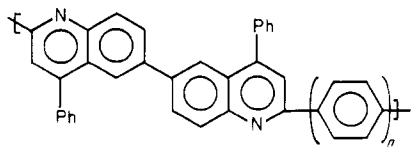
Table IX
X-ray Data on Powder Samples of Polyquinolines 23[a]



polymer	n	d spacing,[a] Å	impurity spacing, Å
23a	1	4.9 (h), 5, 34 (m)	
23b	2	4.9 (h)	
23c	3	4.9 (m), 6.0 (m)	
24d	4	4.9 (m), 4.9 (h)	3.39 (s)

[a] s = sharp diffraction ring, m = medium sharp diffraction ring, h = halo diffraction ring.

obtained. Tensile properties of the "as-spun" and heat-treated fibers are listed in Table V.

Polymer Properties. Viscosity measurements of the polymers were determined in *sym*-TCE, *m*-cresol, concentrated sulfuric acid, or trifluoromethanesulfonic acid at 25.0 ● 0.2 °C, using a Cannon-Ubbelohde viscometer. 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 (10 °C/min) that had first been heated at 50 °C/min under a flowing nitrogen atmosphere to 450 °C and then quenched with liquid nitrogen. Thermogravimetric analyses were obtained with a heating rate of 50 °C/min on pressed powder samples in both flowing air and nitrogen atmospheres.

Dynamic thermomechanical analyses were obtained on film specimens with a Rheovibron (Model DDV-II-C) as described previously.[4] A frequency of 35 Hz was used with an approximate heating rate of 5–10 °C/min in a flowing nitrogen atmosphere.

X-ray diffraction patterns were carried out by Dr. J. B. Lando and D. R. Day, Department of Macromolecular Science, Case Western Reserve University, on powder samples of **23a–d** (Table IX) and fibers of **22b**, using a Statton powder camera with Cu Kα radiation. X-ray data on powder samples of **22b** were carried out by Dr. N. Baenziger, University of Iowa, using a Debye-Scherrer powder camera with Cu Kα radiation.

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Synthesis of (*R*)-Cyclohexylmethyl-*p*-styrylphosphine and the Preparation of Polymer-Bound Optically Active Phosphines

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ABSTRACT: Synthesis of (*R*)-cyclohexylmethyl-*p*-styrylphosphine (1) was accomplished through the resolution of (S_P)-menthyl methyl-*p*-tolylphosphinate (**2a**). The free radical copolymerization of **1** with hydroxyethyl methacrylate and ethylene dimethacrylate afforded cross-linked polymer **14** containing ~0.42 mequiv of optically active monophosphine per gram of polymer. Optically active phosphines such as this polymer-bound cyclohexylmethylphenylphosphine can be used as ligands for rhodium-catalyzed asymmetric syntheses.

Introduction

The use of polymer-bound catalysts for effecting organic reactions has progressed to a point such that the capabilities of the method and the limitations—at least with the present catalytic systems and supports—have been recognized. The unique features and advantages of binding a homogeneous transition-metal complex to an insoluble polymer are evident.[1] When the catalytic reaction is an

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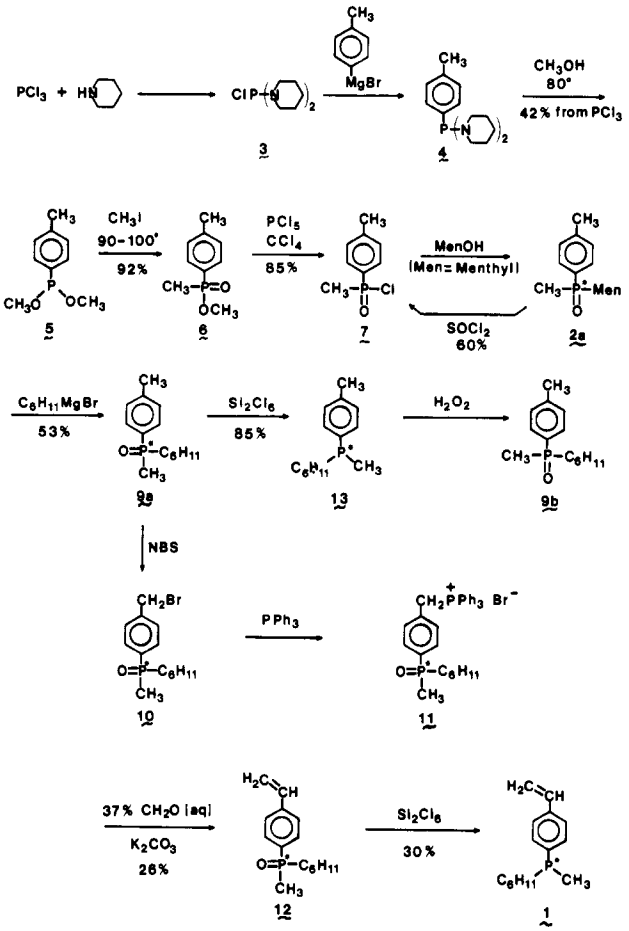


Figure 1. Synthesis of (*R*)-cyclohexylmethyl-*p*-styrylphosphine (1).

asymmetric synthesis that is effected by a transition metal such as rhodium complexed to an optically active phosphine,[2-4] then the attachment of this catalyst to an insoluble polymer support gains even more importance; it is particularly desirable to be able to separate the optically active product in pure form and to be able to recover and reuse not only the transition metal but also the optically active phosphine ligand.

The most challenging problems in polymer-supported catalysis are encountered in the choice of the polymer matrix and the synthesis of the catalyst site in the matrix. Most of the methods that have been reported require the introduction of a reactive site on a cross-linked polystyrene bead followed by the reaction of an optically active phosphine-containing ligand at the site.[5-8] Our approach,[9-13] the synthesis of ligand-bearing monomers, followed by their copolymerizations with a second monomer, has several advantages. First, the optical purity of the ligand on the monomer can be assured. Second, the concentration of the monomer in the polymer can be controlled, and a polymer containing a wide range of ligand concentrations can be synthesized. Third, depending on the comonomer, and thus the reactivity ratios, isolation of the ligand-bearing monomer can be assured. Fourth, the nature of the polymer backbone, polar or nonpolar, for example, can be varied, depending on the comonomer selection. Finally, varying degrees of cross-linking may be introduced.

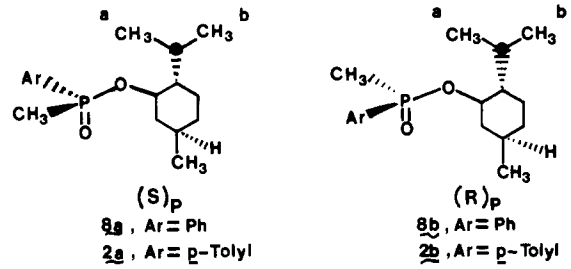
Although a number of vinyl monomers containing optically active chelating phosphines have been synthesized,[9-15] no monomers bearing an optically active monophosphine have been reported; yet there are a wide variety of monophosphines that owe their asymmetry to phosphorus and have been utilized as ligands in homogeneously catalyzed asymmetric reactions.[2b,16-21] In order to make available optically active polymer-bound monophosphines, we have undertaken the synthesis of (*R*)-cyclohexylmethyl-*p*-styrylphosphine (1) and its copolymerization with hydroxyethyl methacrylate and ethylene dimethacrylate.

Results and Discussion

Monomer Synthesis. The synthesis of the optically active styryl monomer was envisioned in two parts, the introduction of the appropriate stereochemistry at phosphorus and the introduction of the styryl moiety. Resolution of diastereomeric menthyl phosphinates has been shown to be an effective method for the preparation of optically active phosphinates and phosphine oxides.[22,23] Therefore, the desired menthyl methyl-*p*-tolylphosphinate (2) was prepared as shown in Figure 1.

The reaction of phosphorus trichloride and piperidine afforded **3**, which was not isolated but was allowed to react with *p*-tolylmagnesium bromide to afford *p*-tolyldipiperidylphosphine (**4**). Displacement of the piperidyl groups in refluxing methanol afforded dimethyl *p*-tolylphosphonite (**5**) in 42% yield from PCl_3. The Arbuzov rearrangement of **5** with methyl iodide afforded **6** in excellent yield and **6** was allowed to react with phosphorus pentachloride to give methyl-*p*-tolylphosphinyl chloride (**7**). The reaction of **7** with (−)-menthol afforded menthyl ester diastereomers **2a** and **2b** which, upon fractional recrystallization, afforded pure **2a**.

By comparison of the sign of the rotation and the ^1H NMR of **2a** with that of (S_P)-menthyl methylphenylphosphinate (**8a**)[24] the stereochemistry at phosphorus was



assigned *S*. The upfield shift of the doublet for H_a (0.34 ppm) for **8a** was shown to be characteristic of the *S* configuration at phosphorus, whereas the doublet for H_a for **8b** was at 0.89 ppm.[24] Correspondingly, **2a** exhibited a doublet at 0.30 ppm; thus the configuration at phosphorus was *S*. The absence of any detectable signals from **2b** in the ^1H NMR, ^{13}C NMR, and ^{31}P NMR spectra and an absence of change of rotation from repeated recrystallizations indicated that **2a** was obtained pure.

The mixture of diastereomers (**2a** and **2b**) in the filtrates, obtained from the fractional recrystallizations, was readily recycled back to racemic **7**, using thionyl chloride in refluxing carbon tetrachloride.[23]

The appropriate stereochemistry and substitution at phosphorus were then obtained by displacement of the menthyl group with cyclohexylmagnesium bromide[22,23] to afford **9a** with net inversion of configuration at phosphorus.

The formation of the styryl moiety was accomplished by bromination of **9a** to form **10**. The bromination reaction was only allowed to proceed to ~60% (via ^1H NMR) to avoid significant amounts of di- and tribromination of **9a**. The phosphonium bromide **11**, obtained from the reaction of crude **10** with triphenylphosphine, was allowed to react with formaldehyde and potassium carbonate[25,26]

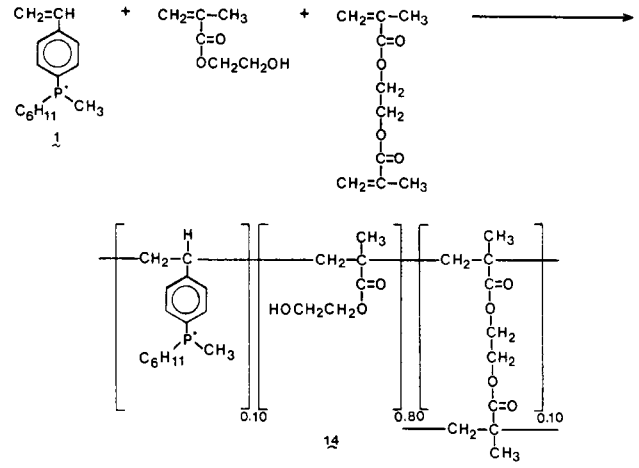


Figure 2. Polymerization of 1 with hydroxyethyl acrylate and ethylene dimethacrylate.

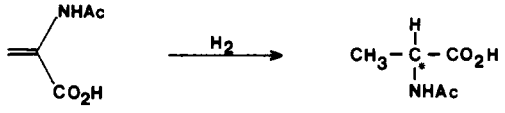
to afford crude styrylphosphine oxide **12**, which was purified by medium-pressure liquid crude chromatography.

Reduction of the tolylphosphine oxide **9a** was carried out with hexachlorodisilane[27] in refluxing benzene for 5.5 min to afford phosphine **13**. The optical purity of **12** was shown to be 81% by the stereospecific oxidation of **13** to **9b**, using hydrogen peroxide.

Reduction of styrylphosphine oxide **12** was carried out under the same conditions to afford styrylphosphine **1**. Since the same reaction conditions were used for the reduction of **12** to **1** as **9a** to **13**, it was assumed that the optical purity of **1** was approximately 80%.

Polymer Synthesis. Styrylphosphines are known to undergo free radical polymerizations with a wide variety of monomers;[28-31] therefore, it was expected that **1** could be incorporated into a variety of polymers possessing different solubility characteristics. The free radical polymerization of **1** was carried out with hydroxyethyl methacrylate and ethylene dimethacrylate to afford insoluble **14** (Figure 2), which would swell in polar solvents, such as alcohols. As expected, polymer **14** was extremely air sensitive, particularly in the presence of complexed rhodium, as the phosphine could be easily oxidized to the phosphine oxide.

Rhodium(I) complexes of polymer **14** and the homogeneous phosphine analogue cyclohexylmethyl-*p*-tolylphosphine (**13**) were prepared by an exchange reaction with bis[chloro(1,5-cyclooctadiene)rhodium]. Hydrogenation of (acylamino)acrylic acid with a rhodium(I) complex of **13** at ambient temperature at 2–3 atm of hydrogen provided complete conversion to *N*-acetylalanine, but in only 13% ee.



These low optical yields are not surprising, since (acylamino)cinnamic acid derivatives are hydrogenated by a rhodium catalyst containing optically pure cyclohexylmethylphenylphosphine ligands in less than 32% ee.[16] By comparison, hydrogenation of (acylamino)acrylic acid substrates generally proceeds in much lower optical yields.[2] For example, tropic acid is converted to hydrotropic acid by this phosphine in only 3% ee.[17]

Experimental Section

Dipiperidylchlorophosphine (3). To a stirred solution of 199.6 g (1.454 mol) of phosphorus trichloride in 1 L of dry oxygen-free ether at 0 °C was added dropwise 495.1 g (5.815 mol) of dry piperidine under a nitrogen atmosphere. After the addition was complete, the slurry was stirred at ambient temperature for 2 h. The piperidine hydrochloride was removed by suction filtration and washed with dry oxygen-free ether under a nitrogen atmosphere. The filtrates containing **3** were used in the next step without further purification.

Pure **3** was obtained by removing the ether in vacuo and distillation of the resultant oil: bp 87.0–90.5 °C (0.025 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.3–1.8 (br, 6), 2.7–3.3 (br, 4); ^{13}C NMR ($CDCl_3$) δ 23.9, 25.7 (d, J_{P-C} = 7.3 Hz), 47.1 (d, J_{P-C} = 14.7 Hz); ^{31}P NMR ($CDCl_3$) δ 153.8. Anal. Calcd for $C_{10}H_{20}ClN_2P$: C, 51.17; H, 8.59; Cl, 15.10; N, 11.93; P, 13.20. Found: C, 51.99; H, 8.99; Cl, 15.19; N, 12.14; P, 13.36.

***p*-Tolyldipiperidylphosphine (4).** To a stirred solution of the ether filtrates of **3** in an ice bath was added dropwise 1.45 mol of *p*-tolylmagnesium bromide in 500 mL of ether under nitrogen, and after addition was complete the gummy slurry was stirred at ambient temperature for 7 h. The precipitate was removed by filtration and the filter cake was washed with dry ether under an argon atmosphere. The solvent was removed in vacuo to afford **4** as a white solid which was used in the next step without further purification: mp 80–82 °C; ^{1}H NMR ($CDCl_3$) δ 1.1–1.8 (br, 10), 2.3 (s, 3), 2.7–3.5 (br, 7), 6.9–7.5 (m, 4).

Dimethyl *p*-Tolylphosphonite (5). To the flask containing **4** was added in small portions 250 mL of dry oxygen-free methanol. The mixture was heated to reflux for 24–48 h, cooled, and filtered under a nitrogen atmosphere. The solvent was removed in vacuo and the resultant oil was distilled to afford 113 g (42% from PCl_3) of **5** as a colorless liquid: bp 68–70 °C (0.35 mmHg); IR (neat) 3980, 3950, 3840, 1610, 1510, 1470, 1460, 1190, 1110, 1050, 1020, 815, 750, 720, 630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3), 3.40 (d, 6, J_{P-O-CH_3} = 10 Hz), 6.77–7.40 (m, 4); ^{13}C NMR ($CDCl_3$) δ 21.3, 52.5 (d, J_{P-O-CH_3} = 8.5 Hz), 128.7 (d, J_{P-C} = 4.8 Hz), 129.5 (d, J_{P-C} = 20.8 Hz), 137.0 (d, J_{P-C} = 20.8 Hz), 139.5; ^{31}P NMR ($CDCl_3$) δ 162.7. Anal. Calcd for $C_9H_{13}O_2P$: C, 58.70; H, 7.11; P, 16.82. Found: C, 58.24; H, 6.98; P, 15.53.

Methyl Methyl-*p*-tolylphosphinate (6). To 1 mL of methyl iodide was added 113 g (0.614 mol) of **5** under a nitrogen atmosphere.[23] After 1–2 mL of **5** was added, the flask was heated with a heat gun until the reaction started as indicated by a violent exotherm. The phosphonite was then added dropwise at a rate to maintain a pot temperature of 90–100 °C. Methyl iodide (~5 mL total) was periodically added to ensure a continuous reaction. After the addition was complete, the temperature was maintained overnight with an oil bath. After the methyl iodide was removed in vacuo, the product was distilled to afford 104 g (92.0%) of **6** as a colorless liquid: bp 115 °C (0.45–0.50 mmHg); IR (neat) 3050, 3020, 2980, 2950, 2870, 1615, 1470, 1460, 1425, 1410, 1310, 1235, 1130, 1050, 900, 795, 745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.60 (d, 3, J_{P-CH_3} = 14 Hz, PCH_3), 2.38 (s, 3, $ArCH_3$), 3.55 (d, 3, J_{P-OCH_3} = 11 Hz, OCH_3), 7.0–7.9 (m, 4, aromatic); ^{13}C NMR ($CDCl_3$) δ 15.3 (d, J_{P-CH_3} = 102.5 Hz), 21.5, 50.5 (d, J_{P-OCH_3} = 6.1 Hz), 127.9 (d, J_{P-C} = 128.2 Hz), 129.2 (d, J_{P-C} = 12.2 Hz), 131.1 (d, J_{P-C} = 11.0 Hz), 142.4 (d, J_{P-C} = 2.4 Hz); ^{31}P NMR ($CDCl_3$) δ 45.7. Anal. Calcd for $C_9H_{13}O_2P$: C, 58.70; H, 7.11; P, 16.82. Found: C, 58.72; H, 7.12; P, 16.19.

Methyl-*p*-tolylphosphinyl Chloride (7). To a stirring solution of 104 g (0.565 mol) of **6** in 400 mL of dry carbon tetrachloride was added 141 g (0.678 mol) of phosphorus pentachloride over 1 h and the mixture was stirred overnight.[23] The mixture was filtered, the solvent was removed in vacuo, and the resultant oil was distilled to afford 91 g (85%) of **7**: bp 125 °C (0.4 mmHg); IR (neat) 1605, 1405, 1302, 1240, 1212, 1115, 895, 880, 810, 755, 622 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.15 (d, 3, J_{P-CH_3} = 14 Hz), 2.35 (s, 3), 7.0–7.9 (m, 4); ^{13}C NMR ($CDCl_3$) δ 21.38 (d, J_{P-C} = 1.8 Hz), 23.55 (d, J_{P-CH_3} = 84.8 Hz), 129.31 (d, J_{P-C} = 14.7 Hz), 129.84 (d, J_{P-C} = 12.2 Hz), 130.21 (d, J_{P-C} = 120.2 Hz), 143.79 (d, J_{P-C} = 3.1 Hz).

(S_P)-Menthyl Methyl-*p*-tolylphosphinate (2a). To a solution of 38 mL (0.48 mol) of pyridine and 74.5 g (0.477 mol) of (−)-menthol in 140 mL of dry ether was added dropwise a solution of 89.8 g (0.477 mol) of **7** in 200 mL of dry ether under a nitrogen atmosphere.[23] The slurry was stirred overnight, after which time the pyridine hydrochloride was isolated by suction filtration and washed with ether. The filtrates were concentrated in vacuo, the

oil was dissolved in pentane, and the trace amounts of pyridine hydrochloride were removed by filtration. The solution was cooled in a freezer to afford 91.3 g of crude **2a**, which was recrystallized twice from pentane to afford 18.8 g of white needles: mp 72.0–73.5 °C; $[\alpha]^{25}_D$ −103.2° (*c* 22, benzene); IR (KBr) 1225, 1015, 995, 905, 805, 765 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.30 (d, *J* = 7 Hz), 0.50–2.50 (m), 0.75 (d, *J* = 7 Hz), 0.85 (d, *J* = 4 Hz), 1.58 (d, J_{P-CH_3} = 14 Hz), 2.30 (s), 3.50–4.25 (m), 6.85–7.75 (m); ^{13}C NMR ($CDCl_3$) δ 14.6, 15.2, 18.7, 21.0, 21.5, 21.9, 22.7, 25.3, 31.5, 34.0, 43.8, 48.6, 48.8, 76.2, 76.5, 126.4, 128.6, 129.1, 130.7, 131.1, 131.6, 141.9, 142.1; ^{31}P NMR ($CDCl_3$) δ 41.3. Anal. Calcd for $C_{18}H_{29}PO_2$: C, 70.13; H, 9.42; P, 10.06. Found: C, 70.31; H, 9.65; P, 10.35

Methyl-*p*-tolylphosphinyl Chloride (7) from Menthyl Methyl-*p*-tolylphosphinate (2). To a solution of 174 g (0.560 mol) of **2a** and **2b** in 240 mL of carbon tetrachloride was added dropwise 165 mL of thionyl chloride under a nitrogen atmosphere.[23] The solution was then heated to reflux for 24 h, during which time it became very dark. The carbon tetrachloride and thionyl chloride were removed by distillation and the resultant dark liquid was distilled to afford 63 g (60%) of **7** as light yellow liquid identical with that obtained above by ^{1}H NMR and IR; bp 125 °C (0.30 mmHg).

(*R*)-Cyclohexylmethyl-*p*-tolylphosphine Oxide (9a). To a stirred solution of 7.97 g (25.9 mmol) of **2a** in 50 mL of dry benzene was added dropwise a solution of 0.105 mol of cyclohexylmagnesium chloride in 120 mL of ether.[23] After the addition was complete, the ether was removed by distillation and the mixture was allowed to reflux for 24 h. After cooling, the reaction was carefully quenched with 100 mL of saturated ammonium chloride, the aqueous layer was separated and washed with benzene (3 × 25 mL), and the organic layers were combined, filtered, concentrated in vacuo, and placed on a dry silica column. Elution with benzene to remove the menthol, followed by ethanol, afforded 4.1 g, which upon recrystallization gave 3.2 g (53%) of **9a** as an amorphous white solid: mp 101.5–102.5 °C; $[\alpha]^{21}_D$ +29.8° (*c* 22, benzene); ^{1}H NMR (CCl_4) δ 0.7–2.1 (br, 11, cyclohexyl), 1.53 (d, 3, J_{P-CH_3} = 12 Hz), 2.41 (s, 3, CH_3Ar), 6.95–7.65 (m, 4, aromatic); ^{13}C NMR ($CDCl_3$) δ 11.99 (d, J_{P-C} = 67.14 Hz), 20.43 (s), 23.88 (s), 24.76 (d, J_{P-C} = 4.88 Hz), 25.39 (s), 37.11 (d, J_{P-C} = 72.02 Hz), 127.68 (d, J_{P-C} = 10.99 Hz), 128.04 (d, J_{P-C} = 93.99 Hz), 129.16 (d, J_{P-C} = 8.4 Hz), 140.35 (d, J_{P-C} = 3.66 Hz); ^{31}P NMR (CCl_4) δ 42. Anal. Calcd for $C_{14}H_{21}OP$: C, 71.16; H, 8.96; P, 13.11. Found: C, 70.90; H, 8.97; P, 12.87.

(*R*)-Cyclohexylmethyl-*p*-styrylphosphine Oxide (12). To a solution of 7.00 g (29.6 mmol) of **9a** in 30 mL of carbon tetrachloride were added 5.27 g (29.6 mmol) of *N*-bromosuccinimide and 0.07 g of benzoyl peroxide. The solution was heated at reflux for 1.5 h, the reaction was cooled to room temperature, and the succinimide was removed by filtration. The filtrate was washed with saturated sodium bicarbonate solution, washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. ^{1}H NMR indicated ~24% **9a** (2.3 ppm), ~62% monobrominated **9a** (4.4 ppm), and 14% dibrominated **9a** (6.8 ppm).

To the bromination products in 35 mL of chloroform was added 7.76 g (29.6 mmol) of triphenylphosphine. The solution was heated at reflux for 16.5 h under a nitrogen atmosphere. The solution was cooled to ambient temperature and concentrated in vacuo to give an oil which was triturated with toluene. The resultant solid was washed with toluene several times and dried in vacuo to afford 12.0 g of **11** as a tan amorphous solid.

To a slurry of the phosphonium bromide in 34 mL of 37% aqueous formaldehyde was added dropwise 10.9 mL of 2.9 M potassium carbonate over 1 h.[25,26] After the mixture was stirred for an additional 4 h, 50 mL of methylene chloride was added, and the organic layer was separated. The organic layer was washed with water (3 × 50 mL), dried (K_2CO_3), and concentrated in vacuo. The resultant solid was subjected to medium-pressure liquid chromatography (SiO_2).[32] Elution with ethyl acetate followed by 10% ethanol in ethyl acetate afforded 3.6 g of **11**, which after recrystallization with hexane/methylene chloride gave 1.9 g (26%) of **12** as white needles: mp 107.0–109.0 °C; $[\alpha]^{24}_D$ +49.2° (*c* 20, benzene); IR (KBr) 3000, 2940, 2870, 1640, 1610, 1450, 1400, 1305, 1205, 1170, 1155, 1115, 1100, 980, 905, 895, 825, 745, 610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.70–2.32 (br, 11, cyclohexyl), 1.65 (d, 3, J_{P-CH_3} = 13.0 Hz, methyl), 5.22 (dd, 1, J_{gem} = 1 Hz, $J_{(Z)-CH=CH_2}$ = 10 Hz, vinyl), 5.70 (dd, 1, J_{gem} = 1 Hz, $J_{(E)-CH=CH_2}$ = 17 Hz, vinyl), 6.45 (dd, 1, $J_{(E)-CH=CH_2}$ = 17 Hz, $J_{(Z)-CH=CH_2}$ = 10 Hz, vinyl), 7.20–7.68 (m, 4, aromatic); ^{13}C NMR ($CDCl_3$) δ 13.0 (d, J_{P-C} = 67.4 Hz), 25.0, 25.7, 25.9, 26.4, 37.3 (d, J_{P-C} = 71.8 Hz), 115.9, 125.7 (d, J_{P-C} = 11.7 Hz), 130.5 (d, J_{P-C} = 8.8 Hz), 131.7 (d, J_{P-C} = 93.8 Hz), 135.7, 140.4; ^{31}P NMR ($CDCl_3$) δ 37.04. Anal. Calcd for $C_{15}H_{21}OP$: C, 72.56; H, 8.52; P, 12.47. Found: C, 72.28; H, 8.36; P, 12.42.

(*R*)-Cyclohexylmethyl-*p*-tolylphosphine (13). To a stirred solution of 1.00 g (4.23 mmol) of **9a** in 20 mL of dry oxygen-free benzene was added 0.96 mL (91.5 g, 5.6 mmol) of hexachlorodisilane under an argon atmosphere.[27] The solution was then heated with stirring in a preheated oil bath (95 °C) for 5.5 min. The solution was then cooled in an ice bath and 13.7 mL of oxygen-free 30% sodium hydroxide was carefully added. In a glovebag, 20 mL of benzene was added to the mixture and the resultant benzene solution was washed with 30% sodium hydroxide (20 mL) and water (4 × 20 mL), dried ($MgSO_4$), and concentrated in vacuo to afford after Kugelrohr distillation [80–85 °C (0.001–0.003 mmHg)] 0.788 g (84.6%) of **13** as a colorless liquid: $[\alpha]^{23}_D$ −4.3° (*c* 19, benzene); IR (neat) 2940, 2860, 1510, 1455, 1430, 880, 870, 810 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.5 (br, 11, cyclohexyl), 1.1 (d, 3, J_{P-CH_3} = 3.5 Hz), 2.1 (s, 3, $ArCH_3$), 6.7–7.5 (m, 4, aromatic); ^{13}C NMR ($CDCl_3$) δ 8.17, 8.76, 20.08, 26.27, 26.57, 27.03, 28.49, 28.96, 29.48, 38.83, 39.18, 128.39, 128.68, 131.66, 132.42, 134.52, 135.05, 137.79; ^{31}P NMR ($CDCl_3$) δ −28.7. Anal. Calcd for $C_{14}H_{21}P$: C, 76.33; H, 9.61; P, 14.06. Found: C, 76.99; H, 9.71; P, 13.61.

To a stirred solution of 0.1 g (0.5 mmol) of **13** in 0.5 mL of oxygen-free benzene was added 0.5 mL of 30% hydrogen peroxide under an argon atmosphere.[27] The solution was stirred for 30 min at room temperature. Benzene (5 mL) was added and the organic layer was separated and washed with water, dried ($MgSO_4$), and concentrated in vacuo to yield 0.1 g (93%) of **9b**; $[\alpha]^{24}_D$ −24.1° (*c* 22, benzene).

(*R*)-Cyclohexylmethyl-*p*-styrylphosphine (1). Styrylphosphine oxide **12** (0.772 g, 2.91 mmol) was reduced with 1.0 g (0.68 mL, 3.8 mmol) of hexachlorodisilane[27] in 20 mL of dry oxygen-free benzene as described for **9a** to afford after Kugelrohr distillation [84 °C (10.4 μmHg)] 0.197 g (29.1%) of **1** as a clear colorless liquid: $[\alpha]^{25}_D$ −6.5° (*c* 2, benzene); ^{1}H NMR ($CDCl_3$) δ 0.80–2.20 (br, 11, cyclohexyl), 1.30 (d, 3, J_{P-CH_3} = 3 Hz), 5.25 (dd, 1, $J_{(E)-CH=CH_2}$ = 18 Hz, J_{gem} = 1 Hz, styryl), 5.75 (dd, 1, $J_{(Z)-CH=CH_2}$ = 11 Hz, J_{gem} = 1 Hz, styryl), 6.8 (dd, 1, $J_{(E)-CH=CH_2}$ = 18 Hz, $J_{(Z)-CH=CH_2}$ = 11 Hz, styryl), 7.40–7.60 (m, 4, aromatic); ^{13}C NMR ($CDCl_3$) δ 7.9, 8.5, 26.3, 26.7, 27.2, 28.6, 29.1, 29.6, 38.8, 39.3, 114.0, 125.5, 125.8, 132.0, 132.7, 136.3, 137.2, 137.7, 138.2; ^{31}P NMR ($CDCl_3$) δ −23.5. Anal. Calcd for $C_{15}H_{21}P$: C, 77.56; H, 9.11. Found: C, 77.63; H, 9.33.

Polymerization. A solution of 0.645 g (4.99 mmol) of 2-hydroxyethyl methacrylate and 0.124 g (0.624 mmol) of ethylene dimethacrylate in 5 mL of dry benzene was degassed via three freeze–pump–thaw cycles. A solution of 0.145 g (0.624 mmol) of **1** in 15 mL of dry oxygen-free benzene and 32 mg of AIBN were added under an inert atmosphere and the solution was stirred at 65 °C for 4.5 h. Benzene (20 mL) was added to the reaction mixture and the polymer was isolated by suction filtration in an inert atmosphere. The white polymer was washed with benzene (3 × 20 mL) and dry oxygen-free hexane (4 × 10 mL) and was dried in vacuo to give 0.75 g (82%). Anal. Calcd for 10% incorporation of **1**: P, 2.13. Found: P, 1.29.

Hydrogenation Reactions. The hydrogenation of (acetylamino)acrylic acid by a rhodium complex of **13** is illustrative of a general procedure. A solution of the catalyst formed from 4.5 mg (0.0091 mmol) of bis[chloro(1,5-cyclooctadiene)rhodium] and 8.2 mg (0.037 mmol) of **13** in 5 mL of ethanol in a pressure bottle was hydrogenated at 9 psi for 15 min. The substrate, 0.235 g (1.82 mmol) of (acetylamino)acrylic acid, and 12.6 μL (9.2 mg, 0.091 mmol) of triethylamine in 11 mL of ethanol was then added. The mixture was then hydrogenated at 2 atm for 5 h to yield 100% (NMR) of *N*-acetylalanine. The solvent was removed under reduced pressure, and the product was taken up in water; $[\alpha]^{23}_D$ −8.4°; 13% ee.

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Synthesis of Poly[3-(4-vinylphenoxy)phthalide-*co*-acrylonitrile] and the Selective Transport Properties of Its Membranes

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ABSTRACT: A new vinyl monomer containing the lactone moiety 3-(4-vinylphenoxy)phthalide (1) was synthesized and copolymerized with acrylonitrile (2). The sequence distributions of the copolymers were investigated by ^{13}C NMR spectroscopy. A penultimate model was used to interpret the propagation process in the copolymerization. The reactivity ratios in the solution polymerization at 45 °C were evaluated: $r_1 = 0.23$, $r_1' = 0.41$, $r_2 = 0.08$, and $r_2' = 0.11$. Radical reactivity indices and frontier electron densities for 1 and 2 were calculated. The membrane prepared from this copolymer showed selective transport properties for alkali metal ions. The selectivity in the transport of alkali metal ions by electrodialysis depended on the fraction of the opened phthalide moiety, i.e., lactone moiety. The present membrane, of which the fraction of opened lactone is small, showed an appreciable ability to separate Li^+ from Na^+ and K^+.

The ability to carry out active and selective transport of ions is of great interest in connection with the technological application of a biomembrane. Many carriers of metal ions, such as cyclic polyethers, chelating reagents, and ionophores, have been considered, but most of them have been investigated in the form of a liquid membrane or a blended membrane. On the other hand, synthetic membranes do not show appreciable selective transport properties for metal ions, except a polyamine sulfone derivative,[1] poly(tetrahydropyran-2,6-diyliminocarbonyl),[2] poly(sodium 3-*O*-vinylbenzylgluconate-*co*-acrylonitrile),[3] poly(3-vinyl-1,4-butyrolactone-*co*-acrylonitrile) (6),[4] and poly[3-[3-(4-hydroxyphenyl)phthalidyl]-4-hydroxystyrene-*co*-4-hydroxystyrene].[5] The selective transport abilities of the former two were revealed by hydrophobic and hydrophilic properties of the membrane, and those of the latter three were caused by the interaction between fixed carriers and metal ions, and the hydrophilic–hydrophobic balance. The last two membranes showed an active transport of alkali metal ions in addition to selective transport. With the lactone-containing polymer membrane, it was proved that the selectivity for alkali metal ion transport depends on both the affinity of the metal ions for the carboxylate formed by the ring opening of a lactone[4] and the hydrophobicity or hydrophilicity of the membrane.[4,5] The hydrophobic membrane, in which the fraction of ring-opened lactone is small, exhibits the following selectivity in alkali metal ion transport: $K^+ > Na^+ > Li^+$.[4] In order to obtain a membrane which has an appreciable selectivity for Li^+, a polymer having phenoxyphthalide as a hydrophobic moiety in the side chain, poly[3-(4-vinylphenoxy)phthalide-*co*-acrylonitrile] (5), was synthesized by a radical copolymerization.

The propagation process in the copolymerization of 3-(4-vinylphenoxy)phthalide (1) and acrylonitrile (2) was found to follow a penultimate model by ^{13}C NMR polymer analysis. The monomer reactivity ratios were also determined. It was assumed that propagation was entirely head-to-tail.

The membrane made of the present copolymer showed an improved selective transport ability for Na^+ and K^+ from Li^+.

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