Tetrahedron Vol. 43, No. 3, pp 451 to 462, 1987
Printed in Great Britain

0040-4020/87 $3.00+.00

NEW CHIRAL POLYSILOXANES PREPARED FROM DERIVATIVES OF (+)- OR (-)-2-PHENYL-3-BUTENOIC ACID, (R)-1-HEPTEN-3-OL AND (R)-1-CYCLOHEXYL-2-PROPEN-1-OL

Sunil K. Aggarwal, Jerald S. Bradshaw*, Masakatsu Eguchi, Scott Parry, Bryant E. Rossiter*, Karin E. Markides, and Milton L. Lee

Department of Chemistry, Brigham Young University, Provo, Utah 84602

(*Received in USA 5 November* 1986)

Abstract. A series of new polysiloxanes containing chiral side groups has been prepared. These polymers were prepared by hydrosilylating chiral alkene derivatives onto polyhydromethylsiloxane. The alkene derivatives were prepared from (+) or (-)-2-phenyl-3-butenoic acid, (R)-1-hepten-3-ol and (R)-1-cyclohexyl-2-propen-1-ol. Polysiloxanes containing racemic substituents were also prepared from derivatives of racemic 3-buten-2-ol. The polysiloxanes containing biphenyl carboxylate derivatives (11a-13a) had liquid crystalline properties. These polymers were prepared for use as stationary phases for capillary gas and supercritical fluid chromatography.

INTRODUCTION

Chromatographic resolution of enantiomers is an area of increasing importance in analytical chemistry. Several research groups have been engaged in the development of enantioselective phases for capillary gas chromatography[1-4] and liquid chromatography.[1,2,5-7] In contrast to tedious classical methods for determining enantiomeric purity, these chiral phases resolve enantiomers of various classes of compounds quickly and reliably using routine chromatographic techniques. Such phases are often capable of providing evidence of absolute configuration of the enantiomers from their elution order.[8] While this area of analysis is in its infancy, it is believed that eventually, most enantiomeric mixtures will be resolvable by some enantioselective chromatographic technique.

The phenomenon of resolution of enantiomers by chromatography is ascribed to the rapid and reversible formation of diastereomeric complexes between the chiral component of the phase and the chiral solutes. If the phase and the chiral solutes differ sufficiently in their free energy of complexation, the resulting differences in partition coefficients will lead to the separation of the enantiomers. It has been shown that such stereoselective complexes can be based on different types of intermolecular forces e.g. hydrogen bonding,[8] charge transfer complexation,[9,10] coordination to metals,[11,12] ionic and dipole-dipole interactions[13] or combinations of two or more such interactions. By these approaches, a variety of compounds such as the amino acids, α, β, and γ-amino acid esters, primary α-amino alcohols, α-hydroxy carboxylic acids, TFA derivatives of sugars, esters of aromatic diols, aromatic diketones, N-acyl/N-TFA derivatives of amines, aromatic sulphoxides, lactones, olefins, etc. have been enantiomerically analyzed on appropriate chiral phases.[8] Some chiral nematic (cholesteric) phases have also been tested as chiral phases in packed column GC.[14,15]

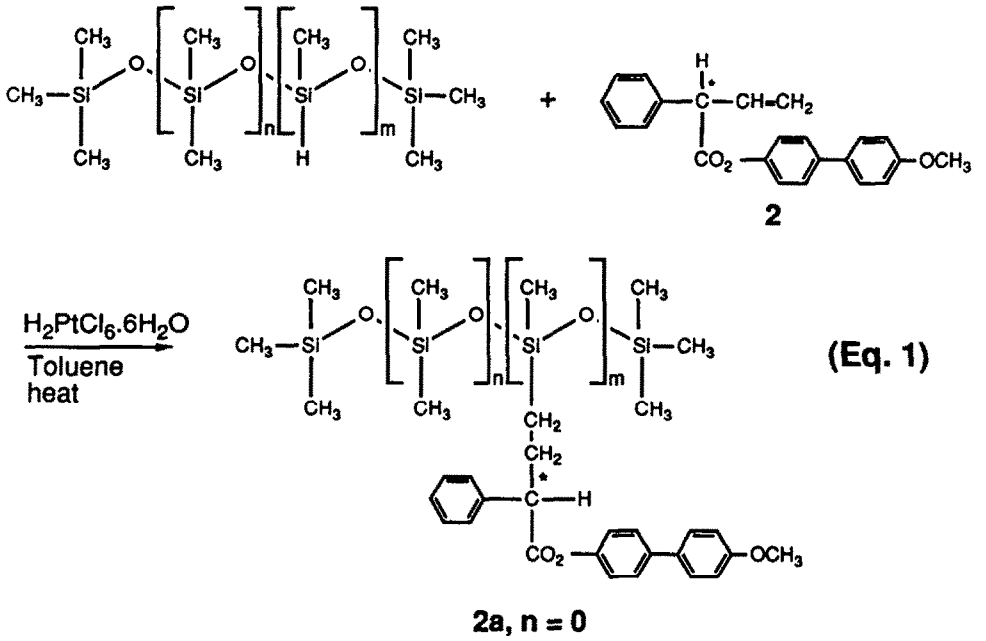
The first example of a chiral cholesteric polymer employed alkoxybenzoate esters of optically active 2-methyl-1-butanol.[16] All attempts in using this type of polymer for

separation of enantiomers have been unsuccessful.[17,18] We felt that we could prepare a variety of similar but more effective chiral phases by designing a chiral center containing (1) a functional group for attaching the liquid crystalline or other complex substituent onto it, (2) an alkene group to attach the chiral center onto a silicon polymer by a hydrosilylation reaction, and (3) an additional group which could be either an aromatic unit for pi-pi and steric interactions with the solute or an aliphatic unit for steric interactions. It is also possible that those materials that are also liquid crystalline will provide for the best resolution of enantiomeric solutes.

This paper reports the synthesis of a series of new polysiloxanes containing chiral side groups. The chiral side groups are composed of derivatives of both (+)- and (-)-2-phenyl-3-butenoic acid (1, Figure 1), (R)-1-hepten-3-ol (5) and (R)-1-cyclohexyl-2-propen-1-ol (6). These derivatives meet the requirements listed above, and the polymers all have substituents with chiral centers close to the polysiloxane backbone. Some of the new chiral polymers are presently being studied as stationary phases for capillary gas and supercritical fluid chromatography.

RESULTS AND DISCUSSION

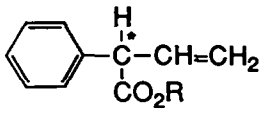
The new polysiloxane materials containing chiral side groups were prepared by a hydrosilylation reaction of a chiral alkene with a polyhydromethylsiloxane as shown in Equation 1 for the preparation of 2a. This reaction has been used extensively to prepare polysiloxanes



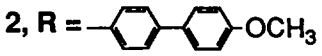
containing a variety of liquid crystalline side groups.[16-20] The chiralities of the polymers were provided by the series of alkenes (2-4, 8, 9, 11, 12, and 14) shown in Figure 1. Racemic alkene derivatives 10 and 13 were prepared for comparison purposes. Table I shows the phase transitions for both the alkene derivatives and the resulting polymers.

(±)-2-Phenyl-3-butenoic acid (1), needed for the preparation of alkenes 2-4, was prepared from cinnamylmagnesium chloride by a previously reported procedure.[21] The (+)- and (-)- forms of 2-phenyl-3-butenoic acid were obtained by crystallization of the (-)-ephedrine and (+)-

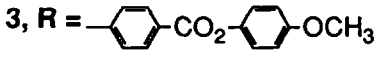
Figure 1. New Chiral Alkenes



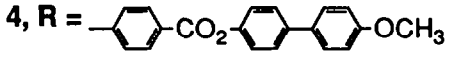
1, R = H



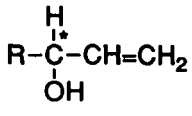
2, R =



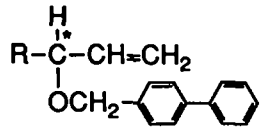
3, R =



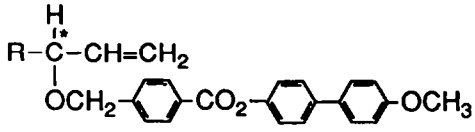
4, R =



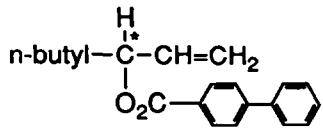
5, R = n-butyl
6, R = cyclohexyl
7, R = methyl (R,S)



8, R = n-butyl
9, R = cyclohexyl
10, R = methyl (R,S)



11, R = n-butyl
12, R = cyclohexyl
13, R = methyl (R,S)



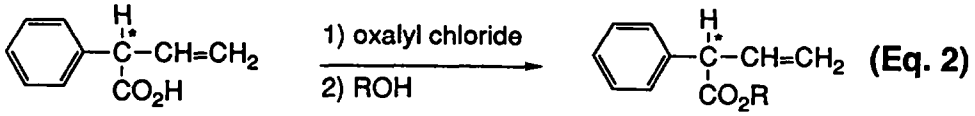
14

Table I. Phase Transitions for the New Chiral Alkenes and the Corresponding Polysiloxanes

Alkene	Phase Transitions (°C)[a]	Polymer	Phase Transitions (°C)[a,b]
2	k 97 i	2a	k 50-98 gum 98-100 i (+62.5°)[b]
3	k 70-71 i	3a	k 95 i (-44.73°)
4	k 85 s 107-108 i	4a	g 78 s 86 i (+25.14°)
8	oil	8a	gum (+10.47°)
9	oil	9a	gum (+3.45°)
10	oil	10a	gum[c]
11	k 108-109 i	11a	82 n* 122 i (+2.61°)
12	k 151-152.5 i	12a	80 s 132 i (-2.9°)
13	k 130-130.5 i	13a	115 n 124 i[c]
14	oil	14a	Hard gum

[a]k-crystalline; s-smectic; n-nematic; n*-cholesteric; i-isotropic; g-glassy
[b]Rotations are given in parenthesis.
[c]Prepared from racemic alcohol

ephedrine salts, respectively, from ethyl acetate followed by treatment with sulphuric acid. The enantiomeric purities of both isomers were determined to be higher than 90% by ^1H NMR spectroscopy using the chiral shift reagent tris-[3-(heptafluoropropylhydroxymethylene)-d-camphorato]europium [Eu(hfc)$_3$]. Compound 1 was converted to three derivatives (2-4) as shown in Equation 2. The 4-hydroxy-4'-methoxybiphenyl needed to prepare 2 was prepared from 4,4'-



1 **2 - 4** **(Eq. 2)**

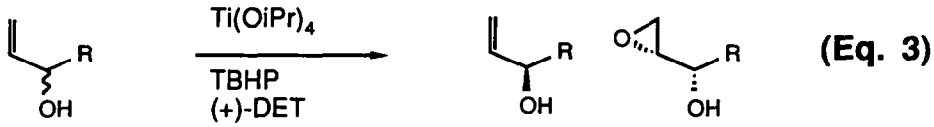
biphenol and dimethylsulfate[19] while 4'-methoxyphenyl-4-hydroxybenzoate (for 3) and 4'-methoxybiphenyl-4-hydroxybenzoate (for 4) were obtained by azeotropic removal of water from the reaction of 4-hydroxybenzoic acid with 4-methoxyphenol and 4-hydroxy-4'-methoxybiphenyl, respectively.

Moss and his coworkers reported the synthesis of (+)- and (-)-p-nitrophenyl-α-methoxyphenyl acetate without racemization using the acid chloride and p-nitrophenol in refluxing toluene.[22] When we used the same conditions for the preparation of esters 2-4 (Equation 2), a considerable amount of decomposition was indicated by the dark red color of the solution and the formation of products other than the ester. We, therefore, performed the reaction at room temperature using dichloromethane (for better solubility of the phenols) and obtained products which had high optical rotations. Table II compares the optical rotations of esters 2-4 obtained both in refluxing toluene and in dichloromethane at room temperature.

Table II. Rotations, $[\alpha]_D^{25}$, of Esters 2-4 Prepared Using Toluene at Reflux Temperature or Methylene Chloride at Room Temperature.

Ester	Precursor Acid	Toluene	CH_2Cl_2
2	+	+12.06°	+48.64°
3	-	-20.23°	-34.46°
4	+	+4.21°	+24.32°

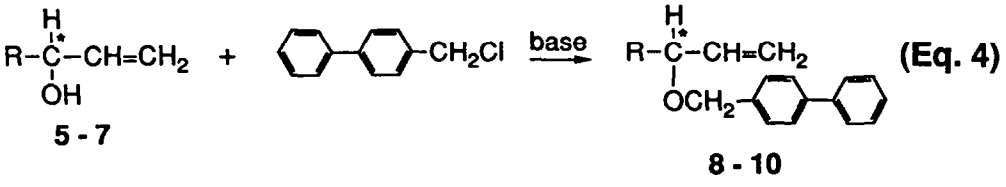
1-Hepten-3-ol (5) and 1-cyclohexyl-2-propen-1-ol (6) were kinetically resolved via the Sharpless epoxidation procedure (Equation 3).[23,24] The optical purity of 5 and 6 were determined by converting both chiral 5 and 6 and their racemic forms into diastereomeric α-methoxy-α-trifluoromethylphenyl acetates and subjecting the derivatives to gas chromatographic



RS-5 & 6 **R-5** **R-6** **(Eq. 3)**

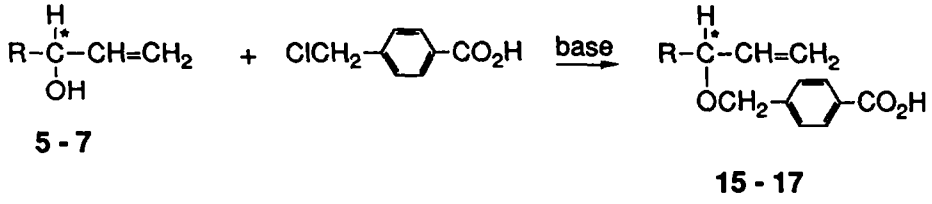
analysis.[25] This analysis indicated an enantiomeric excess of ≥ 90% for both alcohols. Other similar allylic alcohols resolved in this manner were found to have the (R)-configuration.[24]

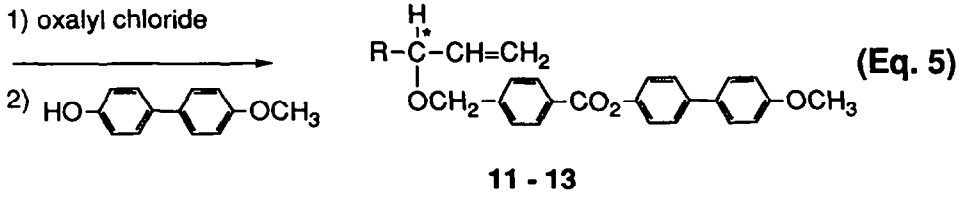
Variously substituted alkene derivatives were prepared from these alcohols as shown in Equations 4-6. In the first case (Equation 4), alcohols 5 and 6 were converted to the



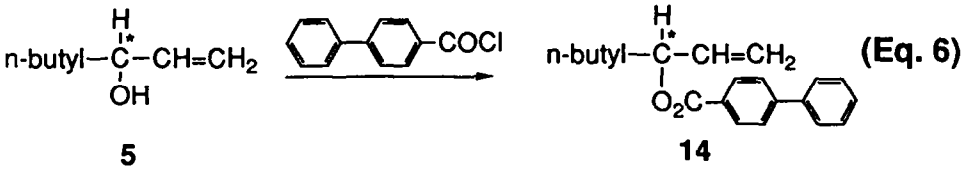
(Eq. 4)

biphenylmethyl ether derivatives 8 and 9 using 4-chloromethylbiphenyl. In the second case (Equation 5), alcohols 5 and 6 were first converted to the p-alkyloxymethylbenzoic acids (15 and 16) using 4-(chloromethyl)benzoic acid. Compounds 15 and 16 were then converted to 11 and 12 as shown in Equation 5. (R substituents are given in Figure 1). Likewise, racemic 3-buten-2-ol (7) was converted to the derivatives 10 (Equation 4) and 13 (Equation 5) respectively. Alcohol 5 was also converted to the 4-biphenylcarboxylate ester (14) as shown in Equation 6.





(Eq. 5)



(Eq. 6)

Polymers 2a-4a and 8a-14a contained about 50% of the chiral substituent (where n=0, see Equation 1) except for 11a mentioned later. Table I lists the physical properties for the starting alkenes and the resulting polymers. The optical purity of 2a was checked by ^{1}H NMR spectroscopy using the chiral shift reagent Eu(hfc)$_3$. The ^{1}H NMR spectrum of the racemic polymer in the presence of shift reagent exhibited two broad signals at δ 4.60 and 5.20 indicative of a CH-unit on the stereogenic carbon. The optically active polymer gave only one signal at δ 5.16 in the NMR spectrum, showing its high optical purity. Apparently, hydrosilylation did not give rise to any significant racemization of the chiral alkene side group.

As shown in Table I, polymers 8a-10a and 14 are gums, whereas polymer 11a is cholesteric

between 82-122°C, a condition required for a good liquid crystalline chiral phase. In an attempt to increase the cholesteric region of this phase, we prepared other polymers from 11 with varying molecular weights and with different percentages of the chiral substituent (by varying the ratio of m and n, see Equation 1). The properties of these polymers are presented in Table III.

Table III. Effect of Varying the Parameters of the Hydropolysiloxane on the Properties of 11a

Sample	Starting SiH Polymer		Phase Transitions
	mol. wt.	SiH(%)[a]	
1	3000	50	82 n* 122 i
2	1500	50	86-88 n* 103-105 i
3	6000 (with 2% 1-octene)	25	74 n* 98 i
4	15000	25	71 n* 97 i

[a]Determines percentage of chiral substituent in the polymer.

It is clear from Table III that the phase transition temperatures were not increased when a lower molecular weight polymer was used, and indeed, the nematic range was decreased when lower percentages of chiral substituents were used. Unfortunately, the polymers 2a-4a (Table I) are isotropic at temperatures below 100°C. In order to check the enantiomeric stability of these polymers, we heated polymer 2a to temperatures above its melting point in an inert atmosphere and noted the change in optical rotation. The results are presented in Table IV. The rotation of 2a was reduced from +62.5° (the initial rotation) to nearly +56° at temperatures up to 210°C, indicating that <5% of the material racemized. The polymer racemized to a slightly greater extent at 240°.

Table IV. Effect of Heat on the Optical Rotation of 2a

Run	Temperature (°C)	$[\alpha]_D^{25}$	Time
1	120	+55.97°	30 minutes
2	150	+55.25°	30 minutes
3	180	+55.75°	30 minutes
4	210	+55.52°	30 minutes
5	240	+53.71°	30 minutes

EXPERIMENTAL SECTION

Infrared (IR) spectra were obtained on a Beckman Acculab 2 Spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded by a JEOL FX 90-Q spectrometer. Phase transitions were obtained on a Thomas-Kofler hot stage microscope using cross polarizers. Optical rotations were obtained on a Perkin-Elmer model 241 polarimeter. Carbon and hydrogen analyses were performed by MHW laboratories, Phoenix, AZ. All compounds, unless otherwise mentioned, were purchased from the Aldrich Chemical Company.

4'-Methoxyphenyl-4-hydroxybenzoate. A mixture of 4-hydroxybenzoic acid (4.9 g, 0.036 mol) and 4.96 (0.04 mol) of 4-methoxyphenol in 20 mL of benzene containing ten drops of sulphuric acid was refluxed for six days. Water was removed using a Dean Stark trap. The reaction was monitored by TLC, and when the 4-hydroxybenzoic acid was consumed, the solid product was filtered. The crude product was dissolved in 250 mL of diethyl ether, washed with saturated aqueous sodium bicarbonate and dried over anhydrous magnesium sulphate. The ether solvent was slowly distilled (about 150 mL) and 100 mL of hexane was added to give 6.80 g (79%) of white crystals: mp 192-194°C; IR (KBr) 3410, 1710 cm^{-1}; NMR (DMSO-d_6) δ 3.84 (3H, s, OCH_3), 6.94-8.16 (8H, m, ArH), 10.44 (1H, broad, OH).

Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.91. Found: C, 68.79; H, 5.10.

4'-Methoxybiphenyl-4-hydroxybenzoate. A mixture of 4-hydroxybenzoic acid (2.5 g, 0.018 mol) and 5.0 g (0.025 mol) of 4-hydroxy-4'-methoxybiphenyl in 60 mL of benzene containing 15 drops of sulphuric acid was refluxed for seven days. Water was removed using a Dean Stark trap. The reaction was monitored by TLC, and when the 4-hydroxybenzoic acid was consumed, the solid was filtered and washed with 25 mL of saturated aqueous sodium bicarbonate solution and twice with 25 mL portions of water. The pinkish white solid thus obtained was dissolved in 1L of refluxing ethanol and filtered. The filtrate on concentration to 250 mL followed by cooling and filtration gave 4.0 g (68.7%) of white crystals: mp 250-252°C; IR (KBr) 3385, 1700 cm^{-1}; NMR (DMSO-d_6) δ 3.80 (3H, s, OCH_3), 6.88-8.12 (12 H, m, ArH), 10.50 (1H, broad, OH).

Anal. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.04. Found: C, 75.13; H, 4.91.

(-)-2-Phenyl-3-butenoic acid [(-)-1]. (1R,2S)-(-)-Ephedrine (6.4 g, 0.039 mol) was dissolved in 70 mL of anhydrous ether and 6.32 g (0.039 mol) of racemic 2-phenyl-3-butenoic acid[21] was added to the solution with stirring. After 10 min, solid started to form and the reaction mixture was kept overnight at room temperature. The ephedrine salt was filtered to give 10.9 g, mp 118-119°C, $[\alpha]_D^{25}$ -29.41° (c 0.918, ethanol). After five crystallizations from ethyl acetate (90 mL for each crystallization), there remained 4.2 g of the salt which exhibited a constant mp of 134°C and $[\alpha]_D^{25}$ -52.96° (c 0.672, ethanol). The salt was treated with 20% sulphuric acid and extracted with ether to give (-)-2-phenyl-3-butenoic acid (2.1 g, 33.2%) as a colorless oil, $[\alpha]_D^{25}$ -82.73° (c 0.612, ethanol). The mother liquor of various batches of the recrystallizations did not give the optically pure (+)-acid.

(+)-2-Phenyl-3-butenoic Acid [(+)-1]. This enantiomer was resolved as above using 3.0 g (0.018 mol) of (1S,2R)-(+)-ephedrine, 45 mL of anhydrous ether, and 2.92 g (0.018 mol) of racemic 2-phenyl-3-butenoic acid. The ephedrine salt (5.2 g), mp 116-117°C, $[\alpha]_D^{25}$ +26.30° (c 1.566, ethanol) was recrystallized six times from ethyl acetate (40 ml for each crystallization) to give 1.50 g of a salt with a constant mp of 132°C, and $[\alpha]_D^{25}$ +52.41° (c 0.477, ethanol). The salt gave 0.8 g (27.4%) of 2-phenyl-3-butenoic acid as a colorless oil, $[\alpha]_D^{25}$ +85.65° (c 0.704 ethanol). The mother liquor of various batches of the recrystallizations did not give optically pure *l*-acid.

Determination of Optical Purity of 1. The racemic and (+)- and (-)- forms of 1 were mixed with tris-[3-heptafluoropropylhydroxymethylene)-d-camphorato]europium [Eu(hfc)$_3$]. In the ^1H NMR spectrum of the racemic acid, the signal corresponding to the vinylic CH_2 appeared as a three peak multiplet at 444.2-471.9 Hz. When the ^1H NMR spectrum of the racemic acid was taken in the presence of the shift reagent at a molar concentration of 1:0.1628 (substrate:reagent), the vinylic CH_2 caused five peaks centered at 516.3, 528.5, 538.5, 549.6 and 557.4 Hz respectively. These peaks can be attributed to an average of the expected six peaks for the vinylic CH_2 signals of the two enantiomers of the acid. It was found that at this concentration, the vinylic CH_2 of the (+)-acid appeared as a well resolved three peak multiplet

centered at 505.2, 516.3 and 530.2 Hz while the peaks for the (-)-acid were present at 510.6, 521.7 and 538.4 Hz respectively. These results show the high optical purity of the resolved acids.

General Procedure for the Esterification of 1. The (+)- or (-)- form of 2-phenyl-3-butenoic acid (1) (1 equivalent) was stirred with 1.5 equivalent of oxalyl chloride at room temperature under anhydrous conditions. After 2 h, the excess oxalyl chloride was removed at reduced pressure to give the crude acid chloride. The product was dissolved in 15 mL of methylene chloride and slowly added to a stirring suspension of equimolar amounts of the appropriate phenol and pyridine (distilled over calcium hydride) in 30 mL of methylene chloride. The solution was stirred for 2 h and then washed with 0.1 N aqueous hydrochloric acid, saturated aqueous sodium bicarbonate and finally with water. The solution was dried over anhydrous magnesium sulphate. The solvent was distilled and the resulting yellow solid was purified by chromatography using toluene as the eluant.

(+)-4-Methoxybiphenyl 2-Phenyl-3-butenoate (2, Equation 2). The (+)- form of 1 (0.81 g, 0.005 mol) and 1.0 g (0.005 mol) of 4-hydroxy-4'-methoxybiphenyl were used. The product was recrystallized from methanol to give white crystals: 0.95 g (55.2%); mp 97°C; $[\alpha]_D^{25}$ + 48.64° (c 3.178, chloroform); IR (KBr) 1735 cm^{-1}; NMR ($CDCl_3$) δ 3.88 (3H, s, OCH_3), 4.56 (1H, d, J=7.4 Hz, -CHPh-), 5.16-5.42 (2H, three peak multiplet, vinyl CH_2), 6.20-6.56 (1H, m, vinyl CH), 6.96-7.64 (13H, m, ArH).

Anal. Calcd for $C_{23}H_{20}O_3$: C, 80.23; H, 5.81. Found: C, 80.20; H, 5.73.

(-)-(4-Methoxyphenoxy)carbonylphenyl 2-Phenyl-3-butenoate (3, Equation 2). The (-)- form of 1 (0.81 g, 0.005 mol) and 1.22 g (0.005 mol) of 4'-methoxyphenyl-4-hydroxybenzoate were used. The product was recrystallized from hexane to give light yellow crystals; 1.05 g (54.1%); mp 70-71°C; $[\alpha]_D^{25}$ -34.46° (c 1.773, chloroform); IR (KBr) 1700, 1730 cm^{-1}; NMR ($CDCl_3$) δ 3.80 (3H, s, OCH_3), 4.56 (1H, d, J=7.4 Hz, -Ph-CH-), 5.16-5.36 (2H, three peak multiplet, vinyl CH_2), 6.12-6.52 (1H, m, vinyl CH), 6.84-8.24 (13 H, m, ArH).

Anal. Calcd for $C_{24}H_{20}O_5$: C, 74.22; H, 5.15. Found: C, 74.29; H, 5.02.

(+)-4-(4-Methoxyphenoxy)phenylcarbonylphenyl 2-Phenyl-3-butenoate (4, Equation 2). The (+)- form of 1 (0.81 g, 0.005 mol) and 1.60 g (0.005 mol) of 4'-methoxybiphenyl-4-hydroxybenzoate were used. The product was recrystallized from methanol to give white crystals: 0.45 g (19.4%); mp 85°C to smectic, 107-108°C to isotropic; $[\alpha]_D^{25}$ + 24.32° (c 0.444, chloroform); IR (KBr) 1730, 1750 cm^{-1}; NMR ($CDCl_3$) δ 3.84 (3H, s, OCH_3), 4.58 (1H, d, J=7.4 Hz, -CHPh-), 5.16-5.40 (2H, three peak multiplet, vinyl CH_2) 6.14-6.52 (1H, m, vinyl CH), 6.94-8.30 (17H, m, ArH).

Anal. Calcd for $C_{30}H_{24}O_5$: C, 77.58; H, 5.17. Found: C, 77.61; H, 5.26.

(R)-1-Hepten-3-ol (5, Equation 3). Dry methylene chloride (200 mL) and 6 mL (0.02 mol) of titanium tetraisopropoxide were placed in a nitrogen purged, 500 mL two-necked round-bottom flask. The mixture was cooled to -15°C and 3.8 mL (0.022 mol) of L-(+)-diethyl tartarate was added. The reaction mixture was stirred for 15 minutes at -15°C and 2.3 g (0.02 mol) of (±) 1-hepten-3-ol was added. Anhydrous 4M tert-butyl hydroperoxide in toluene (5 mL) was then added and the mixture was stirred for an additional 10 minutes at -15°C. The reaction mixture was placed in a -20°C freezer overnight. Analysis by capillary GLC indicated that the reaction was about 55% complete. The reaction mixture was stirred with 200 mL of 10% tartaric acid for 30 min. The aqueous layer was extracted with 200 mL of ether. The organic layers were combined, the solvent was removed and the residue was dissolved in 200 mL of ether. The ether solution was stirred for 30 min with 50 mL of 10% aqueous sodium hydroxide. The layers were separated

and the organic layer was washed with saturated sodium chloride, dried (anhydrous sodium sulfate) and concentrated to give a pale yellow oil. The product was purified by flash chromatography in silica gel using a mixture of hexane:ethyl acetate (4:1) as eluant to give 1.0 g (43.5%) of a clear colorless oil. This oil was further purified by kugelrohr distillation: $[\alpha]_D^{25}$ -6.01° (c 1.0, chloroform); NMR ($CDCl_3$) δ 0.88 (3H, t, J=7.4 Hz, CH_3), 1.20-1.72 (6H, m, 3xCH_2), 2.20-2.84 (1H, b, OH), 3.92-4.28 (1H, m, CH), 5.02-5.36 (2H, m, vinyl CH_2), 5.76-6.08 (1H, m, vinyl CH). This alcohol was used to prepare 8, 11 and 14 each of which gave a satisfactory combustion analysis.

(R)-1-Cyclohexyl-2-propen-1-ol (6, Equation 3). This product was obtained as described for 5 from (±)-1-cyclohexyl-2-propen-1-ol: bp 66-70°C (0.2 mm Hg); $[\alpha]_D^{25}$ -9.50° (c 0.44, chloroform); NMR ($CDCl_3$) δ 1.14-1.88 (11H, m, cyclohexane H), 2.56-2.88 (1H, b, OH), 3.88 (1H, t, J=6.6 Hz, CH), 5.10-5.32 (2H, m, vinyl CH_2), 5.72-6.12 (1H, m, vinyl CH). This alcohol was used to prepare 9 and 12 each of which gave a satisfactory combustion analysis.

Preparation of MTPA Derivatives to Determine the Optical Purity of the Alcohols. The following procedure was used for the small scale preparation of MTPA derivatives for gas chromatographic (GC) analysis. (R)-(+)-MTPA was converted to the (+)-acid chloride and distilled.[26] The reactions were carried out in dry test tubes (dried at 150°C) fitted with rubber septums. The reagents were injected via syringe into the test tubes in the following order: dry pyridine (300 μl, 300 mg); (+)-MTPA-Cl (35 mg, 26 μl, 0.14 mmol), carbon tetrachloride (300 μl) and the substrate alcohol (0.10 mmol). The reaction mixture was then shaken and allowed to stand at room temperature overnight. Excess β-diethylaminoethylamine (ca. 0.20 mmol) was added and the mixture was allowed to stand for five minutes. It was diluted with ether, washed (cold aqueous hydrochloric acid, cold saturated aqueous sodium bicarbonate and saturated aqueous sodium chloride), and dried over anhydrous magnesium sulfate. The filtered ether solution was concentrated at reduced pressure and subjectd to GC anaylsis.

General Procedure for Preparation of Alkene Derivatives (8-10, Equation 4). To a rapidly stirred suspension of 2 equivalents of sodium hydride (60% dispersion) in 25 mL of anhydrous dimethylformamide (dried and distilled over calcium hydride) under an argon atmosphere, was added a solution of 1 equivalent each of the alcohol and 4-(chloromethyl)-biphenyl in 25 mL of anhydrous dimethylformamide over a 15 min period at room temperature. The reaction mixture was stirred for 24 h. The mixture was carefully added to 50 mL of cold water and extracted three times with 40 mL portions of ether. The combined organic extracts were washed with water and dried over anhydrous magnesium sulfate. The filtered ether solution was concentrated under reduced pressure and the residue, a dark yellow oil, was purified by chromatography over silica gel using hexane and a mixture of hexane:toluene (9:1) as eluants. Specific details are given for each derivative (8-10).

(R)-3-(Biphenylmethoxy)-1-heptene (8, Equation 4). The (R)-(-)- form of 5 (0.570 g, 0.005 mol) and 1.01 g (0.005 mol) of 4-(chloromethyl)biphenyl were used to give 0.92 g (79.7%) of the product as a light yellow oil; $[\alpha]_D^{25}$ + 29.11 (c 1.271, chloroform); NMR ($CDCl_3$) δ 0.92 (3H, t, J=4.0 Hz, CH_3), 1.20-1.66 (6H, m, 3xCH_2), 3.64-3.92 (1H, m, -CH), 4.32-4.80 (2H, dd, OCH_2), 5.16-5.40 (2H, m, vinyl CH_2), 5.64-6.04 (1H, m, vinyl CH), 7.24-7.76 (9H, m, ArH).

Anal. Calcd for $C_{20}H_{24}O$: C, 85.71; H, 8.57. Found: C, 85.59; H, 8.51.

(R)-3-(Biphenylmethoxy)-3-cyclohexylpropene (9, Equation 4). The (R)-(-)- form of 6 (0.50 g; 0.0036 mol) and 0.73 g (0.0036 mol) of 4-(chloromethyl)biphenyl were used to give 0.68 g (62.2%) of the product as a light yellow oil; $[\alpha]_D^{25}$ + 23.73° (c 0.535, chloroform); NMR ($CDCl_3$) δ 1.12-2.14 (11H, m, cyclohexane H), 3.52 (1H, t, J=7.4 Hz, -CH), 4.36-4.80 (2H, dd, OCH_2),

5.16-5.44 (2H, m, vinyl CH_2), 5.64-6.04 (1H, m, vinyl CH), 7.32-7.84 (9H, m, ArH).

Anal. Calcd for $C_{22}H_{26}O$: C, 86.27; H, 8.49. Found: C, 86.07; H, 8.29.

(R,S)-3-(Biphenylmethoxy)-1-butene (10 Equation 4). Racemic 7 (0.60 g; 0.0083 mol) and 1.69 g (0.0083 mol) of 4-(chloromethyl)biphenyl were used to give 1.10 g (55.5%) of the product as a colorless oil; NMR ($CDCl_3$) δ 1.28 (3H, d, J=7.0 Hz, CH_3), 3.84-4.02 (1H, m, CH), 4.30-4.68 (2H, dd, OCH_2), 5.10-5.30 (2H, m, vinyl CH_2), 5.62-6.0 (1H, m, vinyl CH), 7.08-7.88 (9H, m, ArH).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.71; H, 7.56. Found: C,85.61 H,7.39.

General Procedure for the Preparation of Benzoic Acid Derivatives 15-17 (Equation 5). To a rapidly stirred suspension of 3.5 equivalents of hexane washed sodium hydride (a 60% dispersion) in 25 mL of anhydrous dimethylformamide under an argon atmosphere, was added a solution of 1 equivalent each of the alcohol and 4-(chloromethyl)benzoic acid in 25 mL of anhydrous dimethylformamide over a 15 min period at room temperature. The reaction mixture was stirred for 24-48 h. The mixture was transferred to 50 mL of cold water and made acidic with 0.1 N aqueous hydrochloric acid which resulted in the formation of a milky solution. The mixture was then extracted 4 times with 40 mL portions of ether. The combined ether extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was distilled and the residue, a yellowish white solid, was crystallized from an appropriate solvent. Specific details are given for 15-17.

(R)-4-(3-Butyl-2-oxa-4-pentenyl)benzoic Acid (15, Equation 5). (R)-(-)-1-Hepten-3-ol (5) (1.14 g, 0.01 mol) and 1.71 g (0.01 mol) of 4-(chloromethyl)benzoic acid were used. The product was dissolved in 250 mL of hot petroleum ether (30-60°) and filtered. The filtrate on concentration to 20 mL followed by cooling, gave 0.95 g (38.6%) of a white crystalline solid: mp 78-80°C; $[\alpha]_D^{25}$ + 26.54° (c 0.380, chloroform), IR (KBr) 2540-2660, 1690 cm^{-1}; NMR ($CDCl_3$) δ 0.90-1.80 (9H, m, methyl, and 3xCH_2), 3.54-3.90 (1H, m, CH), 4.26-4.74 (2H, dd, OCH_2), 5.10-5.40 (2H, m, vinyl CH_2), 5.40-5.52 (1H, m, vinyl CH), 7.26-8.46 (4H, m, ArH), 10.32-11.04 (1H, b, COOH, exchangeable with D_2O).

Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.58; H, 8.06. Found: C, 72.28; H, 8.07.

(R)-4-(3-Cyclohexyl-2-oxa-4-pentenyl)benzoic Acid (16, Equation 5). (R)-(-)-1-Cyclohexyl-2-propen-1-ol (6) (1.25 g, 0.0089 mol) and 1.52 g (0.0089 mol) of 4-(chloromethyl)benzoic acid were used. The product was dissolved in 250 mL of hot petroleum ether (30-60°) and filtered. The filtrate on concentration to 20 mL followed by cooling, gave 0.90 g (36.8%) of a white crystalline solid: mp 99-101°C, $[\alpha]_D^{25}$ + 16.03° (c 0.474, chloroform); IR (KBr) 2540-2660, 1680 cm^{-1}; NMR ($CDCl_3$) δ 1.20-1.98 (11H, m, cyclohexane H), 3.42 (1H, t, J=6.9 Hz, CH), 4.26-4.74 (2H, dd, OCH_2), 5.04-5.52 (2H, m, vinyl CH_2), 5.70-5.96 (1H, m, vinyl CH), 7.44-8.16 (4H, m, ArH), 10.26-10.74, (1H, b, COOH, exchangeable with D_2O).

Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.45; H, 8.03. Found: C, 74.47; H, 8.04.

(R,S)-4-(3-Methyl-2-oxa-4-pentenyl)benzoic Acid (17, Equation 5). Racemic 7 (1.5 g, 0.013 mol) and 2.24 g (0.013 mol) of 4-(chloromethyl)benzoic acid were used. The product was dissolved in 250 mL of hot hexane and filtered. The filtrate on concentration to 25 mL followed by cooling, gave 1.25 g (46.1%) of a white crystalline solid: mp 98-99°C; IR (KBr) 2540-2660, 1690 cm^{-1}; NMR ($CDCl_3$) δ 1.36 (3H, d, J=7.5 Hz, CH_3), 3.84-4.16 (1H, m, CH), 4.44-4.84 (2H, dd, OCH_2), 5.16-5.40, (2H, m, vinyl CH_2), 5.72-6.04 (1H, m, vinyl CH), 7.52-8.16 (4H, m, ArH), 11.7-12.0, (1H, b, COOH, exchangeable with D_2O).

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.90; H, 6.79. Found: C, 69.93; H, 6.61.

(R)-4-Methoxybiphenyl 4-(3-Butyl-2-oxa-4-pentenyl)benzoate (11, Equation 5). This material was prepared as above for 2 from 0.95 g (0.0038 mol) of 15 and 0.77 g (0.0038 mol) of 4-hydroxy-4'-methoxybiphenyl. The white solid obtained by silica gel chromatography using hexane:toluene (1:1) as eluant, was crystallized from absolute ethanol to give 0.48 g (29.1%) of a white solid: mp 108-109°C; $[\alpha]_D^{25}$ + 22.61° (c 0.252, chloroform); IR (KBr) 1725 cm^{-1}; NMR ($CDCl_3$) δ 0.80 (3H, t, J=4.0 Hz, CH_3), 1.32-1.60 (6H, m, 3xCH_2), 3.45-3.80 (1H, m, CH), 3.90 (3H, s, OCH_3), 4.40-4.84 (2H, dd, OCH_2), 5.16-5.36 (2H, m, vinyl CH_2), 5.64-6.02 (1H, m, vinyl CH), 7.00-8.32 (12H, m, ArH).

Anal. Calcd for $C_{28}H_{30}O_4$: C, 78.13; H, 6.97. Found: C, 77.90; H, 7.16.

(R)-4-Methoxybiphenyl 4-(3-Cyclohexyl-2-oxa-4-pentenyl)benzoate (12, Equation 5). This material was prepared as above for 2 from 1.4 g (0.0051 mol) of 16 and 1.02 g (0.0051 mol) of 4-hydroxy-4'-methoxybiphenyl. The white solid obtained by silica gel chromatography using hexane:toluene (1:1) as eluant, was crystallized from ethanol to give 0.88 g (37.8%) of a solid: mp 151-152.5°C; $[\alpha]_D^{25}$ + 14.06° (c 0.526, chloroform); IR (KBr) 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.16-2.12 (11H, m, cyclohexane H), 3.48 (1H, t, J=5.5 Hz, CH), 3.88 (3H, s, OCH_3), 4.32-4.80 (2H, dd, OCH_2), 5.14-5.40 (2H, m, vinyl CH_2), 5.60-5.96 (1H, m, vinyl CH), 6.96-8.28 (12H, m, ArH).

Anal. Calcd for $C_{30}H_{32}O_4$: C, 78.94; H, 7.01. Found: C, 78.83; H, 7.21.

(R,S)-4-Methoxybiphenyl 4-(3-Methyl-2-oxa-4-pentenyl)benzoate (13, Equation 5). This compound was prepared as above for 2 from 1.2 g (0.0058 mol) 17 and 1.16 g,(0.0058 mol) of 4-hydroxy-4'-methoxybiphenyl. The white solid obtained by silica gel chromatography using a mixture of hexane:toluene (1:1) as eluant was crystallized from ethanol to give 0.65 g (28.8%) of a solid: mp 130-130.5°C; IR (KBr) 1725 cm^{-1}; NMR ($CDCl_3$) δ 1.36 (3H, d, J=4.0 Hz, CH_3), 3.60-4.20 (4H, m, CH and OCH_3), 4.44-4.84 (2H, dd, OCH_2), 5.16-5.36 (2H, m, vinyl CH_2), 5.68-6.04 (1H, m, vinyl CH), 7.00-8.32 (12H, m, ArH).

Anal. Calcd for $C_{25}H_{24}O_4$: C, 77.32; H, 6.19. Found: C, 77.36; H, 6.26.

(R)-1-Hepten-3-yl 4-Biphenylcarboxylate (14, Equation 6). A mixture of 4-biphenylcarboxylic acid (1.74 g, .0088 mol), one drop of dimethylformamide and 3.2 g (0.027 mol) of freshly distilled thionyl chloride was stirred at room temperature for 4 h. The excess thionyl chloride was removed under vacuum using toluene to remove any residual thionyl chloride. The light yellow colored solid thus obtained was dissolved in 25 mL of dry methylene chloride and the solution was added dropwise to an ice cooled solution of 1.0 g (0.0088 mol) of 5 and 0.69 g (0.0087 mol) of pyridine in 25 mL of dry methylene chloride. The reaction mixture was stirred for 2 h at 0°C and for 1 h at room temperature. The mixture was washed with 0.1N aqueous hydrochloric acid, saturated aqueous sodium bicarbonate and water and then dried over anydrous magnesium sulfate. The solvent was evaporated and the product, a light yellow oil, was purified by silica gel chromatography using a mixture of hexane:toluene (19:1) as eluant to give 0.90 g (34.9%) of an oil: $[\alpha]_D^{25}$ -8.36° (c 0.275, chloroform); IR (neat) 1715 cm^{-1}; NMR ($CDCl_3$) δ 1.00 (3H, t, J=6.5 Hz, CH_3), 1.32-2.00 (6H, m, 3xCH_2), 5.20-5.36 (1H, m, CH), 5.48-5.64 (2H, m, vinyl CH_2) , 5.80-6.12 (1H, m, vinyl CH), 7.44-8.24 (9H, m, ArH).

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.63; H, 7.48; Found: C,81.70; H,7.47.

General Procedure for the Synthesis of Polysiloxane Materials. The alkene (1.1 mmol) and 1 mmol of the appropriate polyhydromethylsilane were dissolved or suspended in 2 mL of toluene in a PTFE vial. Chloroplatinic acid (40 μL) (0.4% solution of chloroplatinic acid dissolved in 98 parts of tetrahydrofuran and 1 part of ethanol) was added, and the vial was filled with argon gas. The mixture was heated at 80°C for 24-36 h. The progress of the reaction was monitored by IR spectroscopy at regular intervals. The disappearance of an absorption band at

2060-2080 cm^{-1} (Si-H) indicated the completion of the reaction. The final traces of Si-H were removed by bubbling ethylene gas into the reaction mixture for 10-15 min followed by further heating for 0.5 h. The polymers were obtained by precipitation with an equal volume of methanol. The products were purified by dissolving them in 2 mL of methylene chloride and precipitation with 5 mL of methanol. This process was repeated two times. The polymers were dissolved in methylene chloride, filtered (5-10 μm pore size) and the solvent was evaporated followed by drying in vacuum at 40±5°C overnight. The physical properties of the polymers are given in Table II.

Acknowledgement: This work was supported by National Science Foundation Grant No. CHE-8314769.

REFERENCES AND NOTES

1. Lochmuller, C.H.; Souter, R.W. J. Chromatogr. 1975, 113, 283.
2. Blaschke, G. Angew. Chem. Int. Ed. Engl. 1980, 19, 13.
3. Konig, W.A. J. High Resolut. Chromatogr. and Chromatogr. Commun. 1982, 5, 588.
4. Schurig, V. Angew. Chem. Int. Ed. Engl. 1984, 23, 747.
5. Krull, I.S. Adv. Chromatogr. 1978, 16, 175.
6. Pirkle, W.H.; House, D.W. J. Org. Chem. 1979, 44, 1957.
7. Davankov, V.A.; Kurganov, A.A.; Bochkov, A.S. Adv. Chromatogr. 1983, 22, 71.
8. Gil-Av, E. J. Chromatogr. Library, 1985, 32, 111 and references therein.
9. Newman, M.S.; Lednicer, D. J. Amer. Chem. Soc. 1956, 78, 4765.
10. Pirkle, W.H.; House, D.W.; Finn, J.M. J. Chromatogr. 1980, 192, 143 and references therein.
11. Schurig, V. "Asymmetric Synthesis"; Morrison, J.D. Ed.; Vol. 1, Academic Press: London, 1983, pp. 59.
12. Gil-Av, E.; Weinstein, S. "Handbook of HPLC For The Separation of Amino Acids, Peptides and Proteins"; Hancock, W.S. Ed.; Vol. 1, CRC Press Inc.: Boca Raton, FL; pp. 429.
13. Smith, G.G.; Wonnacott, D.M. Anal. Biochem. 1980, 109, 414.
14. Kelker, H. Adv. Liq. Cryst. 1978, 3, 237.
15. Porcaro, P.J.; Shubiak, P. J. Chromatogr. Sci. 1971, 9, 690.
16. Finkelmann, H.; Rehage, G. Makromol. Chem. Rapid Commun. 1982, 3, 859.
17. Jones, B.A.; Bradshaw, J.S.; Nishioka, M.; Lee, M.L. J. Org. Chem. 1984, 49, 4947.
18. Bradshaw, J.S.; Schregenberger, C.; Chang, K.H.C.; Markides, K.E.; Lee, M.L. J. Chromatogr. 1986, 358, 95.
19. Apfel, M.A.; Finkelmann, H.; Janini, G.M.; Laub, R.J.; Luehmann, B.H.; Price, A.; Roberts, W.L.; Shaw, T.J.; Smith, C.A. Anal. Chem. 1985, 57, 651.
20. Adams, N.W.; Bradshaw, J.S.; Bayona, J.M.; Markides, K.E.; Lee, M.L. Mol. Cryst. Liq. Cryst., in press.
21. Friedrich, L.E.; Cormier, R.A. J. Org. Chem. 1971, 36, 3011.
22. Moss, R.A.; Sunshine, W.L. J. Org. Chem. 1974, 39, 1083.
23. Rossiter, B.E. "Asymmetric Synthesis"; Morrison, J.D. Ed.; Vol. 5, Academic Press: New York, 1985, pp. 193.
24. Martin V.S.; Woodard, S.S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K.B. J. Amer. Chem. Soc. 1981, 103, 6237.
25. Dale, J.A.; Mosher, H.S. J. Amer. Chem. Soc. 1973, 95, 512.
26. Dale, J.A.; Dull, D.L.; Mosher, H.S. J. Org. Chem. 1969, 34, 2543.