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Asymmetric Epoxidation of α,*β*-Unsaturated Ketones Catalyzed by Chiral Polybinaphthyl Zinc Complexes: Greatly Enhanced Enantioselectivity by a Cooperation of the Catalytic Sites in a Polymer Chain

Hong-Bin Yu, Xiao-Fan Zheng, Zhi-Ming Lin, Qiao-Sheng Hu, Wei-Sheng Huang, and Lin Pu*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

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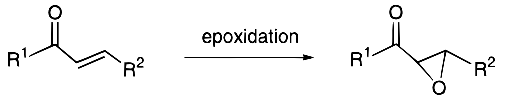
Polybinaphthyl zinc *catalysts* have been developed for the asymmetric epoxidation of α,*β*-unsaturated ketones in the presence of *tert*-butyl hydroperoxide. Up to 81% ee has been achieved for the epoxidation of α,*β*-unsaturated ketones containing *β*-aliphatic substituents by using a binaphthyl polymer combined with diethylzinc. A very interesting positive cooperative effect of the catalytic sites in the polymer chain is observed which leads to greatly increased enantioselectivity over the corresponding monomer ligands.

Introduction

The asymmetric epoxidation of α,*β*-unsaturated ketones (**1**) is a very important organic transformation since the resulting chiral α,*β*-epoxy ketones (**2**) are versatile precursors to many natural products and drug molecules (Scheme 1).[1−6] In 1980, Julia et al. discovered that the use of an excess amount of polypeptides and hydrogen peroxide could promote the asymmetric epoxidation of chalcone and its derivatives with both good enantioselectivity and diastereoselectivity.[1a] However, this epoxidation process is found to be mostly limited for the reaction of aryl-substituted α,*β*-unsaturated ketones.[1,2] The polypeptide reagents cannot carry out the epoxidation of α,*β*-unsaturated ketones with *β*-alkyl groups other than *tert*-butyl or cyclopropyl. Recently, important progress has been made by Lygo,[3a] Taylor,[3b] and Arai[3c,d] on using chiral phase transfer catalysts for the asymmetric epoxidation of both alkyl- and aryl-substituted α,*β*-unsaturated ketones.

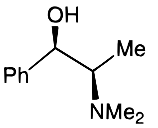
In 1996, Enders et al. reported an epoxidation of α,*β*-unsaturated ketones under oxygen for substrates containing alkyl substituents with good enantioselectivity.[4] The reaction was conducted in the presence of a stoichiometric amount of a zinc complex generated from the reaction of a chiral amino-alcohol **3** with diethylzinc. When substrates contained only aromatic substituents, this process showed only modest enantioselectivity. Later, Jackson and co-workers found that when (+)-diethyl tartrate (**4**) was treated with dibutylmagnesium, it catalyzed the epoxidation of aryl-substituted α,*β*-unsaturated ketones with high enantioselectivity in the presence of *t*-BuOOH.[5] Recently, Shibasaki and co-workers reported a catalytic asymmetric epoxidation of α,*β*-unsaturated ketones by using hydroperoxides and catalysts made from the reaction of the chiral binaphthyl ligands **5** with La(O-i-Pr)$_3$ and Yb(O-i-Pr)$_3$.[6] These lanthanoid catalysts showed very good enantioselectivity for substrates containing either alkyl or aryl substituents.

Scheme 1. The Epoxidation of α,*β*-Unsaturated Ketones



1 **2**

1a: $R^1 = R^2 = Ph$. **1b**: $R^1 = Ph$, $R^2 = i\text{-Pr}$.
1c: $R^1 = Ph$, $R^2 = n\text{-Pr}$. **1d**: $R^1 = Ph$, $R^2 = p\text{-MePh}$
1e: $R^1 = Ph$, $R^2 = p\text{-ClPh}$. **1f**: $R^1 = Ph$, R^2 = 2-naphthyl
1g: $R^1 = Ph$, $R^2 = t\text{-Bu}$. **1h**: R^1 = 2-naphthyl, $R^2 = Ph$



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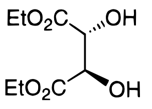

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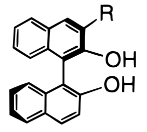

5, R = H or CH$_2$OH

In our laboratory, we are interested in studying asymmetric reactions catalyzed by chiral polymers. We have used binaphthyl structures to construct a class of chiral rigid polymers[7−9] and have applied these materials to a number of catalytic asymmetric reactions.[9−11] Catalysts based on these polymers have exhibited very high enantioselectivity for the organozinc addition to aldehydes,[10] the hetero Diels−Alder reaction of ethyl glyoxylate with

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(2) For reviews on the polypeptide-mediated epoxidation of α,*β*-unsaturated ketones, see: (a) Pu, L. *Tetrahedron: Asymmetry* **1998**, *9*, 1457. (b) Ebrahim, S.; Wills, M. *Tetrahedron: Asymmetry* **1997**, *8*, 3163.

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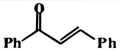
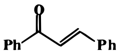
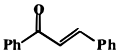
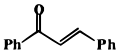
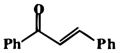
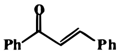
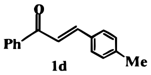
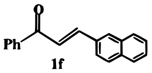
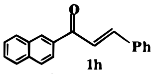
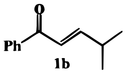
(7) Pu, L. *Chem. Rev.* **1998**, *98*, 2405.

10.1021/jo990749w CCC: $18.00

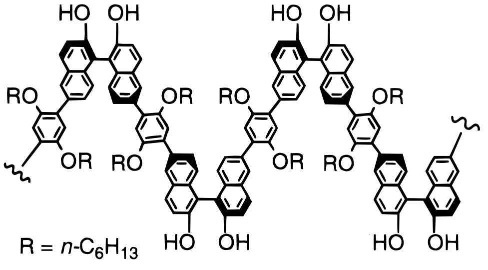
Table 1. Epoxidation of α,*β*-Unsaturated Ketones in the Presence of the Polybinaphthyl (*R*)-6, Diethylzinc, and Oxygen

Entry	Ketone	Yield [%]	*ee* [%]	Solvent	Temperature (^oC)	Mole Ratio [(*R*)-**6**/Et_2Zn/ketone]
1	 **1a**	41	71	CH_2Cl_2	0	1:0.95:0.90
2	 **1a**	99	50	CH_2Cl_2	0	1:1.9:0.90
3	 **1a**	64	49	CH_2Cl_2	-30	1:1.9:0.90
4	 **1a**	11	58	CH_2Cl_2	r.t.	1:1.9:0.90
5	 **1a**	34	37	Toluene	0	1:0.95:0.90
6	 **1a**	0	0	THF	0	1:1.9:0.90
7	 **1d**	34	54	CH_2Cl_2	-15	1:1.9:0.90
8	 **1f**	75	54	CH_2Cl_2	0	1:1.9:0.90
9	 **1h**	91	47	CH_2Cl_2	0	1:1.9:0.90
10	 **1b**	18	25	Toluene	0	1:0.95:0.90

2-methyl-1,3-butadiene,[11a] and the 1,3-dipolar cycloaddition of nitrones with vinyl ethers.[11b] Herein, we report our discovery that the polybinaphthyls can also catalyze the asymmetric epoxidation of α,*β*-unsaturated ketones. An interesting cooperative effect of the catalytic sites in a binaphthyl polymer chain is found to greatly enhance the enantioselectivity over the corresponding monomer ligands.

Results and Discussion

1. The Asymmetric Epoxidation of α,*β*-Unsaturated Ketones in the Presence of Diethylzinc, Oxygen, and a Stoichiometric Amount of a Chiral Binaphthyl Polymer. Previously, we have prepared a polybinaphthyl (*R*)-**6** from the Suzuki coupling of an optically pure binaphthyl monomer with a phenylene linker.[10b] Analogous to Enders's study of **3**,[4] we have used polymer (*R*)-**6** combined with diethylzinc and oxygen to carry out the asymmetric epoxidation of α,*β*-unsaturated ketones. Table 1 summarizes the use of (*R*)-**6** for the epoxidation of various substrates[12] under various conditions. As shown in entry 1, 1 equiv (based on the binaphthyl unit) of the polymer after treated with 0.95 equiv of diethylzinc was used to oxidize chalcone (**1a**) in methylene chloride under oxygen. After 18 h at 0 °C, the epoxy product **2a** was obtained in 41% yield. Its ee was determined to be 71% by HPLC−Chiracel OD column. The absolute configuration of the product was 2*S* and 3*R* by comparing its optical rotation with the literature data.[4] When increasing the amount of diethylzinc, although the yield became much higher, the ee was significantly reduced (entry 2). No epoxidation was observed when the reaction was conducted in THF (entry 6), probably because THF reduced the reactivity of the polybinaphthyl zinc complex, formed from the reaction of the polymer with diethylzinc, through coordination to the zinc center. Both the ee and yield were very low for



(*R*)-**6**

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(8) (a) Hu, Q.-S.; Vitharana, D.; Liu, G.; Jain, V.; Wagaman, M. W.; Zhang, L.; Lee, T. R.; Pu, L. *Macromolecules* **1996**, *29*, 1082. (b) Ma, L.; Hu, Q.-S.; Vitharana, D.; Wu, C.; Kwan, C. M. S.; Pu, L. *Macromolecules* **1997**, *30*, 204. (c) Hu, Q.-S.; Vitharana, D.; Liu, G.; Jain, V.; Pu, L. *Macromolecules* **1996**, *29*, 5075. (d) Ma, L.; Hu, Q.-S.; Musick, K.; Vitharana, D.; Wu, C.; Kwan, C. M. S.; Pu, L. *Macromolecules* **1996**, *29*, 5083. (e) Musick, K. Y.; Hu, Q.-S.; Pu, L. *Macromolecules* **1998**, *31*, 2933.

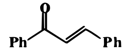
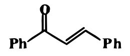
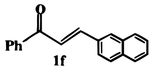
(9) (a) Hu, Q.-S.; Zheng, X.-F.; Pu, L. *J. Org. Chem.* **1996**, *61*, 5200. (b) Hu, Q.-S.; Vitharana, D.; Zheng, X.-F.; Wu, C.; Kwan, C. M. S.; Pu, L. *J. Org. Chem.* **1996**, *61*, 8370.

(10) (a) Huang, W.-S.; Hu, Q.-S.; Zheng, X.-F.; Anderson, J.; Pu, L. *J. Am. Chem. Soc.* **1997**, *119*, 4313. (b) Hu, Q.-S.; Huang, W.-S.; Vitharana, D.; Zheng, X.-F.; Pu, L. *J. Am. Chem. Soc.* **1997**, *119*, 12454. (c) Huang, W.-S.; Hu, Q.-S.; Pu, L. *J. Org. Chem.* **1998**, *63*, 1364. (d) Hu, Q.-S.; Huang, W.-S.; Pu, L. *J. Org. Chem.* **1998**, *63*, 2798. (e) Huang, W.-S.; Pu, L. *J. Org. Chem.*. **1999**, *64*, 4222. (f) Huang, W.-S.; Hu, Q.-S.; Pu, L. *J. Org. Chem.* **1999**, *64*, 7940−7956.

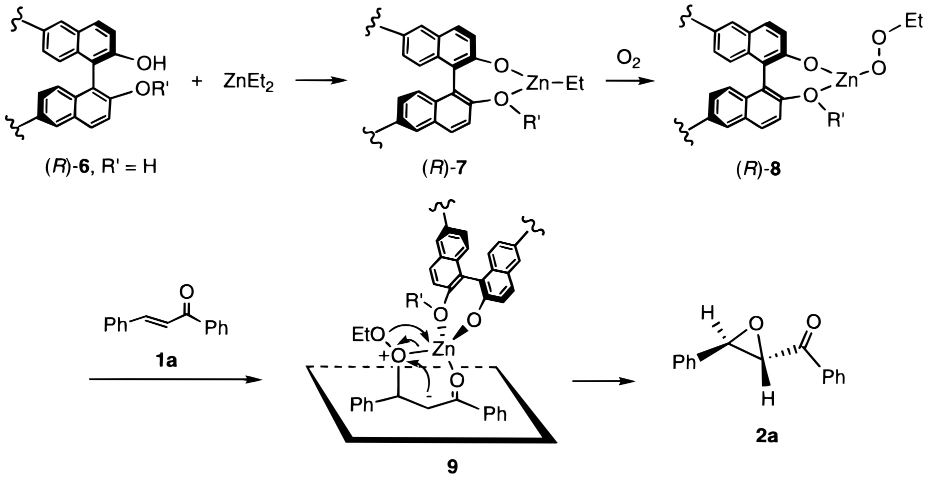
(11) (a) Johannsen, M.; Jørgensen, K. A.; Zheng, X.-F.; Hu, Q.-S.; Pu, L. *J. Org. Chem.* **1999**, *64*, 299. (b) Simonsen, K. B.; Jorgensen, K. A.; Hu, Q.-S.; Pu, L. *J. Chem. Soc., Chem. Commun.* **1999**, 811.

(12) References about the α,*β*-unsaturated ketones: (a) See ref 4b for **1b** and **1c**. (b) For **1d** and **1e**: Krauss, S. R.; Smith, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 141. (c) For **1f**: Ross, D. R.; Waight, E. S. *J. Chem. Soc.* **1965**, 6710. (c) For **1g**: Bowers, K. W.; Giese, R. W.; Grimshaw, J.; House, H. O.; Kolodny, N. H.; Kronberger, K.; Roe, D. K. *J. Am. Chem. Soc.* **1970**, *92*, 2783. (c) For **1h**: Shotter, R. G. *Tetrahedron* **1973**, *29*, 2163.

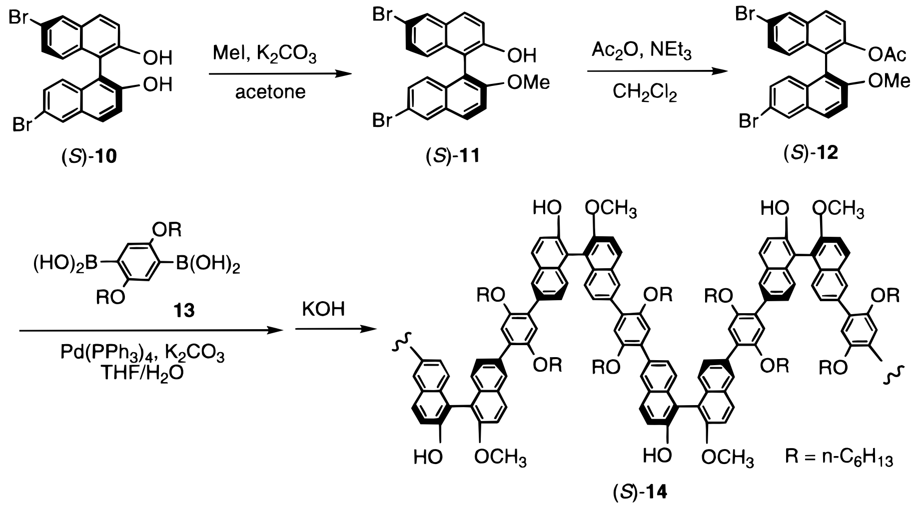
Table 2. Asymmetric Epoxidation of α,*β*-Unsaturated Ketones in the Presence of the Polymer (*S*)-14, Diethylzinc, and Oxygen

Entry	Ketone	Yield (%)	*ee* (%)	Solvent	Temperature (°C)	Mole Ratio [(*S*)-**14**/Et_2Zn/ketone]
1	 **1a**	>90	35	CH_2Cl_2	0	1:0.95:0.9
2	 **1a**	>90	38	CH_2Cl_2	0	1:0.95:0.9
3	 **1f**	95	33	CH_2Cl_2	0	1:0.95:0.9

Scheme 2. A Proposed Mechanism for the Polybinaphthyl-Mediated Epoxidation of Chalcone



Scheme 3. Synthesis of a Monomethylated Chiral Binaphthol Polymer (*S*)-14

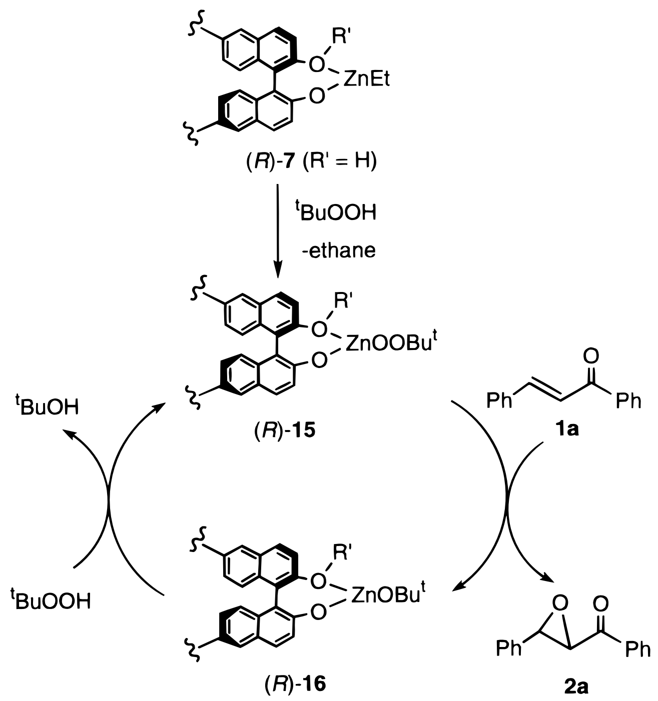


the substrate containing a *β*-aliphatic substituent (**1b**) (entry 10). In all the reactions, only one diastereomer was formed from each enone.

On the basis of Enders's study on the amino alcohol–diethylzinc-mediated epoxidation,[4] a mechanism for the asymmetric epoxidation promoted by polymer (*R*)-**6** is proposed (Scheme 2). The reaction of (*R*)-**6** with diethylzinc can lead to (*R*)-**7** which can be oxidized by oxygen to give the zinc peroxy complex (*R*)-**8**. Enders's work indicates that the rate-limiting step is probably the conversion from such a zinc peroxy complex to a Michael addition type intermediate like **9**. Formation of intermediate **9** explains the exclusive production of the *trans*-epoxide from the (*E*)-α,*β*-unsaturated ketone. This intermediate generates (2*S*,3*R*)-**2a** as the major enantiomer.

We have modified the polymer by introducing a methyl group (R′ = Me) into the binaphthyl unit of (*R*)-**6**–(*R*)-**8**. As shown in Scheme 3, monomethylation of 6,6′-dibromo-1,1′-bi-2-naphthol [(*S*)-**10**][9] gave (*S*)-**11** which was then converted to a binaphthyl acetate monomer (*S*)-**12**. The Suzuki coupling of (*S*)-**12** with a diboronic acid **13** followed by hydrolysis led to the formation of polymer (*S*)-**14** with monomethylated binaphthol units. The molecular weight of this polymer was $M_w = 36\,000$ and $M_n = 12\,800$ (PDI = 2.8) as measured by gel permeation chromatography (GPC) relative to polystyrene standards.

Scheme 4. A Proposed Mechanism for the Polybinaphthyl-*Catalyzed* Asymmetric Epoxidation of Chalcone



Its specific optical rotation was $[\alpha]_D = -301.1$ ($c = 0.5$, CH_2Cl_2). This polymer had better solubility than (*R*)-**6** in organic solvents.

Polymer (*S*)-**14** was used for the asymmetric epoxidation of α,*β*-unsaturated ketones in the presence of diethylzinc and oxygen (Table 2). This polymer showed largely improved yield for the epoxidation without using excess diethylzinc. The diastereoselectivity also remained very high (>99% de). However, introduction of the methyl group to the binaphthyl unit of the polymer did not improve the enantioselectivity.

2. Development of a *Catalytic* Asymmetric Epoxidation of α,*β*-Unsaturated Ketones Using Polybinaphthyls, Diethylzinc, and *tert*-Butyl Hydroperoxide. As shown above, when the epoxidation of α,*β*-unsaturated ketones was carried out by using the binaphthyl polymeric zinc complexes and oxygen, the results were not satisfactory. Although up to 71% ee was obtained, the conversion was low (Table 1, entry 1). On the other hand, when high conversions were achieved, the ee's became small (Table 2). In all cases, the use of a stoichiometric amount of the chiral binaphthyl polymers was necessary.

To improve the polybinaphthyl-mediated epoxidation, we decided to use *t*-BuOOH in place of oxygen as the oxidants. This led to our discovery of a *catalytic* asymmetric epoxidation of α,*β*-unsaturated ketones by using the polybinaphthyl zinc complexes. In the presence of 5 mol % of polymer (*R*)-**6** and 10 mol % of diethylzinc in methylene chloride at 0 °C, chalcone (**1a**) was oxidized by *t*-BuOOH[13] to the corresponding epoxide **2a** in 95% isolated yield and with >99% de and 28% ee. Scheme 4 shows a possible mechanism for this catalytic process. The key step that enables this zinc-mediated epoxidation to be catalytic may be the equilibrium between zinc peroxide (*R*)-**15** and zinc *tert*-butoxide (*R*)-**16** in the presence of *t*-BuOOH. In this step, (*R*)-**16** reacts with *t*-BuOOH to regenerate chiral zinc peroxide (*R*)-**15** which oxidizes **1a** to **2a**.

We have tested the use of two monomer ligands (*R*)-**17**[10c] and (*R*)-**18**[10f] for the epoxidation of a *β*-propyl-substituted enone **1c**. Both (*R*)-**17** and (*R*)-**18** contain 3,3′-aryl substituents on the binaphthyl units which was expected to provide increased chiral barrier and better steric control. However, when the epoxidation of **1c** was conducted in the presence of *t*-BuOOH and diethylzinc, neither of the monomer ligands showed improvement on the enantioselectivity. At room temperature, (*R*)-**17** converted **1c** to **2c** in 75% yield and 30% ee, and (*R*)-**18** did in 83% yield and 21% ee.

Although these monomer ligands gave very low enantioselectivity, when (*R*)-**19**, a polymer containing monomer ligand (*R*)-**17** as its structural unit was used to catalyze the epoxidation of **1c**, the corresponding epoxy product **2c** was obtained in 91% yield and 76% ee (Table 3, entry 1). Thus, from the monomer to the polymer, there is a dramatic enhancement in enantioselectivity. Table 3 summarizes the use of polymer (*R*)-**19** for the asymmetric epoxidation of various α,*β*-unsaturated ketones.[12] As shown in Table 3, up to 81% ee (entry 8) was observed for the asymmetric epoxidation of the α,*β*-unsaturated ketones containing aliphatic substituents, and over 70% ee was observed in general for the epoxidation of the α,*β*-unsaturated ketones containing only aromatic substituents. In most of the reactions, 20 mol % of the polymer (based on the binaphthyl unit) was used. When a stoichiometric amount of (*R*)-**19** was used, no improvement on the enantioselectivity was observed (entry 6). The configuration of the major enantiomers of the epoxy products is 2*R* and 3*S* as determined by comparing their optical rotations with the literature data. This is opposite to that of the products generated in the presence of polymer (*R*)-**6**, even though both of the polymers contain *R* binaphthyl units. Factors causing this difference remain to be investigated.

To understand the origin of the greatly enhanced enantioselectivity of polymer (*R*)-**19** versus monomer (*R*)-**17**, we have studied the use of another polymer (*R*)-**20**[10d] for the asymmetric epoxidation. Under the conditions of entry 1 in Table 3, (*R*)-**20** converted **1c** to **2c** with 37% ee and 99% yield, and **1b** to **2b** with 55% ee and 88% yield. Thus, the enantioselectivity of (*R*)-**20** is very similar to that of monomer (*R*)-**17** and much lower than that of polymer (*R*)-**19**. This indicates that the steric and electronic environments of the monomer catalyst are mostly preserved in polymer (*R*)-**20** and are quite different from those of polymer (*R*)-**19**. The high enantioselectivity of polymer (*R*)-**19** over monomer (*R*)-**17** is not merely due to the increased size of the macromolecules.

We propose that the much better enantioselectivity of polymer (*R*)-**19** over monomer (*R*)-**17** and polymer (*R*)-**20** might arise from the structure of the polymeric zinc complex (*R*)-**21** probably formed when (*R*)-**19** is treated with diethylzinc. In (*R*)-**21**, the *p*-dialkoxylphenylene linker acts as a dual ligand to coordinate to the zinc centers on the two adjacent binaphthyl units. Thus, there is a cooperative effect between the neighboring catalytic sites in the polymer chain which has greatly increased the enantioselectivity of the catalyst. However, neither monomer (*R*)-**17** nor polymer (*R*)-**20** could achieve such

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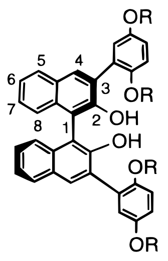
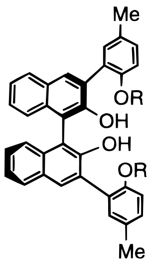
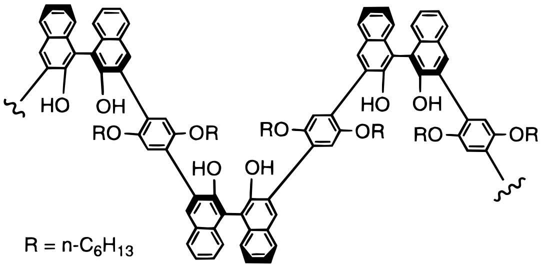
[13] The commercially obtained *t*-BuOOH was treated before use: Hill, J. G.; Rossiter, B. E.; Sharpless, K. B. *J. Org. Chem.* **1983**, *48*, 3607.



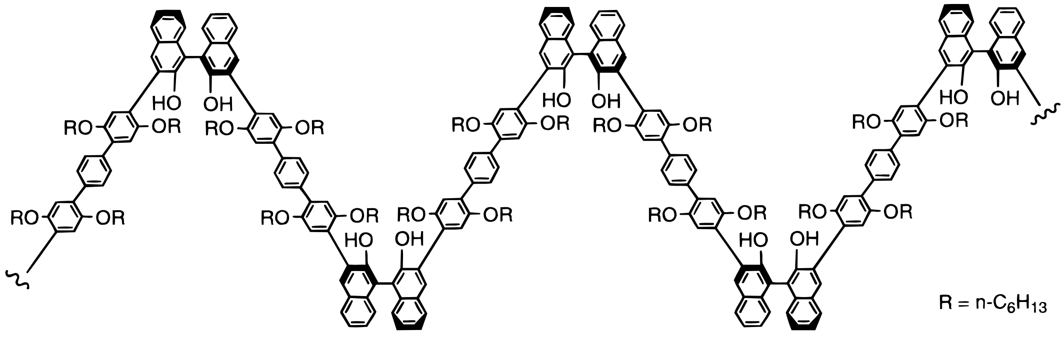
(*R*)-**17**



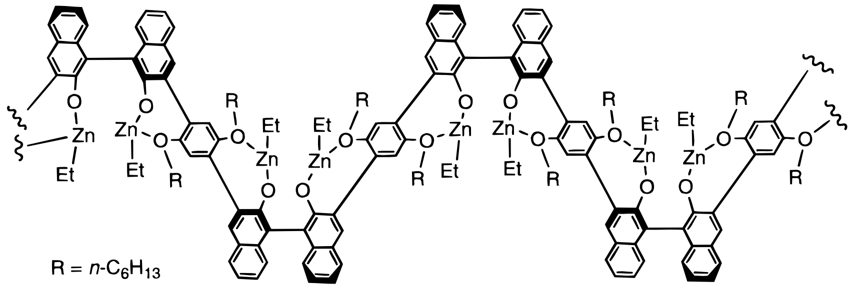
(*R*)-**18**



(*R*)-**19**



(*R*)-**20**



(*R*)-**21**

a site cooperation and each of their binaphthyl units should function independently. The cooperative effect as shown in (*R*)-**21** might have changed the electronics as well as the steric conformation of both the catalytic sites and the polymer chain. Earlier, we had observed that this cooperation of the catalytic sites led to negative effects on the asymmetric reaction of diethylzinc with aldehydes, i.e., both monomer (*R*)-**17** and polymer (*R*)-**20** had much better enantioselectivity than (*R*)-**19**.[10a−d] Thus, interaction of the neighboring catalytic sites in the polymer chain of (*R*)-**21** has imposed very different effects on different reactions.

3. Summary

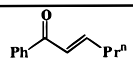
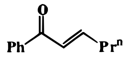
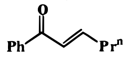
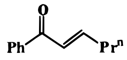
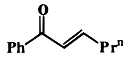
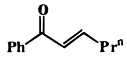
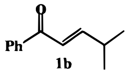
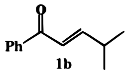
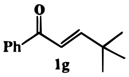
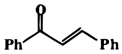
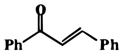
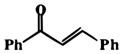
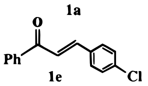
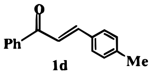
In summary, polybinaphthyl zinc *catalysts* have been developed for the asymmetric epoxidation of α,β-unsaturated ketones. A binaphthyl polymer has shown up to 81% ee for the epoxidation of α,β-unsaturated ketones containing β-aliphatic substituents. These substrates failed to undergo epoxidation when using the previously reported polypeptide reagents. In addition, only a catalytic amount of the binaphthyl polymer is used in our new epoxidation process but excess polypeptides (based on the monomer units) were required previously. A very interesting positive cooperative effect of the catalytic sites in the polybinaphthyl chain is observed, which leads to greatly increased enantioselectivity over the corresponding monomer ligands. Understanding of this cooperative effect in the binaphthyl polymer could allow the design of new and highly enantioselective polymeric catalysts for asymmetric synthesis.

Experimental Section

General Data. All the solvents were dried according to the standard methods prior to use. Chalcone was purchased from Aldrich and dried under vacuum for 10 h. *t*-BuOOH was purchased from Aldrich and was treated according to literature[13] before use. Diethylzinc and palladium tetrakis(triphenylphosphine) were purchased from Strem. Molecular weights of the polymers were measured with gel permeation chromatography by using THF eluent and polystyrene standards.

Preparation and Characterization of (*S*)-11. To a suspension of (*S*)-**10** (7.75 g, 17.5 mmol) and K_2CO_3 (3.6 g, 26.3 mmol) in acetone was added CH_3I (1.2 mL, 24.2 mmol) at room temperature. The mixture was stirred at room temperature for 32 h and monitored by ^1H NMR spectroscopy. When the dimethylated side product started to form, the reaction was stopped by pouring the mixture into H_2O. After extraction with ethyl acetate (3 × 100 mL), the combined organic layer was washed with brine (3 × 20 mL) and dried over Na_2SO_4. The solvent was then removed in a vacuum, and the crude product was purified by flash chromatography on silica gel (EtOAc/hexane: 20:1) to give (*S*)-**11** as a white crystalline solid in 40% yield (3.1 g). mp 92−94 °C. $[\alpha]_D = 113.3$ ($c = 0.5$, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz) δ 3.80 (s, 3H, CH_3), 4.90 (s, 1H, OH), 6.86 (d, $J = 8.9$ Hz, 1H), 6.99 (d, $J = 8.8$ Hz, 1H), 7.28 (dd, $J = 1.9$, 8.9 Hz, 1H), 7.34 (m, 2H), 7.48 (d, $J = 9.1$ Hz, 1H), 7.81 (d, $J = 8.9$ Hz, 1H), 7.95 (d, $J = 9.2$ Hz, 1H), 8.01 (d, $J = 1.9$ Hz, 1H), 8.05 (d, $J = 1.9$ Hz, 1H). Anal. Calcd for $C_{21}H_{14}O_2Br_2$: C, 55.02; H, 3.06. Found: C, 55.93; H, 3.33.

Table 3. Asymmetric Epoxidation of α,β-Unsaturated Ketones Catalyzed by Polymer (*R*)-19[a]

Entry	Ketone	Solvent	Temperature	Time (h)	Isolated Yield (%)	ee[b] (%)	[α]D (c, CH_2Cl_2)
1	 1c	Et_2O	r.t.	5	92	76	1.7 (1.0)
2	 1c	${}^tBuOMe$	r.t.	4.5	89	71	
3	 1c	${}^nBuOMe$	r.t.	3.5	87	62	
4	 1c	Anisole	r.t.	6	98	48	
5	 1c	THF	r.t.	6	97	0	
6[c]	 1c	Et_2O	r.t.	4.5	81	73	
7	 1b	Et_2O	r.t.	3.5	93	78	26.6 (0.9)
8[d]	 1b	Et_2O	r.t.	3.5	94	81	27.1 (0.9)
9	 1g	Et_2O	r.t.	8	67	64	14.0 (0.36)[e]
10	 1a	Toluene	0 °C	3	89	39	
11	 1a	Et_2O	0 °C	5	95	74	
12	 1a	Et_2O	r.t.	3	92	73	-151.1 (1.0)
13	 1e	Et_2O	r.t.	5.5	81	79	-176.8 (0.7)
14	 1d	Et_2O	r.t.	8	93	70	-171.0 (1.1)

a. All reactions used 20 mol% of (*R*)-**19** (based on the repeating unit), 36 mol% of Et_2Zn, 1.2 equiv of *t*-BuOOH unless indicated otherwise. b. Determined by HPLC with a Chiracel-OD column. c. 1.0 equiv of (*R*)-**19**, 1.8 equiv of Et_2Zn and 1.0 equiv of *t*-BuOOH were used. d. 40 mol% of the polymer and 72 mol% of Et_2Zn were used. e. Measured in $CHCl_3$.

Preparation and Characterization of (*S*)-12. To a solution of (*S*)-**11** (0.54 g, 1.2 mmol) and Et_3N (1 mL) in CH_2Cl_2 was added Ac_2O (0.5 mL) at 0 °C. The mixture was stirred at room temperature for 4 h, and the reaction was monitored by ^1H NMR spectroscopy. After the reaction was complete, the mixture was poured into H_2O and extracted with EtOAc. The combined organic layer was washed with brine (5 mL), 1 N HCl (2 × 10 mL), brine (5 mL), saturated sodium bicarbonate solution (10 mL), and brine (5 mL) and dried over Na_2SO_4. After evaporation of the solvent, the residue was recrystallized from EtOAc/hexanes (1:3) to give (*S*)-**12** as a white crystalline solid in 87% yield (0.51 g). mp 164−165 °C. $[\alpha]_D = +85.9$ ($c = 0.5$, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz) δ 1.79 (s, 3H), 3.76 (s, 3H), 6.95 (d, $J = 8.9$ Hz, 1H), 7.05 (d, $J = 9.1$ Hz, 1H), 7.29 (dd, $J = 1.9, 9.2$ Hz, 1H), 7.34 (dd, $J = 1.7, 8.9$ Hz, 1H), 7.43 (s, 1H), 7.45 (s, 1H), 7.88 (d, $J = 3.0$ Hz, 1H), 7.90 (d, $J = 3.5$ Hz, 1H), 8.01 (d, $J = 1.6$ Hz, 1H), 8.10 (d, $J = 1.6$ Hz, 1H). Anal. Calcd for $C_{23}H_{16}O_3Br_2$: C, 55.20; H, 3.20. Found: C, 55.40; H, 3.12.

Preparation and Characterization of Chiral Polybinaphthyl (*S*)-14. Under nitrogen, a mixture of (*S*)-**12** (0.50 g, 1.0 mmol), diboronic acid **13** (1.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) in THF (5 mL)/1 N K_2CO_3 (5 mL) was heated at reflux. After 48 h, KOH (0.56 g) was added, and the mixture was heated at reflux for another 12 h under nitrogen. The organic layer was then separated and combined with CH_2Cl_2 (500 mL). After washed with brine and dried over Na_2SO_4, the solvent was removed, and the residue was redissolved in a minimum amount of CH_2Cl_2. Methanol was then added to precipitate out the polymer. This process was repeated three times to give (*S*)-**14** as a yellow solid in 75% yield. GPC: $M_w = 36\,000$ and $M_n = 12\,800$ (PDI = 2.8). $[\alpha]_D = 301.1$ ($c = 0.5$, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz) δ 0.80 (s, 6H with a shoulder at 0.92), 1.24 (m, 10H), 1.38 (m, 4H), 1.70 (m, 4H), 3.92 (m, 7H), 5.02 (br, 1H), 7.13 (s, 2H, small peaks at 6.93, 7.04), 7.19 (m, 1H), 7.32 (m, 1H), 7.40 (m, 1H), 7.58 (m, 3H), 7.98 (m, 1H), 8.15 (m, 3H). Anal. Calcd for $(C_{39}H_{42}O_4)_n$: C, 81.53; H, 7.32. Found: C, 81.47; H, 7.50.

A Typical Procedure for the Asymmetric Epoxidation in the Presence of Polymer (*R*)-6, Diethylzinc, and Oxygen. Epoxidation of *trans*-Chalcone (1a). In a drybox, diethylzinc (38 μL, 0.38 mmol, 0.95 equiv) was added to a solution of (*R*)-**6** (224 mg, 0.40 mmol, 1.0 equiv) in dry CH_2Cl_2 (15 mL) in a 50 mL Schlenk flask at room temperature while stirring. After 90 min, the reaction mixture was cooled to 0 °C and was placed under a balloon filled with O_2. The nitrogen inside the flask should not be displaced. After stirred for 2 h, the reaction mixture was cooled to −78 °C, and *trans*-chalcone (80 mg, 0.38 mmol, 0.95 equiv) was added. The reaction mixture was stirred for 30 min at this temperature and then rapidly warmed to 0 °C while stirring. The reaction progress was followed by thin-layer chromatography. After 18 h, saturated aqueous NH_4Cl (5 mL), 10% aqueous Na_2SO_3 (5 mL), and Et_2O (50 mL) were sequentially added to the reaction mixture, and the organic phase was separated. The polymer was precipitated out of the diethyl ether solution with methanol and recovered. The organic solution was evaporated and was combined with more diethyl ether extracts from the aqueous solution. The combined organic extracts were washed with saturated brine and dried over Na_2SO_4. The solvent was then removed under reduced pressure. After purification by flash chromatography on silica gel (hexane/EtOAc: 15:1), the chiral epoxide was obtained in 41% yield. Its ee was 71% as determined by HPLC−Chiracel OD column. The recovered polymer was redissolved into CH_2Cl_2, washed with 1 N HCl (10 mL) and brine, and dried over Na_2SO_4. The solvent was removed, and the residue was redissolved in a minimum amount of CH_2Cl_2. Methanol was added to precipitate out the polymer which was then dried under vacuum. This process gave the recovered (*R*)-**6** in 90% yield.

A Typical Procedure for the Asymmetric Epoxidation in the Presence of Polymer (*R*)-19, Diethylzinc, and *tert*-Butyl Hydroperoxide. Under nitrogen, to a diethyl ether solution (10 mL) of polymer (*R*)-**19** (0.1 mmol based on the repeating unit) was added diethylzinc (18 μL, 0.18 mmol) at room temperature. After stirring for 15 min, an α,β-unsaturated ketone (0.5 mmol) and *t*-BuOOH (135 μL, 4.43 M in toluene, 0.6 mmol) were added, and the resulting solution was stirred at room temperature for the time shown in Table 3. The reaction was quenched with 1 N HCl and extracted with ethyl acetate. The organic layer was washed with aqueous saturated sodium hydrogensulfite, brine, aqueous sodium bicarbonate, and brine. After the solution was concentrated, the polymer was precipitated out with addition of methanol. The solution was concentrated under vacuum, and the residue was purified by column chromatography to give the epoxidation product.

Determination of the ee's of the Epoxidation Products 2 Formed by Using Polymer (*R*)-19 as the Catalyst. All the ee's were determined by Chiral HPLC: Chiracel OD column with hexanes/2-propanol as eluent and 254 nm UV detector.

2a ($R^1 = R^2 = Ph$). Flow rate: 1.0 mL/min. Eluent: hexane:*i*-PrOH = 90:10. Retention time: minor 10.6 min, major 11.3 min. ee: 73%. $[\alpha]_D = -151.1$ (*c* = 1.0, CH_2Cl_2). Literature[4b] $[\alpha]_D = -130.0$ (*c* = 1.1, CH_2Cl_2).

2b ($R^1 = Ph$, $R^2 = i$-Pr). Flow rate: 1.0 mL/min. Eluent: hexane:*i*-PrOH = 90:10. Retention time: minor 6.5 min, major 7.3 min. ee: 78%. $[\alpha]_D = +26.6$ (*c* = 0.93, CH_2Cl_2). Literature[4b] $[\alpha]_D = +32.0$ (*c* = 1.3, CH_2Cl_2).

2c ($R^1 = Ph$, $R^2 = n$-Pr). Flow rate: 1.0 mL/min. Eluent: hexane:*i*-PrOH = 90:10. Retention time: minor 7.0 min, major 7.4 min. ee: 76%. $[\alpha]_D = +1.7$ (*c* = 1.0, CH_2Cl_2) Lit.[4b] $[\alpha]_D = +0.9$ (*c* = 1.1, CH_2Cl_2).

2d ($R^1 = Ph$, $R^2 = p$-CH_3Ph). Flow rate: 0.5 mL/min. Eluent: hexane:*i*-PrOH = 90:10. Retention time: minor 18.6 min, major 20.2 min. ee: 70%. $[\alpha]_D = -171.0$ (*c* = 1.08, CH_2Cl_2). Literature[5] $[\alpha]_D = -210$ (*c* = 1, CH_2Cl_2).

2e ($R^1 = Ph$, $R^2 = p$-ClPh). Flow rate: 0.5 mL/min. Eluent: hexane:*i*-PrOH = 98:2. Retention time: minor 38.5 min, major 40.6 min. ee: 79%. $[\alpha]_D$ =-176.8 (*c* = 0.70, CH_2Cl_2). Literature[5] $[\alpha]_D = -195$ (*c* = 1, CH_2Cl_2).

2 g ($R^1 = Ph$, $R^2 = t$-Bu). Flow rate: 0.5 mL/min. Eluent: hexane:*i*-PrOH = 90:10. Retention time: minor 11.3 min, major 13.4 min. ee: 64%. $[\alpha]_D = +14$ (*c* = 0.36, $CHCl_3$). Literature[14] $[\alpha]_D = +10$ (*c* = 0.53, $CHCl_3$).

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