Rigid and Sterically Regular Chiral 1,1′-Binaphthyl Polymers in Asymmetric Catalysis

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Abstract: Optically active 1,1′-binaphthyl structures have been used to synthesize novel, rigid and sterically regular polymeric catalysts for asymmetric catalysis. Good to excellent enantioselectivties have been achieved for reactions including the organozinc addition to aldehydes, the reduction of ketones with catecholborane, the hetero-Diels–Alder reaction of ethyl glyoxylate with a conjugated diene, the epoxidation of α,β-unsaturated ketones, and the 1,3-dipolar cycloaddition of nitrones with alkenes. The studies on the use of polymers (*R*)-**4**, (*R*)-**8**, (*R*)-**9**, and (*R*)-**15** and monomer (*R*)-**11** in asymmetric catalysis have introduced two new concepts for the development of enantioselective polymer catalysts: 1) the microenvironment of the catalytic sites in rigid and sterically regular polymers can be systematically modified to produce highly enantioselective polymeric catalysts; 2) the enantioselectivity of a monomeric catalyst can be maintained in a polymer catalyst by the use of a rigid and sterically regular polymer backbone. Compared with the traditional polymer-supported catalysts for which flexible and sterically irregular polymers are used, this new approach can better preserve the catalytic environment of the monomeric catalysts in the polymer as long as the catalytically active species are not aggregates of the monomers. These strategies not only make it possible to obtain easily reusable and highly enantioselective polymeric catalysts for many asymmetric reactions, but also can be further extended to construct polymeric chiral catalysts that are capable of multiple asymmetric catalytic reactions by incorporating different catalytic species in a polymer chain.

Keywords: aldehydes · asymmetric catalysis · 1,1′-binaphthyls · catalysts · chiral polymers

Introduction

During the past two decades, tremendous progress has been made in the field of asymmetric catalysis.[1–3] A number of highly enantioselective as well as practical catalysts have been developed for the synthesis of chiral organic compounds including drug molecules and agricultural products. Because the optically active catalysts are often quite expensive to prepare, it is highly desirable if they can be easily recovered and reused. For this purpose, the application of both heterogeneous and homogeneous polymer-supported chiral catalysts to asymmetric synthesis has been studied.[4–6] The large size differences between macromolecules and small molecules make it easy to recycle the chiral polymer catalysts. The heterogeneous polymer-supported chiral catalysts are recovered by simple filtration and the homogeneous polymer-supported chiral catalysts by either membrane filtration or precipitation with poor solvents followed by filtration. The polymer-supported catalysts can also be used for continuous production of chiral products in flow reactors or flow membrane reactors. Traditionally, the polymer-supported chiral catalysts are prepared by anchoring highly enantioselective monomeric catalysts to flexible and sterically irregular polymer supports. Although a few enantioselective polymer catalysts have been obtained in this manner, a significant reduction of enantioselectivity is often observed after a monomeric catalyst is attached to a polymer support. This indicates that the microenvironment of the polymer is very important for the stereoselectivity of the catalyst. Because of the stereo-irregularity and flexibility of the traditional polymeric chiral catalysts, their catalytic sites do not have well-defined microenvironment. It is very difficult to *systematically* modify the microenvironment of the catalytic sites in these polymers to improve their enantioselectivity.

Discussion

Recently, we have carried out a program to use optically pure 1,1′-binaphthyl molecules[7] to build novel rigid and sterically regular chiral polymers[8, 9] and have studied their applications as asymmetric catalysts.[10–16] Polymer **1** represents a general structure for the binaphthyl-based polymeric chiral catalysts.

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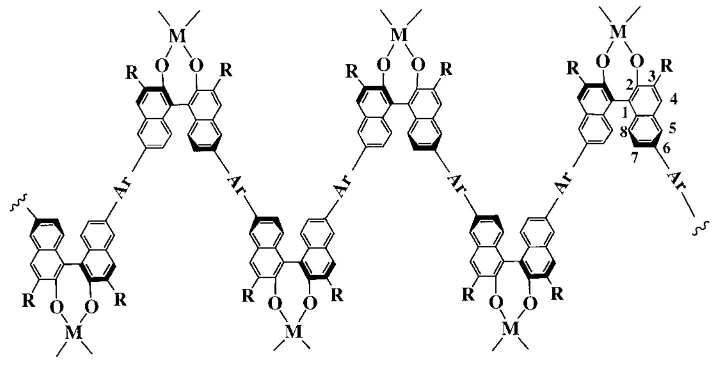

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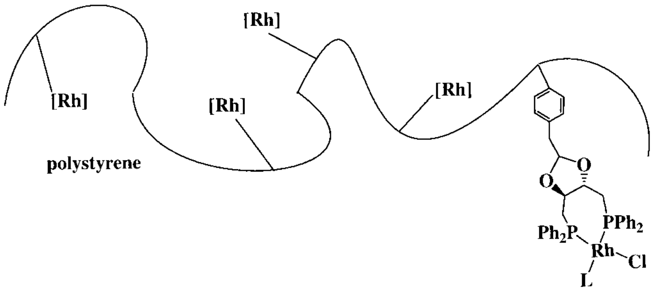

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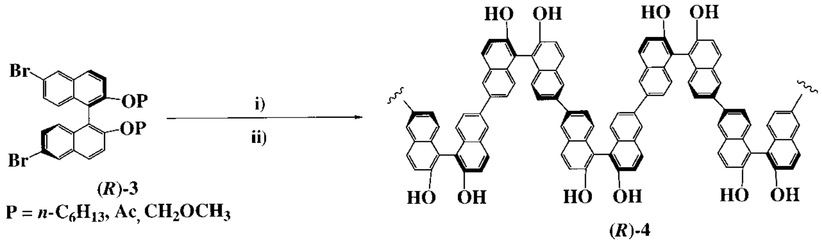
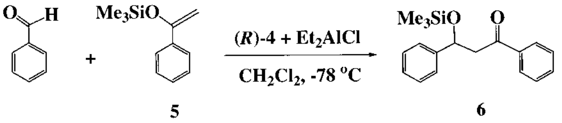
Owing to the rigidity and stereoregularity of the polymer, its metal centers, that is, the catalytic sites, have much better defined microenvironments compared with those in the traditional polymer catalyst **2**.[6] Therefore, when the polymer catalyst **1** does not perform satisfactorily in an asymmetric reaction, it is possible to *systematically* vary the R groups and/or the Ar linkers of **1** to modify both the steric and electronic environments of the catalytic sites to improve the stereoselectivity. The development of enantioselective polymeric catalysts is thus reduced to be very similar to the development of normal monomeric chiral catalysts. Using this strategy, we have obtained highly enantioselective polymer catalysts. We have further demonstrated that the rigid and sterically regular polymer chains can be used to preserve the catalytic properties of enantioselective monomer catalysts.

Polymer (*R*)-**4** is the first binaphthyl polymer prepared in our laboratory for asymmetric catalysis.[10, 11] It is synthesized from the Ni^0 or Ni^{II}/Zn mediated polymerization of 6,6′-dibromo binaphthyl monomers (*R*)-**3** followed by hydrolysis (Scheme 1). Polymer (*R*)-**4** is soluble in benzyl alcohol, DMF, and basic aqueous solution, but insoluble in methylene chloride, chloroform, benzene, toluene, and THF. This polymer, after treatment with diethyl aluminum chloride, was used to catalyze the Mukaiyama aldol condensation of benzaldehyde with **5** to give **6** (Scheme 2). Although both the aluminum complexes made from polymer (*R*)-**4** and the monomer (*R*)-1,1′-bi-2-naphthol showed no enantioselectivity for this reaction, the polymer-based Lewis acid complex had a greatly enhanced catalytic activity over the monobinaphthyl complex. The high activity of the polybinaphthylaluminum complex probably results from the empty p orbitals on its Al^{III} centers, which cannot form the intermolecular Al–O–Al bridging bonds as in the monomer case and are thus available to activate the carbonyl group of benzaldehyde.



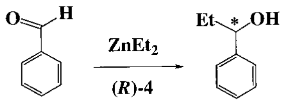
Scheme 1. Synthesis of the 1,1′-binaphthol polymer (*R*)-**4**. i) Ni^0 or Ni^{II}/Zn; ii) hydrolysis.

We have also examined the application of (*R*)-**4** to the asymmetric reaction of diethylzinc with benzaldehyde to produce a secondary chiral alcohol **7** (Scheme 3).[12, 13] This polymer again showed very low chemoselectivity as well as enantioselectivity. Besides the addition product **7**, a side-product, benzyl alcohol, was also generated from the reduction of benzaldehyde. This reaction was carried out in methylene chloride, in which (*R*)-**4** was insoluble and acted as a heterogeneous catalyst. In order to improve the catalytic properties of the polymer catalyst, a soluble polymer (*R*)-**8** was prepared by linking the binaphthyl units at the 6,6′-position with phenylene spacers containing flexible hexyloxyl groups through a Suzuki coupling polymerization.[12, 13] This polymer was used to catalyze the reaction of benzaldehyde with diethylzinc. Although improvements were seen, both the chemoselectivity and enantioselectivity were still low.



5 **6**

Scheme 2. A Mukaiyama reaction catalyzed by the polybinaphthyl aluminum complex.



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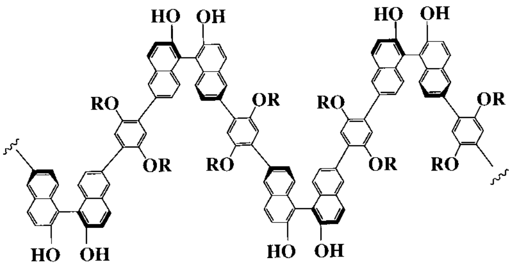
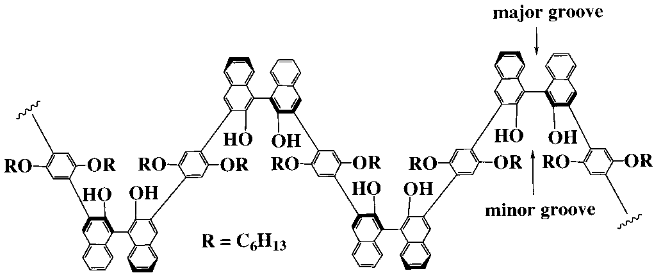
Scheme 3. An asymmetric diethylzinc addition to benzaldehyde catalyzed by the polybinaphthyl zinc complex.

In catalysis conducted by polymers (*R*)-**4** and (*R*)-**8**, the catalytically active species should be the in situ generated zinc complexes from the reaction of diethylzinc with the binaphthyl hydroxyl groups of the polymers. Therefore, the steric and electronic environments around the binaphthyl-zinc centers



R = n-C_6H_{13} (*R*)-**8**

need to be modified to adjust the catalytic properties of the polymers. A polymer (*R*)-**9** with a molecular weight of either MW = 6700 (PDI = 1.5) or MW = 24,300 (PDI = 2.5) (measured by gel permeation chromatography relative to polystyrene standards) was then prepared.[12, 13] This polymer



(*R*)-**9**

possesses two features that are different from polymers (*R*)-**4** and (*R*)-**8**: 1) The phenylene spacers in (*R*)-**9** are linked at the 3,3′-positions of the binaphthyl units rather than the 6,6′-positions. This is expected to provide better steric control at the catalytic sites. 2) The hexyloxyl groups in (*R*)-**9** not only make this polymer soluble in organic solvents, but also can act as ligands to coordinate to the metal centers introduced to the binaphthyl units. Thus, the catalytic sites in (*R*)-**9** are both sterically and electronically different from those of (*R*)-**4** and (*R*)-**8**.

When (*R*)-**9** was used to catalyze the reaction of diethylzinc with benzaldehyde, both the chemoselectivity and enantioselectivity were greatly enhanced. At 0 °C in toluene solution, (*R*)-**9** (5 mol% based on the binaphthyl unit) catalyzed the formation of (*R*)-**7** with high yield and excellent *ee* (92%). No benzyl alcohol side product was observed. This polymer was also found to catalyze the diethylzinc addition to a number of para-substituted benzaldehydes with excellent *ee*'s ($\geq$90%). For the reaction of aliphatic aldehydes, up to 83% *ee* was observed. (*R*)-**9** was easily recovered by precipitation with methanol. The recovered polymer showed the same catalytic properties as the original polymer. We have also found that the enantioselectivity of the reaction is independent of the method used to prepare the polymer, the polymer molecular weight, and the molecular weight distribution.

Polymers (*R*)-**4** and (*R*)-**8** are prepared by carrying out the polymerization at the major-groove of the binaphthyl monomers, and are designated as the major-groove polybinaphthyls. Polymer (*R*)-**9** is thus the minor-groove polybinaphthyl. The UV spectra of the polymers show that there is a blue-shift going from the major-groove polymer (*R*)-**8** to the minor-groove polymer (*R*)-**9**. This indicates a reduced conjugation in the minor-groove polymer, probably arising from the steric interaction between the alkoxyl groups on the phenylene spacer and the hydroxyl groups on the binaphthyl unit; this disrupts the planarity of the arylene repeating unit. The major-groove polymer (*R*)-**8** does not have this steric interaction, leading to a better conjugation within the repeating units. We have shown that the conjugation of the binaphthyl-based chiral conjugated polymers are identical to that of their repeating units with no extended conjugation across the 1,1′-binaphthyl bonds.[8b,c]

Although both (*R*)-**8** and (*R*)-**9** contain the same *R* binaphthyl units in the polymer chain, their positive and negative circular dichroism (CD) signals in solution are completely inverted, with the signals of (*R*)-**8** red-shifted because of better conjugation. It has been previously observed that an optically active 2,2′-substituted 1,1′-binaphthyl molecule can exist in either *cisoid* or *transoid* conformation.[17-20] As shown in Figure 1, the *cisoid* conformation has a dihedral angle of less than 90° between the two naphthyl rings and the *transoid* conformation greater than 90°. Molecules containing 2,2′-substituents that are either small or capable of intramolecular hydrogen bonding prefer the *cisoid* conformation. Whereas, increased steric interaction between the 2,2′-substituents will favor the *transoid* conformation. These two conformations gave the opposite CD signals even though the chiral configuration of the compounds are the same. Therefore, the observed opposite CD effects of the minor-groove polymer (*R*)-**9** versus the major-groove polymer (*R*)-**8** suggest that the minor-groove polymer might contain *transoid* binaphthyl units because of the large steric interaction among the alkoxyl groups on the phenylene spacer and the binaphthyl dihydroxyl groups, but the major-groove polymer might have *cisoid* binaphthyl units.

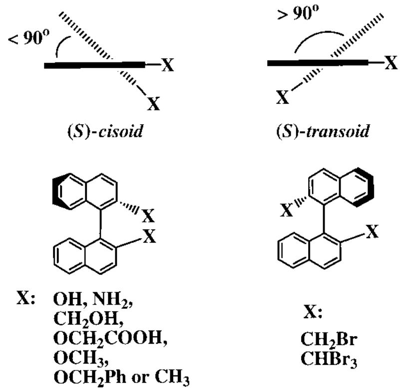
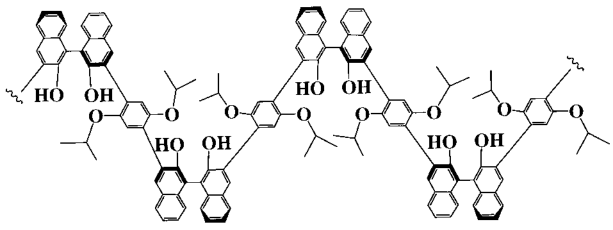


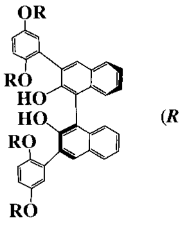
Figure 1. *Cisoid* and *transoid* conformations of 1,1′-binaphthyl molecules.

In order to study the effect of the size of the alkoxyl groups in the minor-groove polybinaphthyl (*R*)-**9** on the catalytic property, a polymer (*R*)-**10** containing isopropyloxyl groups was synthesized.[21] When this polymer was used to catalyze the reaction of benzaldehyde or cyclohexanecarboaldehyde with diethylzinc, it exhibited both slightly lower catalytic activity and enantioselectivity. This indicates that merely increasing the steric bulkiness at the catalytic sites of the polymer cannot further enhance the enantioselectivity.

We have also prepared (*R*)-**11** as the monomeric model compound of (*R*)-**9**.[14] When used in the diethylzinc addition,



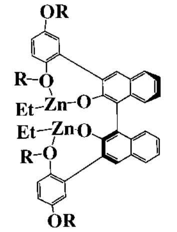
(*R*)-10



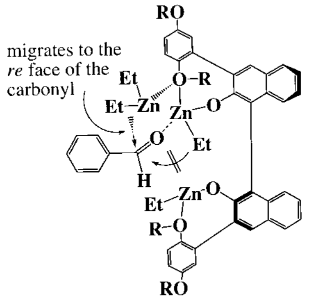
(*R*)-11

this monobinaphthyl compound shows very general enantioselectivity for the reaction of a broad range of aldehydes. Over 90% *ee*'s were observed for the reactions of many aromatic, aliphatic and α,β-unsaturated aldehydes. The enantioselectivity of (*R*)-**11** is much more general than that of polymer (*R*)-**9**.

Unlike the amino alcohol catalysts that were found to exist as dimers when treated with diethylzinc,[22] (*R*)-**11** exists as a monobinaphthyl compound in solution after treatment with two equivalents of diethylzinc as revealed by a cryoscopic experiment.[16] (*R*)-**12** is the proposed structure for the zinc complex, which can be a mixture of diastereomers because of the increased rotation barriers around the naphthyl–phenyl bonds. (*R*)-**12** cannot react with one equivalent benzaldehyde to give the alcohol product **7**. This indicates that the ethyl groups in (*R*)-**12** cannot migrate to the carbonyl group of the aldehyde substrate. When the concentration of (*R*)-**11** was reduced from 5 mol% to 0.5 mol%, although the reaction became very slow, there was no change in enantioselectivity. We have further found that there is a linear relationship between the *ee* of (*R*)-**11** and the *ee* of the product (*R*)-**7** from the reaction catalyzed by (*R*)-**11**. All these evidences support the assumption that in the reactions carried out with (*R*)-**11**, the catalytically active species should be monomeric rather than the monomer aggregate. A transition state **13** is proposed for the reaction. In **13**, the ethyl group from the coordinated diethylzinc migrates to the *re* face of the coordinated benzaldehyde to generate the corresponding (*R*)-**7**. It is not clear whether there is a cooperative effect between the two zinc centers in (*R*)-**12**.



(*R*)-12



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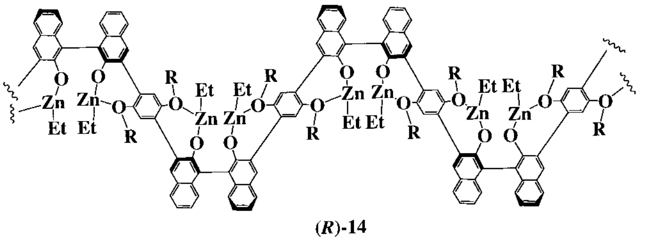
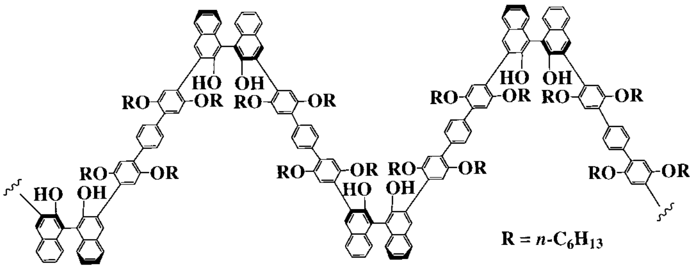
Structure (*R*)-**14** is proposed as the catalytically active species for the diethylzinc addition catalyzed by polymer (*R*)-**9**. Since both of the alkoxyl oxygens on the phenylene spacer of (*R*)-**9** can coordinate to the zinc atoms in the adjacent binaphthyl units, the resulting electronic and steric environment of the catalytic sites in (*R*)-**14** is different from that of (*R*)-**12**. This could explain the significantly different enantioselectivity between monomer (*R*)-**11** and polymer (*R*)-**9**. Monomer (*R*)-**11** is good for almost all types of aldehyde substrates, but the high enantioselectivity of (*R*)-**9** is limited to *para*-substituted benzaldehydes.



(*R*)-14
R = *n*-C_6H_{13}

In order to avoid the interference between the adjacent binaphthyl units as shown in (*R*)-**14**, we have designed and synthesized a new polymer (*R*)-**15** that contains long and rigid triphenylene linkers for the asymmetric reaction of aldehydes with organozincs.[15] The molecular weight of this polymer is MW = 25,800 (PDI = 1.8) as measured by gel permeation chromatography relative to polystyrene standards. In this polymer, both the steric and electronic environments of the monomeric catalyst (*R*)-**11** are mostly preserved. We thus expect that the catalytic properties of (*R*)-**11** should also be preserved in (*R*)-**15**.

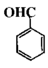
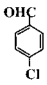
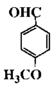
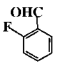
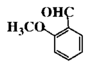
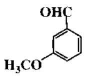
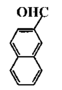
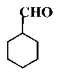
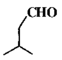
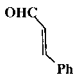
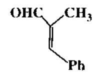


R = *n*-C_6H_{13}

(*R*)-15

Indeed, polymer (*R*)-**15** has exhibited excellent enantioselectivity for the diethylzinc addition to many types of aldehydes including *para*-, *ortho*-, or *meta*-substituted aromatic aldehydes, linear or branched aliphatic aldehydes, and α,β-unsaturated aldehydes. The catalytic properties of (*R*)-**15** are almost identical to those of the monomeric catalyst (*R*)-**11**. Table 1 shows the selected results obtained by using the chiral binaphthyl polymers (*R*)-**4**, (*R*)-**8**, (*R*)-**9**, and (*R*)-**15** in the asymmetric organozinc additions to aldehydes. As shown in the table, a systematic improvement of the enantioselectivity from the major-groove binaphthyl polymers to the minor-groove binaphthyl polymers is observed. In addition to the diethylzinc reaction, polymer (*R*)-**15** also shows high enantioselectivity for the reaction of dimethylzinc and diphenylzinc with aldehydes.[1b] (*R*)-**15** can be easily recovered by precipitation with methanol and the recycled catalyst shows the same catalytic properties as the original polymer. This polymer is the best catalyst yet reported for the reaction of

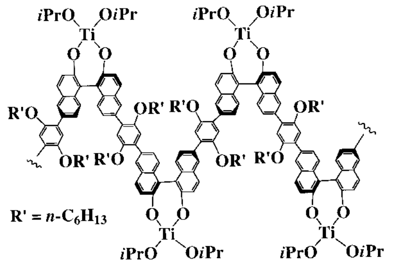
Table 1. Selected enantiomeric excess' [%] for the asymmetric reactions of aldehydes with organozinc reagents catalyzed by the chiral binaphthyl polymers.

Chiral Polymer	Zinc Reagent	Aldehyde 							R–CHO				
(*R*)-**4**	$ZnEt_2$	13											
(*R*)-**8**	$ZnEt_2$	40											
(*R*)-**9**	$ZnEt_2$	92	93	88	35	59			74[a]	83		90	
	$ZnMe_2$	79											
(*R*)-**15**	$ZnEt_2$	98	98	97	91	93	98	96	98[a]	98	98	92	97
	$ZnMe_2$	93							89[b]				
	$ZnPh_2$			92					85[c]				

[a] $R = n\text{-}C_5H_{11}$. [b] $R = n\text{-}C_7H_{11}$. [c] $R = C_2H_5$.

aldehydes with organozinc reagents to generate chiral secondary alcohols.

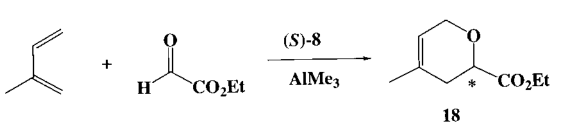
As we have discussed earlier, the major-groove polybinaphthyl (*R*)-**8** is not a good catalyst for the diethylzinc addition to benzaldehyde.[12, 13] However, with the addition of $[Ti(OiPr)_4]$, (*S*)-**8** can catalyze the reaction with both high chemoselectivity (100%) and high enantioselectivity (86% ee).[23] The catalytic properties of the polybinaphthyl-titanium complex (*S*)-**16**, generated from the reaction of (*S*)-**8** with $[Ti(OiPr)_4]$, are very similar to those of the titanium complex derived from the monomer 1,1'-bi-2-naphthol.[24] Thus, the rigid polymer structure of (*S*)-**16** has preserved the catalytic properties of the monomeric catalyst.



(*S*)-**16**

The use of the mono- and polybinaphthyl zinc complexes for the asymmetric reduction of prochiral ketones has been studied. In the presence of a zinc complex generated from the reaction of (*S*)-**9** with diethylzinc, catecholborane reduced acetophenone to 1-phenylethanol (**17**) with 67% *ee* (Scheme 4).[16] When monomer (*R*)-**11** was used, the *ee* was significantly increased to 81%. Polymer (*R*)-**15** showed almost the same enantioselectivity as (*R*)-**11** for the catalytic reduction of acetophenone (80% *ee*). This again demonstrates that the steric and electronic environment of monomer (*R*)-**11** is maintained in polymer (*R*)-**15**. This polymer also catalyzed the asymmetric reduction of other aryl methyl ketones in the presence of diethylzinc with 70–80% *ee*.

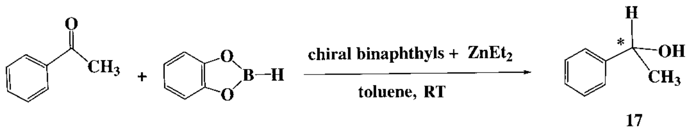
Through collaboration with Jørgensen and co-workers, it was found that an aluminum complex of the major-groove binaphthyl polymer (*S*)-**8** prepared by treatment with trimethyl aluminum catalyzed the hetero-Diels–Alder reaction of ethyl glyoxylate with 2-methyl-1,3-butadiene to give **18** with up to 95% *ee* (Scheme 5).[25] The enantioselectivity of this polymer catalyst is much higher than that prepared from the insoluble polymer (*R*)-**4**. The catalytic properties of (*S*)-**8** are very similar to those of the monomeric 1,1'-bi-2-naphthol-aluminum complex.[26]



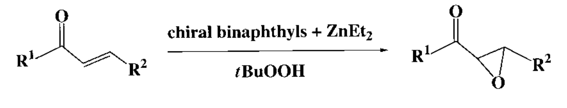
Scheme 5. An asymmetric hetero-Diels–Alder reaction catalyzed by the polybinaphthyl aluminum complex.

The zinc complex of polybinaphthyl (*R*)-**9** can also catalyze the asymmetric epoxidation of *α*,*β*-unsaturated ketones in the presence of *t*BuOOH with up to 81% ee as well as complete diastereoselectivity (Scheme 6).[27] In this case, the enantioselectivity of both the long linker polymer (*R*)-**15** and monomer (*R*)-**11** is much lower than that of (*R*)-**9**, indicating a positive cooperative effect between the adjacent binaphthyl units in (*R*)-**9**.

Collaboration with Jørgensen and co-worker led to the discovery that polymer (*R*)-**9** in combination with $AlMe_3$ had excellent regio-, diastereo- and enantioselectivity for the 1,3-dipolar cycloaddition of nitrones **19** with alkenes **20** (Scheme 7).[28] Table 2 summarizes the results for the use of (*R*)-**9** + $AlMe_3$ in the 1,3-dipolar cycloaddition. The reaction was carried out at room temperature in methylene chloride in the presence of 20 mol% of (*R*)-**9** + $AlMe_3$ unless indicated otherwise. After precipitation and centrifugation to remove the polymer catalyst at the completion of the reaction, the isoxazolidine products **21** were essentially both chemically and enantiomerically pure. This demonstrates that using the polymeric catalyst not only makes it easy to recover the chiral catalyst, but also greatly simplifies the purification of the product. The catalytic properties of (*R*)-**9** are almost identical to those of monomer (*R*)-**11**. This indicates that the catalytic

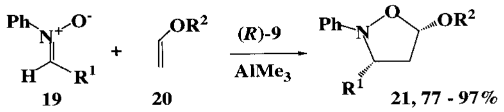


Scheme 4. An asymmetric reduction of acetophenone catalyzed by the polybinaphthyl zinc complexes.



R^1 and R^2 = alkyl or aryl

Scheme 6. An asymmetric epoxidation of *α*,*β*-unsaturated ketones catalyzed by the polybinaphthyl zinc complexes.



Schema 7. An asymmetric 1,3-dipolar cycloaddition catalyzed by the polybinaphthyl aluminum complex.

Table 2. The reaction of **19** with **20** catalyzed by (*R*)-**9** + $AlMe_3$ (20 mol %).

	R^1	R^2	Isolated Yield [%]	*exo*:*endo*[a]	*ee* (*exo*)[b] [%]
1	Ph	Et	97	> 98:2	99
2[c]	Ph	Et	80	> 98:2	94
3	Ph	*t*Bu	86	> 98:2	95
4	*p*-tolyl	*t*Bu	77	> 98:2	94
5	Ph	Bn	72	> 98:2	93

[a] Determined by ^1H NMR. [b] Determined by HPLC using Chiralcel OD column. [c] 10 mol % of (*R*)-**9** + $AlMe_3$ was used.

environment of the polymeric aluminum complex is the same as that of the monomer and the interference between the adjacent binaphthyl units shown in the zinc complex (*R*)-**14** does not exist in the aluminum complex.

In summary, using optically active 1,1′-binaphthyl structures, we have developed novel rigid and sterically regular polymeric catalysts for asymmetric catalysis. Good to excellent enantioselectivties have been achieved for reactions including the organozinc addition to aldehydes, the reduction of ketones with catecholborane, the hetero-Diels–Alder reaction of ethyl glyoxylate with a conjugated diene, the epoxidation of α,β-unsaturated ketones, and the 1,3-dipolar cycloaddition of nitrones with alkenes. Our studies on the use of polymers (*R*)-**4**, (*R*)-**8**, (*R*)-**9**, and (*R*)-**15** and monomer (*R*)-**11** in asymmetric catalysis have introduced two new concepts for the development of enantioselective polymer catalysts: 1) The microenvironment of the catalytic sites in rigid and sterically regular polymers can be systematically modified to produce highly enantioselective polymeric catalysts. 2) The enantioselectivity of a monomeric catalyst can be maintained in a polymer catalyst by using a rigid and sterically regular polymer backbone. Compared with the traditional polymer-supported catalysts where flexible and sterically irregular polymers are used, this new approach can better preserve the catalytic environment of the monomeric catalysts in the polymer as long as the catalytically active species are not aggregates of the monomers. These strategies not only make it possible to obtain easily reusable and highly enantioselective polymeric catalysts for many asymmetric reactions, but also can be further extended to construct polymeric chiral catalysts that are capable of multiple asymmetric catalytic reactions by incorporating different catalytic species in a polymer chain.

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