Polystyrene Resins Incorporating BINOL Units: New Materials For Asymmetric Catalysis

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The radical crosslinking polymerization of styrene with (*R*)-divinyl-BINOL derivatives results in the formation of reticulated polystyrene networks containing protected (*R*)-BINOL entities at each junction of the polystyrene chains. The generation of polystyrene-immobilized free (*R*)-BINOL was performed by cleaving the protecting ether groups under acidic conditions. The resulting materials containing optically active BINOL units were tested as chiral ligands in the enantioselective addition of diethylzinc to benzaldehyde. The catalytic properties of the polymer gels were shown to be highly dependent on the degree of reticulation: in the best cases, the resins incorporating (*R*)-BINOL units showed activities and selectivities similar to those of molecular (*R*)-BINOL.

1. Introduction

Enantioselective catalysis is among the most powerful and challenging tools in organic chemistry.[1] The optimization of catalyst performance in terms of activity and selectivity and the elaboration of new catalytic materials can result in improved synthetic processes and the reduction of waste. The elaboration of polymer-supported (PS) reagents and catalysts is a field of intense research activity.[2] The immobilization of catalysts on polymeric supports offers a simple means of catalyst recovery and should facilitate catalyst reuse. Numerous chiral ligands derived from, for example, bis(oxazoline)s,[3] salen-type ligands[4] or binaphthyls[5] have been fixed on polymer supports and used as catalysts in asymmetric hydrogenations, additions, dihydroxylations and epoxidations.[6] In particular, the catalytic addition of diethylzinc to aldehydes[7] is a widely used test reaction for the evaluation of enantioselective PS catalysts.[8] However, PS catalyst systems show fundamental differences from their nonpolymeric counterparts, due to (a) hindered diffusion of the reactants through the polymer network, and (b) interactions of the support with reactants and immobilized catalyst species. These parameters can affect both activity and selectivity of the PS catalyst and often result in decreases in reaction rates and enantiomeric excesses.[9]

Since the first utilization of nonracemic 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) in asymmetric synthesis by Noyori et al.,[10] this chiral ligand has been shown to be extremely useful in numerous stoichiometric and catalytic asymmetric reactions.[11] The synthesis of polymer-supported BINOL has already been reported,[12] BINOL-containing linear polymers with main chain chirality in particular having been intensively studied.[13]

For several years we have been investigating BINOL-containing materials and polymers. For example, we have developed silica hybrid materials incorporating BINOL entities.[14] We have demonstrated that catalytic species can be stabilized in a silica matrix: the catalytic properties of materials incorporating rhodium are far superior to those of the corresponding molecular complex in homogeneous solution. The chiral loading affects the enantioselectivity of these materials in asymmetric catalysis: silica hybrid materials with a high chiral loading showed enhanced enantioselectivity relative to xerogels with lower concentrations of incorporated chiral entities. We attributed these results to a supramolecular effect of the chiral matrix. We have also recently reported the immobilization of (*R*)-BINOL crown ether units for molecular recognition.[15]

Here we report on the immobilization of (*R*)-BINOL entities in organic polymer materials by radical crosslinking copolymerization of divinyl-BINOL derivatives with styrene. To the best of our knowledge, only one example of immobilization of BINOL moieties by this method has been reported.[16] We were interested in the preparation of organic polymers with various degrees of crosslinking and loading in order to explore the influence of the support on the catalytic properties. Our approach permits the large-scale synthesis of chiral crosslinkers and the copolymerization of various ratios between the chiral crosslinking agent and the co-monomer styrene. In this way, the loading of the reticulated polymer with chiral groups can easily be varied.

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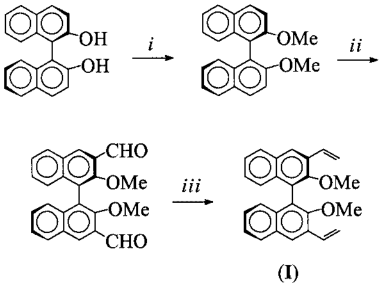
It has been shown that substitution on the BINOL unit may influence the catalytic performance of the chiral ligand.[17] The polystyrene chains can be viewed as bulky substituents on the BINOL unit and may affect the catalytic properties of the polymer-supported chiral ligand.

2. Results and Discussion

2.a. Monomer Synthesis

We present the synthesis of several (*R*)-divinyl-BINOL crosslinking agents by a general three-step method. The synthesis of 2,2′-bis(methoxy)-3,3′-divinyl-BINOL (**I**) from (*R*)-BINOL[18] by a methylation[19] − lithiation/formylation[20] − Wittig sequence is represented in Scheme 1.

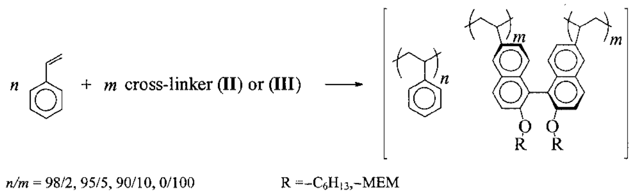


Scheme 1. Synthesis of 2,2′-bis(methoxy)-3,3′-divinyl-1,1′-binaphthyl (**I**); reactions and conditions: *i*: methyl iodide, acetone, potassium carbonate, reflux, 24 h, 97%; *ii*: *n*-butyllithium, TMEDA, diethyl ether, reflux, then DMF/H$^+$, 61%; *iii*: potassium *tert*-butoxide, methyltriphenylphosphonium bromide, THF, 66%

The synthesis of the crosslinkers **II** and **III** was carried out in a similar way, also from (*R*)-BINOL. Bromination quantitatively gave (*R*)-6,6′-dibromo-1,1′-binaphthyl.[21] The next steps (protection,[22,23] lithium/bromine exchange followed by formylation,[24] and Wittig reaction) gave the desired products in high yields (Scheme 2). The precursors **II** and **III** are functionalized with different protecting groups: whereas the hydroxy functions in precursor **II** are protected with hexyl groups, precursor **III** is etherified with methoxyethoxymethyl (MEM) groups. We have already shown that MEM ethers are useful protecting groups for the hydroxy functions of BINOL, allowing the synthesis of a protected trialkoxysilylated precursor and related hybrid materials.[23] Furthermore, the MEM group is easier to cleave than alkyl aryl ethers. The characterization of the crosslinkers **I** and **II** by chiral HPLC indicated optical purities of > 99%.

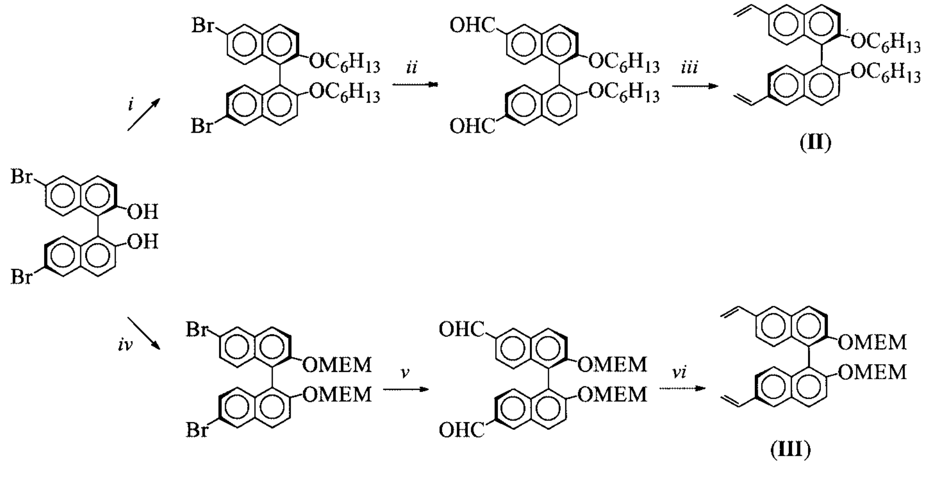
2.b. Polymer Syntheses

Polymers with different degrees of crosslinking were prepared either by radical crosslinking polymerization of the crosslinkers **I**−**III** with styrene[12c] or by thermal bulk polymerization of the pure crosslinkers **II** and **III**. The radical copolymerizations were carried out in toluene at 60 °C. AIBN was used as initiator (Scheme 3).



Scheme 3. Crosslinking polymerization of the chiral precursors **II** and **III** with styrene

In this way, polymers with different loadings of chiral building blocks were prepared. The polymers **1** and **2** were prepared from styrene and the crosslinker **I**. Because of the lower reactivity of the vinyl groups in the crosslinker **I**, copolymerization with styrene took longer than with the 6,6′-divinyl-BINOL precursors **II** or **III**. However, characterization of the polymers **1** and **2** by FT-IR spectroscopy, solid-state ^{13}C CP-MAS NMR spectroscopy and elemental ana-



Scheme 2. Synthesis of the crosslinkers **II** and **III**; reactions and conditions: *i*: BrC_6H_{13}, K_2CO_3, acetone, reflux, 95%; *ii*: *n*BuLi, Et_2O, −80 → 0 °C, then DMF/H$^+$, 86%; *iii*: potassium *tert*-butoxide, methyltriphenylphosphonium bromide, THF, 89%; *iv*: NaH, MEMCl, THF, 0 °C → room temp.; *v*: *n*BuLi, THF, −80 °C, then DMF/H$^+$, 98%; *vi*: potassium *tert*-butoxide, methyltriphenylphosphonium bromide, THF, 86%

lysis confirmed the incorporation of the chiral entity in the polymer network.

The formation of three-dimensional networks in the cases of the copolymerization reactions of the crosslinkers **II** and **III** with styrene was indicated by the gelation of the reaction medium during the polymerization. Unlike the copolymers, the polymers **6** and **9**, made up exclusively of the chiral precursors, were prepared by thermal bulk polymerization. Heating of the pure crosslinkers **II** or **III** to 100 °C for 24 h under vacuum firstly gave rubber-like intermediates and finally afforded hard and glassy products. Table 1 gives the monomer ratios and the loading of the prepared crosslinked polymers.

Table 1. Synthesis of polystyrene resins crosslinked by the chiral divinylic compounds **I**−**III**

Polymer	Crosslinker	Amount of the crosslinker in the reaction mixture (%) vs. styrene[a]	Loading[b] [mmol g^{-1}] Calcd.	Found
1	**I**	4	0.34	0.52
2	**I**	8	0.60	0.72
3	**II**	2	0.18	0.21
4	**II**	5.2	0.40	0.92
5	**II**	11	0.69	0.94
6	**II**	100	1.97	2.22
7	**III**	5.3	0.40	0.53
8	**III**	11	0.69	0.85
9	**III**	100	1.94	1.92

[a] Molar ratio. [b] Determined by elemental analysis by determination of oxygen.

The elemental analysis data of the polymers show that the oxygen values found are in all cases higher than expected, and the crosslinker was incorporated preferentially. This result can be explained by a higher reactivity of the double vinylic functionalized compound.

The polymers were also characterized by FT-IR spectroscopy and solid-state ^{13}C CP-MAS NMR spectroscopy. Characterization of the polymers by FT-IR spectroscopy and comparison with polystyrene and the pure monomer confirmed the incorporation of the chiral crosslinker into the network.

The optical purities of the incorporated BINOL moieties could not be established directly, due to the insolubility of the materials. However, Seebach et al. reported that unprotected divinylic (*R*)-BINOL derivatives probably undergo racemization during the radical polymerization whereas the protected (*R*)-BINOL counterparts are conformationally stable.[16] We therefore assume that the protected precursors **I**−**III** do not racemize in the course of the radical crosslinking polymerization. This supposition is confirmed by the results of the use of the crosslinked polymers in asymmetric catalysis (vide infra).

2.c. Deprotection of the Crosslinked Polymers

The methyl and hexyl ethers in the polymers **1**−**6** were cleaved with boron tribromide. The cleavage was confirmed by FT-IR and solid-state ^{13}C CP-MAS NMR spectroscopy. Figure 1 shows the FT-IR spectra of polymer **5** and the corresponding deprotected polymer **5**-OH. The generation of free hydroxy groups in **5**-OH is reflected by new signals at 3520 cm^{-1} [ν(O−H)] and 1144cm^{-1} [δ(O−H)]. Additionally, the characteristic signal of aryl alkyl ethers, visible in the spectrum of polymer **5** at 1243 cm^{-1}, completely disappeared in the spectrum of **5**-OH. Because of the elimination of the hexyl groups of the incorporated BINOL units, the signal intensity of the [ν(C−H)] absorption (2950−2850 cm^{-1}) is considerably lower in polymer **5**-OH than in polymer **5**.

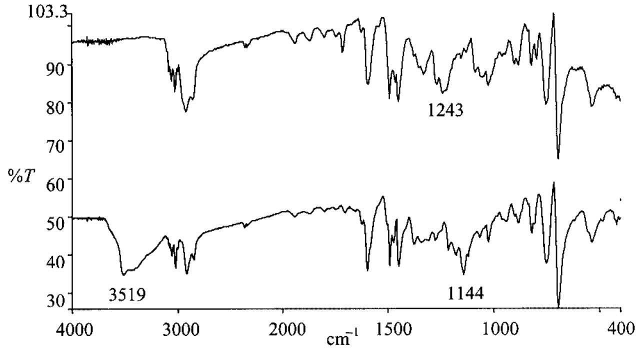


Figure 1. FT-IR spectra of polymer **5** (top) and the corresponding deprotected material **5**-OH (bottom)

Comparison of the solid-state ^{13}C CP-MAS NMR spectra of polymer **5** and of **5**-OH confirms the cleavage of the alkyl aryl ethers in the polymers. Figure 2 shows the solid-state ^{13}C CP-MAS NMR spectra of polymers **5** and **5**-OH. The spectrum of polymer **5** shows intense signals due to the polystyrene matrix at $\delta = 41.5$ and 129 ppm. The presence of the chiral crosslinker in the material is indicated by resonances at $\delta = 15.2$, 24.0, 26.7 and 31.2 ppm (hexyl ether), but also by a resonance at $\delta = 155.7$ ppm due to the aromatic carbon atom in the position *ipso* to the hexyloxy group. After treatment of polymer **5** with boron tribromide,

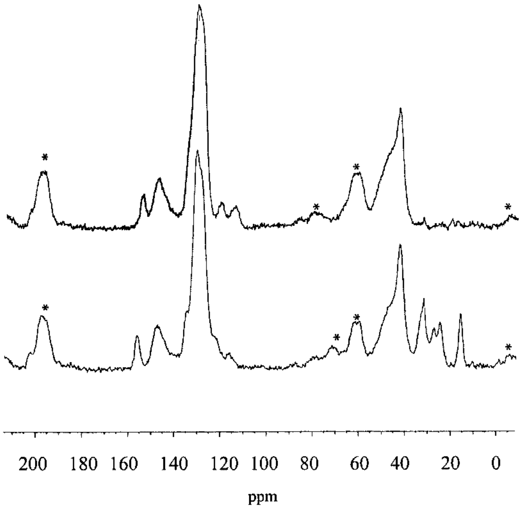


Figure 2. Solid-state ^{13}C CP-MAS NMR spectra of polymers **5**-OH (top) and **5** (bottom); spinning side-bands are marked by asterisks

the signals of the hexyloxy chains had completely disappeared in the spectrum of polymer **5**-OH, whereas the signals of the polystyrene matrix were unchanged. This result shows that the cleavage of the hexyl ethers had occurred quantitatively in the crosslinked material and indicates good accessibility of the reactive sites in the polymer network.

In the case of the deprotection of polymer **6**, both the FT-IR and the ^{13}C CP-MAS NMR spectra of the corresponding material **6**-OH indicated that deprotection had not completely taken place in this material. This may be due to hindered diffusion of the reactants through the highly reticulated polymer network.

Similar results were obtained with the precursor **III** as crosslinking agent. The characterization of the polymers **7**−**9** by FT-IR and solid-state ^{13}C CP-MAS NMR spectroscopy confirms the incorporation of the chiral entities into the polymer network.

MEM ethers can be cleaved under milder conditions than hexyl ethers. Free hydroxy groups were generated in the MEM-containing polymers by swelling the polymers **7**, **8** and **9** in THF and treatment of the swollen gels with 4 N hydrochloric acid at 50 °C. After acidic treatment, the characteristic signals indicating the presence of MEM groups in the polymers **7**-OH and **8**-OH had completely disappeared. In contrast, the spectra of polymer **9**-OH always showed absorptions due to the protective group, indicating incomplete cleavage of the MEM ethers, similarly to the case of the material **6**-OH.

These results indicate that the cleavage of the alkyl aryl ethers in the reticulated polymers took place quantitatively, both for hexyl ethers and for MEM ethers, if the polymers could be swollen in an organic solvent. In contrast, the cleavage reaction was found to be incomplete for the materials with high degrees of crosslinking. The cleavage of the hexyl ether required vigorous treatment with stoichiometric amounts of boron tribromide whereas MEM ethers could be cleaved with 4 N hydrochloric acid.

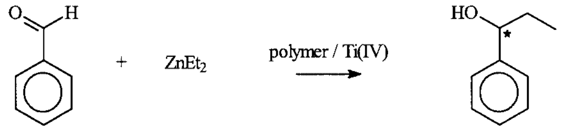
2.d. Test in Asymmetric Catalysis

The catalytic activity of the reticulated materials was tested in the addition of diethylzinc to benzaldehyde.[25] The results are summarized in Table 2.

These results indicate that the (BINOL)Ti^{IV} complex is a very efficient catalyst for the addition of diethylzinc to benzaldehyde, affording 1-phenylpropan-1-ol in quantitative yield (Entry 1). However, we found a slightly lower enantiomeric excess (80% *ee*) than reported by Chan et al. under our standard reaction conditions.[25] The formation of the catalytic (BINOL)Ti(O*i*Pr)$_2$ complex takes place very quickly with molecular (*R*)-BINOL, but needs a longer time with the immobilized BINOL species. We therefore chose a considerably longer reaction period for catalyst formation with the reticulated polymers [15 h instead of 10 min with (*R*)-BINOL].

The catalytic activities of the reticulated materials were generally high, except in the cases of the polymers **6**-OH and **9**-OH. These highly reticulated polymers afforded (*R*)-1-phenylpropanol in yields of 50−60% and with 17 or 4% *ee*, respectively (Entries 8/11). The polymer **6**-OH was allowed to react for 5 h; longer reaction times did not result in higher conversions and selectivities. These reduced catalytic activities and selectivities can be explained by the incomplete deprotection reactions (vide supra); only small quantities of free 2,2′-dihydroxybinaphthyl entities are formed in the course of the deprotection reaction. The polymers **6**-OH and **9**-OH mainly contain monodeprotected 2′-alkoxy-2-hydroxybinaphthyl and even 2,2′-dialkoxybinaphthyl entities and therefore show strongly decreased catalytic properties. Another important aspect is the presence of free Ti(O*i*Pr)$_4$ in the reaction medium. The conversion rates and selectivities of the **6**-OH/Ti(O*i*Pr)$_4$ and **9**-OH/Ti(O*i*Pr)$_4$ sys-

Table 2. Additions of diethylzinc to benzaldehyde catalyzed by various [(*R*)-BINOL]Ti^{IV} complexes



Entry[a]	Chiral ligand	Cocatalyst	Conversion	*ee*[b]	Configuration[b]
1	(*R*)-BINOL	Ti(O*i*Pr)$_4$	> 99%[c]	80%	(*R*)
2	(*R*)-BINOL	−	no reaction[c]	−	−
3	**1**-OH	Ti(O*i*Pr)$_4$	> 99%[c]	24%	(*R*)
4	**2**-OH	Ti(O*i*Pr)$_4$	> 99%[c]	20%	(*R*)
5	**3**-OH	Ti(O*i*Pr)$_4$	> 99%[c]	73%	(*R*)
6	**4**-OH	Ti(O*i*Pr)$_4$	90%[c]	78%	(*R*)
7	**5**-OH	Ti(O*i*Pr)$_4$	> 99%[c]	77%	(*R*)
8	**6**-OH	Ti(O*i*Pr)$_4$	53%[d]	17%	(*R*)
9	**7**-OH	Ti(O*i*Pr)$_4$	> 99%[c]	78%	(*R*)
10	**8**-OH	Ti(O*i*Pr)$_4$	> 99%[c]	69%	(*R*)
11	**9**-OH	Ti(O*i*Pr)$_4$	64%[d]	4%	(*R*)

[a] General reaction conditions: benzaldehyde/"(*R*)-BINOL"/Ti(O*i*Pr)$_4$/Et$_2$Zn = 1.0:0.1:0.7:3 (molar ratio), reaction time 20 h except for Entry **8** (reaction time 5 h). [b] Determined by HPLC on a Daicel Chiralcel OD column. [c] Determined by gas chromatography on a HP-50+ column. [d] Determined by ^{1}H NMR spectroscopy.

tems are only slightly higher than those of free Ti(O*i*Pr)$_4$, without any added BINOL.[25] We therefore assume that only small amounts of Ti(O*i*Pr)$_4$ are coordinated to the immobilized (*R*)-BINOL entities because of (a) incomplete cleavage of the protecting alkyl ether groups in the strongly reticulated polymer, and (b) hindered diffusion processes of the reactants through the rigid polymer network.

The selectivities of the polymers strongly depend on the substitution pattern of the immobilized BINOL species. The polymers **1**-OH and **2**-OH, incorporating BINOL units substituted in the 3,3′-positions, show considerably lower enantioselectivity than the polymers made up of 6,6′-disubstituted BINOL entities (Entries 3/4).

In the other cases of asymmetric addition of diethylzinc to benzaldehyde with reticulated polymers (Entries 5−7, 9 and 10), we observed degrees of conversion of > 99%; only the polymer **4**-OH (Entry 6) gave a slightly lower degree of conversion of 90%. The enantioselectivities of the reticulated polymers are in a range from 69−79% *ee* and are also slightly lower than in the case of molecular (*R*)-BINOL. This slightly reduced enantioselectivity may be due to a substitution effect of the polystyrene chains in the 6,6′-positions on the catalytic properties of the BINOL units.

The catalytic activity of the immobilized BINOL resins in the asymmetric addition of diethylzinc to benzaldehyde depends particularly on two parameters:

1. The position of the polystyrene chains on the (*R*)-BINOL unit: BINOL moieties substituted in positions 3,3′ show considerably lower enantioselectivies than materials made up of BINOL units substituted in positions 6,6′.

2. The degree of reticulation of the polymer network: High levels of reticulation limit diffusion through the polymer network and do not allow complete deprotection of the immobilized 2,2′-dialkoxy-1,1′-binaphthyls. After deprotection, the strongly reticulated polymers contain only partially deprotected immobilized BINOL species and show low catalytic activity and selectivity. In contrast, the protecting ether groups of immobilized 2,2′-alkoxy-1,1′-binaphthyls in lightly reticulated materials can be cleaved quantitatively. The deprotected materials show high catalytic activity and selectivity.

In this context, we wish to point out that rhodium-containing silica hybrid materials display completely different behavior in heterogeneous asymmetric catalysis. These materials exhibit high catalytic activities even with high degrees of crosslinking, as the polar and porous silica matrix permits better accessibility of the catalytic sites than the completely organic polystyrene resin throughout the three-dimensional network.

The nature of the synthetic pathway, either by deprotection of the hexyloxy precursor **II** with boron tribromide or by deprotection of the MEM precursor **III** with hydrochloric acid, does not affect the catalytic properties of the polymers.

Experimenal Section

General: All reactions were performed under nitrogen or argon by Schlenk tube techniques. ^{1}H and ^{13}C NMR spectra in solution were recorded with Bruker AC 200 and AC 250 spectrometers. Deuterated chloroform was used as NMR solvent, and chemical shifts are reported as δ values in ppm relative to tetramethylsilane; *J* values are in Hz. IR spectra were determined with a Perkin−Elmer SPECTRUM 1000 FT-IR spectrometer. Mass spectra were measured with a JEOL MS-DX 300 mass spectrometer. Optical rotations were measured with a Perkin−Elmer polarimeter 241. Elemental analyses were carried out by the "Service Central de Micro-Analyse du CNRS" at Vernaison (France). Enantiomeric excess of the crosslinkers **I** and **II** and the 1-phenylpropanol were determined by chiral HPLC with a Waters 515 HPLC pump, a Waters 2487 UV detector and a Daicel Chiralcel OD column. All reagents were obtained from commercial sources and used without purification. In experiments requiring dry solvents, THF, toluene and diethyl ether were distilled from sodium/benzophenone, DMF was distilled from CaH$_2$, dichloromethane was distilled from P$_2$O$_5$, and alcohols were distilled from Mg. The preparation of (*R*)-6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthyl,[21] (*R*)-6,6′-dibromo-2,2′-bis(hexyloxy)-1,1′-binaphthyl,[22] (*R*)-6,6′-dibromo-2,2′-bis[(methoxyethoxy)methyloxy]-1,1′-binaphthyl[23] and (*R*)-2,2′-bis(methoxy)-1,1′-binaphthyl-3,3′-dicarbaldehyde[20] were carried out as described in the literature.

Syntheses of the Binaphthyl Crosslinkers I, II and III

(*R*)-2,2′-Bis(methoxy)-3,3′-divinyl-1,1′-binaphthyl (I): Methyltriphenylphosphonium bromide (1.45 g, 4.05 mmol) was added at 0 °C to a suspension of potassium *tert*-butoxide (0.45 g, 4.05 mmol) in freshly distilled THF (30 mL). The resulting yellow suspension was stirred for 3 h at this temperature. After the mixture had then been cooled to −80 °C, a solution of (*R*)-2,2′-bis(methoxy)-1,1′-binaphthyl-3,3′-dicarbaldehyde (500 mg, 1.35 mmol) in THF was added. The solution was stirred at −80 °C for 30 min and was than allowed to warm to room temperature overnight. The reaction mixture was quenched by addition of 30 mL of water and extracted with EtOAc (3 × 30 mL), and the combined organic phases were washed successively with water (2 × 30 mL) and brine (1 × 30 mL) and finally dried with sodium sulfate. After evaporation of the solvents, flash chromatography of the crude product (silica gel, hexane/EtOAc, 93:7) afforded the title compound. Yield: 330 mg, 0.9 mmol (66%). ^{1}H NMR (CDCl$_3$): δ = 3.39 (s, 6 H), 5.45 (dd, ^1J = 11.0, ^2J = 1.4 Hz, 2 H1 Hz), 6.03 (dd, ^1J = 17.7, ^2J = 1.4 Hz, 2 H2 Hz), 7.10−7.42 (m, 8 H), 7.90 (d, *J* = 8.2 Hz, 2 H), 8.14 (s, 2 H) ppm. ^{13}C NMR (CDCl$_3$): δ = 61.1, 115.9, 125.0, 125.1, 125.7, 126.2, 126.3, 128.2, 130.8, 131.5, 132.6, 133.9, 154.3. IR (KBr): ṽ = 2993, 2960, 2931, 2850, 1592, 1493, 1453, 1392, 1356, 1239, 1148, 1101, 1004, 896, 758 cm^{-1}. HRMS (FAB): calcd. for $C_{26}H_{22}O_2$ [M + H]$^+$ 366.1620, found 366.1612. $[\alpha]_D^{25}$= −30.5 (*c* = 1.017, CH$_2$Cl$_2$); *ee* > 99.9% (chiral HPLC, solvent: hexane/2-propanol, 9:1).

(*R*)-2,2′-Bis(hexyloxy)-6,6′-divinyl-1,1′-binaphthyl (II): This compound was prepared in a similar way, starting from (*R*)-2,2′-bis(hexyloxy)-1,1′-binaphthyl-6,6′-dicarbaldehyde (1.86 g, 3.64 mmol). Yield: 1.64 g, 3.24 mmol (89%). ^{1}H NMR (CDCl$_3$): δ = 0.74 (t, 6 H), 0.98 (m, 12 H), 1.40 (m, 4 H), 3.92 (m, 4 H), 5.24 (dd, ^1J = 11.7, ^2J = 0.8 Hz, 2 H), 5.75 (dd, ^1J = 17.5, ^2J = 0.8 Hz, 2 H), 6.85 (dd, ^1J = 17.6, ^2J = 11.7 Hz, 2 H), 7.12 (d, *J* = 8.8 Hz, 2 H), 7.37 (dd, ^1J = 9.0, ^2J = 2.0 Hz, 2 H), 7.38 (d, *J* = 9.0 Hz, 2 H), 7.77 (d, *J* = 1.6 Hz, 2 H), 7.89 (d, *J* = 9.0 Hz, 2 H) ppm. ^{13}C NMR (CDCl$_3$): δ = 13.9, 22.5, 25.3, 29.4, 31.3, 69.7, 112.9, 116.0, 120.7, 123.4, 124.8, 126.4, 129.2, 129.3, 132.7, 134.0, 137.0, 154.8 ppm. IR (KBr): ṽ = 3086, 2930, 2858, 1631, 1588, 1466, 1336, 1275, 1250, 1093, 1053, 988, 888 cm^{-1}. $[\alpha]_D^{25}$ = 81.3 (*c* = 1.30, CH$_2$Cl$_2$); *ee* = 99.1% (chiral HPLC, solvent: hexane).

$C_{36}H_{42}O_2$ (506.73): calcd. C 85.33, H 8.35, O 6.31; found C 84.81, H 8.38, O 6.20.

(*R*)-2,2′-Bis[(2-methoxyethoxy)methoxy]-1,1′-binaphthyl-6,6′-dicarbaldehyde: (*R*)-6,6′-Dibromo-2,2′-bis[(methoxyethoxy)methoxy]-1,1′-binaphthyl (4.00 g, 6.5 mmol) was dissolved in THF (30 mL) under an inert gas in a Schlenk tube. This solution was cooled to −80 °C, and BuLi (1.6 M in hexanes, 11 mL) was added dropwise. The yellow reaction mixture was stirred at this temperature for 45 min, and DMF (1.7 mL) was then added dropwise. The reaction mixture was stirred for 30 min at −80 °C and then for 2 h at room temperature. The suspension was poured into 200 mL of crunched ice/100 mL hydrochloric acid (2 N) and stirred for 30 min at 0 °C. The product was extracted with 3 × 50 mL of ethyl acetate. Drying with magnesium sulfate and evaporation of the solvents under reduced pressure yielded an off-white solid. Column chromatography of the crude product (silica gel, hexane/EtOAc, 70:30) afforded the pure title compound. Yield: 3.28 g, 6.3 mmol (98%). ^1H NMR ($CDCl_3$): $\delta = 3.29-3.52$ (m, 14 H), 5.13 (d, $J = 7.1$ Hz, 2 H), 5.26 (d, $J = 7.1$ Hz, 2 H), 7.18 (d, $J = 8.8$ Hz, 2 H), 7.69 (dd, $J = 8.7$, 1.5 Hz, 2 H), 7.75 (d, $J = 9.2$ Hz, 2 H), 8.15 (d, $J = 9.2$ Hz, 2 H), 8.39 (d, $J = 1.4$ Hz, 2 H), 10.10 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 59.0$, 67.7, 71.3, 93.6, 117.4, 120.2, 123.4, 126.1, 128.7, 131.6, 136.6, 134.9, 137.1, 155.3, 192.0 ppm. IR (KBr): $\tilde{\nu} = 3039$, 2930, 2886, 2821, 1698, 1619, 1477, 1231, 1013 cm^{-1}. $[\alpha]_D^{25} = -62.7$ ($c = 1.022$, CH_2Cl_2). $C_{30}H_{30}O_8$ (518.56): calcd. C 69.49, H 5.83; found C 69.48, H 5.88.

(*R*)-2,2′-Bis[(2-methoxyethoxy)methoxy]-6,6′-divinyl-1,1′-binaphthyl (III): This compound was prepared similarly to the divinylic compounds **I** and **II**, starting from (*R*)-2,2′-bis[(methoxyethoxy)methoxy]-1,1′-binaphthyl-6,6′-dicarbaldehyde (2.96 g, 5.7 mmol). Yield: 2.52 g (86%). ^1H NMR ($CDCl_3$): $\delta = 3.24-3.52$ (m, 14 H), 5.05 (d, $J = 6.9$ Hz, 2 H), 5.19 (d, $J = 6.9$ Hz, 2 H), 5.26 (dd, $^1J = 10.9$, $^2J = 1.3$ Hz, 2 H), 5.76 ("d", $J = 17.6$ Hz, 2 H), 6.84 (dd, $^1J = 17.6$, $^2J = 10.9$ Hz, 2 H), 7.08 (d, $J = 8.9$ Hz, 2 H), 7.37 (dd, $^1J = 8.9$, $^2J = 1.6$ Hz, 2 H), 7.55 (d, $J = 8.0$ Hz, 2 H), 7.79 (br. s, 2 H), 7.92 (d, $J = 9.1$ Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 58.9$, 67.5, 71.4, 94.3, 113.6, 117.7, 121.2, 123.7, 125.8, 126.4, 129.6, 129.9, 133.4, 133.6, 136.8, 152.9 ppm. IR (KBr): $\tilde{\nu} = 3086$, 2926, 2851, 1631, 1591, 1480, 1232, 1105, 1029, 966, 908 cm^{-1}. MS [FAB (+)]: *m/z* (%) = 514 (8) [M^+]. $[\alpha]_D^{25} = -263.7$ ($c = 0.46$, CH_2Cl_2). $C_{32}H_{34}O_6$ (514.62): calcd. C 74.69, H 6.66, O 18.65; found C 74.85, H 6.73, O 18.41.

Polymer Syntheses: All polymers except for polymers **6** and **9** were prepared by radical copolymerization of styrene with the crosslinkers **I−III**. AIBN was added to a toluene solution of styrene and the crosslinker. The resulting homogeneous solution was degassed and heated to 60 °C. The products were isolated either by precipitation of the toluene solution in methanol, for soluble polymers, or by filtration and washing with ethanol. The exact amounts of styrene, the crosslinkers, the initiator AIBN and the yields are listed in Table 3. Polymers **6** and **9** were prepared by simple heating of the precursors **II** and **III** to 100 °C under vacuum. After 24 h at this temperature, the resulting material was powdered and washed with methanol. After drying, the polymers were isolated in quantitative yield.

Spectroscopic Properties of Polymer 2: IR (KBr): $\tilde{\nu} = 3060$, 3026, 2924, 2850, 1601, 1494, 1453, 1356, 1261, 1235, 1100, 1013, 804, 751, 699 cm^{-1}. ^{13}C CP-MAS NMR: $\delta = 156.5$, 146.2, 127.4, 41.6 ppm (the signal of the OCH_3 group linked to the binaphthyl rings is masked by rotational side bands of the aromatic carbon atoms. Elemental analysis: found C 86.25, H 7.17, O 2.31.

Spectroscopic Properties of Polymer 5: IR (KBr): $\tilde{\nu} = 3025$, 2922, 1594, 1493, 1451, 1330, 1243, 1027, 755, 696 cm^{-1}. ^{13}C CP-MAS NMR: $\delta = 155.7$, 146.6, 129.1, 59.3, 41.5, 31.2, 26.7, 24.0, 15.2 ppm. Elemental analysis: found C 88.78, H 8.11, O 3.00.

Spectroscopic Properties of Polymer 8: $\tilde{\nu}$ (KBr)/cm^{-1} 3059, 3025, 2920, 1599, 1493, 1452, 1229, 1105, 1072, 1025, 758, 698. ^{13}C CP-MAS NMR: $\delta = 153.6$, 146.8, 128.9, 97.6, 72.5, 68.8, 40.7. Elemental analysis: found C 83.90, H 7.21, O, 8.13.

Cleavage of the Polymer-Supported Methyl, Hexyl and MEM Ethers: Deprotection of the polymers was carried out either with stoichiometric amounts of boron tribromide (polymers **1−6**) or with 4 N hydrochloric acid (polymers **7−9**).

General Procedure for Cleavage with Boron Tribromide: The polymer (500 mg) was swollen in ca. 10 mL of dichloromethane and stirred at room temperature for 10 min. The resulting suspension was cooled to −80 °C, and a stoichiometric amount of BBr_3 was added. The heterogeneous mixture was allowed to reach room temperature overnight, quenched by pouring into crunched ice and filtered. The resulting polymer was washed several times with methanol and finally dried in vacuo.

Spectroscopic Properties of Polymer 2-OH: IR (KBr): $\tilde{\nu} = 3512$, 3049, 3026, 2922, 1601, 1493, 1425, 750, 698 cm^{-1}. ^{13}C CP-MAS NMR: $\delta = 156.6$, 146.7, 127.5, 41.4 ppm. Yield: 380 mg.

Spectroscopic Properties of Polymer 5-OH: IR (KBr): $\tilde{\nu} = 3519$, 3059, 3024, 2918, 1599, 1492, 1451, 1144, 755, 697 cm^{-1}. ^{13}C CP-MAS NMR: $\delta = 153.0$, 146.2, 129.2, 119.0, 112.6, 41.6 ppm. Yield: 400 mg.

General Procedure for Cleavage with Hydrochloric Acid: The polymer (500 mg) was swollen in a mixture of ca. 10 mL THF/1 mL 4 N hydrochloric acid and stirred at 50 °C for 18 h. After this time, the reaction mixture was cooled to room temperature, poured into methanol and filtered. The resulting polymer was washed several times with methanol and finally dried in vacuo.

Table 3. Composition of the reaction mixtures for the syntheses of the copolymers **1−5**, **7** and **8**

Polymer	Styrene	Crosslinker Type	Amount	AIBN	Yield [g]	[%]
1	1.26 g, 12.1 mmol	**I**	180 mg, 0.49 mmol	110 mg	0.93	65
2	1.26 g, 12.1 mmol	**I**	360 mg, 0.98 mmol	110 mg	1.04	64
3	5.21 g, 50 mmol	**II**	510 mg, 1 mmol	168 mg	3.19	56
4	2.60 g, 25 mmol	**II**	665 mg, 1.31 mmol	100 mg	1.46	45
5	2.60 g, 25 mmol	**II**	1.40 g, 2.76 mmol	51 mg	3.37	84
7	2.60 g, 25 mmol	**III**	677 mg, 1.32 mmol	25 mg	2.23	59
8	1.29 g, 12.5 mmol	**III**	714 mg, 1.39 mmol	30 mg	1.55	77

Spectroscopic Properties of Polymer 8-OH: IR (KBr): $\tilde{\nu}$ = 3530, 3060, 3026, 2922, 1600, 1494, 1452, 1219, 1151, 1028, 758, 699 cm^{-1}. ^{13}C CP-MAS NMR: δ = 153.4, 146.7, 129.0, 41.1 ppm. Yield: 440 mg .

General Procedure for the Asymmetric Addition of Diethylzinc to Benzaldehyde: The reaction was carried out according to the literature procedure.[26] A Schlenk tube, equipped with a stirring bar, was charged with the reticulated polymer corresponding to 0.025 mmol of (*R*)-BINOL. After drying in vacuo, the solvent (dichloromethane, 2 mL) and Ti(O*i*Pr)$_4$ (60µL, 0.175 mmol) were added. The resulting mixture was stirred at ambient temperature for 15 h, and diethylzinc (1 M in hexane, 0.75 mL) was then added. The resulting suspension was stirred for another 15 min and cooled to 0 °C. At this temperature, benzaldehyde (26 µL, 0.25 mmol) was added and the reaction mixture was stirred at 0 °C. The reaction was stopped by addition of hydrochloric acid (2 N, 5 mL) and the polymer was filtered and washed. The diethyl ether extract was dried and the yield and *ee* value were determined by GC and HPLC (Chiralcel OD, hexane/2-propanol, 9:1), respectively.

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