mL of ethanol containing 10% of triethylamine and chopped in a blender. The resultant yellow fibrous polymer was extracted with ethanol in a Soxhlet extractor for 24 h and dried at 100 °C under reduced pressure for 24 h (Table III).

General Procedure for Macromolecular Phosphination. To 20 mL of liquid ammonia was added 0.078 g (0.340 mmol) of sodium to afford a dark blue solution; then 0.63 g (0.34 mmol) of diphenylphosphine was added, followed by the addition of 20 mL of THF. An orange solution was generated in a few minutes. The ammonia was driven off as described above. The phosphide solution was added rapidly to the mixture of **13** in 30 mL of THF at room temperature with stirring overnight and then heated to reflux for 1 h. After the mixture cooled, the polymer was precipitated in ethanol, extracted with ethanol under nitrogen for 24 h, and dried at 100 °C under reduced pressure for 24 h (Table III).

General Procedure for the Catalytic Reactions. All catalytic reactions were carried out in a 100-mL stainless steel bomb with a glass cylinder and a glass cylinder lid. The catalyst, substrate, and solvent were charged into the cylinder. The bomb was purged with synthesis gas 3–5 times before heating. After the reaction, the bomb was cooled thoroughly by a dry ice/2-propanol bath, and then the pressure was released very slowly. The mixture was vacuum transferred and then examined by GLC and/or other means such as NMR or IR.

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Registry No. **2**, 17219-94-2; **3**, 85565-99-7; **4**, 85566-00-3; **5**, 85566-01-4; **6**, 85565-95-3; **7**, 85566-02-5; **8**, 85565-97-5; **10**, 39705-76-5; **13**, 85565-96-4; **14**, 85565-98-6; phenanthrene, 85-01-8; ethylene glycol, 107-21-1; *o*-bis(diphenylphosphino)benzene, 13991-08-7; *o*-dichlorobenzene, 95-50-1; 1-pentene, 109-67-1; hexanal, 66-25-1; 2-methylpentanal, 123-15-9; $[Rh(CO)_2Cl]_2$, 14523-22-9; $[Rh(COD)_2Cl]_2$, 12092-47-6.

References and Notes

(1) Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419.

(2) Daroda, R. J.; Blackborow, J. R.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1980**, 1098.

(3) Daroda, R. J.; Blackborow, J. R.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1980**, 1101.

(4) Bozik, J. E.; Kobylinski, T. P.; Pretzer, W. R. U.S. Pat. 4 239 924, Dec 16, 1980.

(5) Bozik, J. E.; Kobylinski, T. P.; Pretzer, W. R. U.S. Pat. 4 239 925, Dec 16, 1980.

(6) Dumas, H.; Levisalles, J.; Rudler, H. *J. Organomet. Chem.* **1980**, *187*, 405.

(7) Keister, J. B.; Geutile, R. *J. Organomet. Chem.* **1981**, *222*, 143.

(8) Sugi, Y.; Bando, K.; Takami, Y. *Chem. Lett.* **1981**, 63.

(9) Knifton, J. F. *CHEMTECH* **1981**, 609.

(10) Murata, K.; Matsuda, A.; Bando, K.; Sugi, Y. *J. Chem. Soc., Chem. Commun.* **1979**, 785.

(11) Okano, T.; Kobayashi, T.; Konishi, H.; Kiji, J. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3799.

(12) Pittman, C. U., Jr. In "Polymer Supported Reactions in Organic Synthesis"; Hodge, P., Sherrington, D. C., Eds.; Wiley: New York, 1980; Chapter 5.

(13) See: Sherrington, D. C. Ref 12, Chapter 1. See also: International Workshop on Heterophase Attached Homogeneous Catalysis, Grenoble, France, 1977 (CNRS and NSF).

(14) Stille, J. K. *Macromolecules* **1981**, *14*, 870 and references therein.

(15) Carey, J. G.; Millar, I. T. *J. Chem. Soc.* **1959**, 3144.

(16) Girdler, R. B.; Gore, P. H.; Thadani, C. K. *J. Chem. Soc. C* **1967**, 2619.

(17) Holsten, J. R.; Pitts, E. H., Jr. *J. Org. Chem.* **1961**, *26*, 4151.

(18) Blackburn, E. V.; Loader, C. E.; Timmons, C. J. *J. Chem. Soc. C* **1968**, 1576.

(19) Swartz, J. E.; Bunnett, J. F. *J. Org. Chem.* **1979**, *44*, 340.

(20) Swartz, J. E.; Bunnett, J. F. *J. Org. Chem.* **1979**, *44*, 4673.

(21) Kosolapoff, G. M.; Maier, L. "Organophosphorus Compounds"; Wiley: New York, 1972; Vol. 1.

(22) Chiswell, B.; Venenzi, L. M. *J. Chem. Soc. A* **1966**, 417.

(23) Hart, F. A. *J. Chem. Soc.* **1960**, 3324.

(24) Gillespie, D. G.; Walker, B. J.; Stevens, D.; McAuliffe, C. A. *Tetrahedron Lett.* **1976**, 1905.

(25) Chow, K. K.; Halfpenney, M. T.; McAuliffe, C. A. *J. Chem. Soc., Dalton Trans.* **1973**, 147.

(26) "Rodd's Chemistry of Carbon Compounds III^{H}", 2nd ed.; Coffey, S., Ed.; Elsevier: Amsterdam, 1979; p 119.

Synthesis of High Molecular Weight Ring Polystyrenes[†]

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ABSTRACT: The reaction of two-ended living polystyrylsodium with dimethyldichlorosilane was used to prepare narrow molecular weight distribution ring polymers. The molecular weight of the samples ranged from 5×10^3 to 4.5×10^5. It was found that ring and linear polymers of the same molecular weight can be fractionally precipitated. Ultracentrifugation sedimentation and gel permeation chromatography were used to monitor the purity of the ring polymers.

Introduction

It was discovered in 1962 that certain DNA molecules occur in nature in a circular form.[1] DNA molecules, however, are complex molecules and their circularity imposes certain constraints on their conformations. A particularly illuminating introduction to the peculiar aspects of circular DNA conformations was written by Cantor and Schimmel.[2] It was soon recognized that it would be useful to study ring polymers that occur normally as flexible random coils,[3] but the challenge of their synthesis had to be rekindled.[4]

Ring polymers are formed in the polymerization of certain heterocyclics and during polycondensation reac-

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