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Polymeric Cinchona Alkaloids for the Heterogeneous Catalytic Asymmetric Dihydroxylation of Olefins : The Influence of the Polymer Backbone Polarity on the Compatibility between Polymer Support and Reaction Medium

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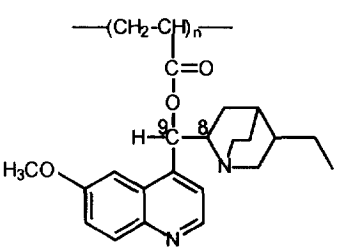
Abstract: Heterogeneous catalytic asymmetric dihydroxylation of olefins using homo- and co-polymeric cinchona alkaloids has been reported. The benzoate type homopolymers **2a, b** showed high enantioselectivity in the heterogeneous ADH reactions, but their catalytic efficiency was largely dependent on the solvent system which may relate to the accessibility of the active catalytic site. The influence of polymer backbone polarity on the compatibility with the reaction medium was investigated using copolymers **3a, b** and **4** having polar polymer backbone. The reaction rates and optical yields were dramatically increased by increasing the polarity of the polymer backbone in NMO-acetone/H_2O system.

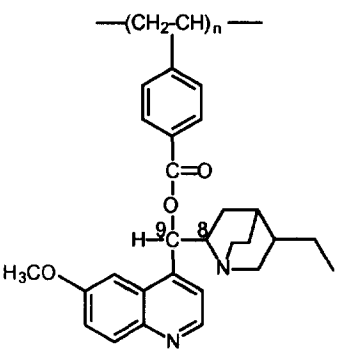
The Sharpless catalytic asymmetric dihydroxylation (ADH) of olefins using catalytic amounts of osmium tetroxide in the presence of cinchona alkaloid derivatives, allows access to a wide variety of enantiomerically pure vicinal diols.[1] However, there are limitations to performing the catalytic ADH reaction on a large scale due to toxicity and high cost of osmium tetroxide and cinchona alkaloid derivatives. Heterogeneous catalytic system could overcome these problems by the repetitive use of osmium and the cinchona alkaloids. An interesting development in this context is the use of polymeric cinchona alkaloids in the catalytic ADH reactions. Recently, several polymeric cinchona alkaloid derivatives have been prepared for this purpose.[2] However, most of the polymers needed complicated synthetic manipulations and their catalytic efficiency was, usually, not sufficient for practical purposes. Thus, development of synthetically simple and efficient polymers for heterogeneous ADH is strongly required. Especially, we are interested in the catalytic ADH of *trans*-cinnamate derivatives since it can provide the key intermediates for the preparation of important pharmaceuticals such as Taxol side chain,[3] Diltiazem[4] and Chloramphenicol.[5] To our best knowledge, the heterogeneous catalytic ADH of *trans*-cinnamate derivatives was not studied extensively. Recently, Lohray *et al.* reported that copolymer of dihydroquinidine 4-vinylbenzoate (DHQD 4-VB) and styrene provided moderate enantioselectivity (45 % ee) for the catalytic ADH of methyl *trans*-cinnamate. He also reported that ADH of *trans*-stilbene using the homopolymer of the DHQD 4-VB **2a** furnished racemic product concluding an increase in the amount of immobilized alkaloid on the polymer support led to an exponential decrease in the rate and enantiomeric purity of diols.[2e] However, suprisingly, during our own efforts to find an efficient polymeric catalysts for the heterogeneous ADH reactions, we found that, in contrast with the observation of Lohray, the homopolymer **2** exhibited

excellent enantioselectivity (max. 93% ee for *trans*-stilbene and 91% ee for methyl *trans*-cinnamate). More interestingly, it has been found that its catalytic efficiency was largely dependent on the secondary oxidant and solvent system which may relate to the compatibility between polymer support and the reaction medium. To probe this, the influence of the polymer backbone polarity on the compatibility with the reaction medium was investigated using copolymer **3** and **4** having polar polymer backbone, and here we wish to report the results.

Homopolymers **1a** and **2a, b** were easily prepared by polymerization of dihydroquinidine acrylate, dihydroquinidine 4-vinylbenzoate and dihydroquinine 4-vinylbenzoate in benzene under reflux in the presence of AIBN, respectively. The heterogeneous ADHs using homopolymers **1a** and **2a, b** for methyl *trans*-cinnamate and *trans*-stilbene were conducted under standard conditions, i.e. in acetone/H_2O and *t*-BuOH/H_2O using NMO and $K_3Fe(CN)_6$ as secondary oxidant, respectively. The results are summarized in Table 1.



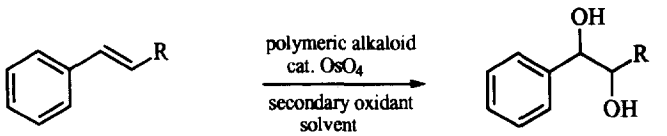
1a: poly(DHQD acrylate); (8*R*, 9*S*)



2a: poly(DHQD 4-VB); (8*R*, 9*S*)
2b: poly(DHQN 4-VB); (8*S*, 9*R*)

As shown in Table 1, the optical yields and reaction rates depend on the monomeric structure of the polymer. The benzoate type monomeric structure (polymer **2a** and **2b**) exhibited higher optical yields than those of acrylate type structure (polymer **1**) in both reaction conditions (entry 1 *vs.* entry 3 and 6, entry 2 *vs.* entry 4 and 7). A similar trend has been shown that in homogeneous catalytic ADH, i.e. hydroquinidine *p*-chlorobenzoate gave generally better results than hydroquinidine acetate.[6,7] More interestingly, the cataytic reactivity and enantioselectivity of polymer 2-Os complex was largely dependent on the solvent system. When the heterogeneous ADH of the methyl *trans*-cinnamate was carried out in *t*-BuOH/H_2O using $K_3Fe(CN)_6$, the reaction was completed in 18 hrs with excellent enantioselectivity (91% ee in entry 4 and 87% ee in entry 7). However, in acetone/H_2O-using NMO, the reaction proceeded very slowly (60 hrs) and gave a much lower optical yield (45% ee in entry 3 and 51% ee in entry 6). In order to examine the generality of the solvent and secondary oxidant effects on the enantioselectivity, *trans*-stilbene, one of the most common reactive substrates for the ADHs, was subjected to the heterogeneous catalytic ADH using homopolymer **2a** and **2b**. Similar phenomina with methyl *trans*-cinnamate have been observed. In acetone/H_2O-NMO system, the diol product was obtained in moderate optical yields (entry 8 and 10), but not racemic as indicated by Lohray. Whereas excellent enantoselectivities were observed in *t*-BuOH/H_2O-$K_3Fe(CN)_6$ system (entry 9 and 11). In acetone-H_2O (10:1 v/v) solvent system, the homopolymers **2a, b**

Table 1. Heterogeneous catalytic ADH of olefins using homopolymeric cinchona alkaloids **1-2**[a]



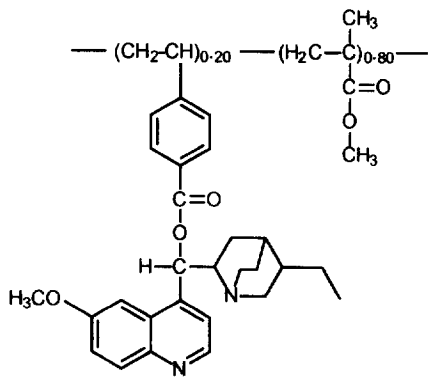
Entry	Polymers	Olefins (R=)	Secondary oxidant	Reaction time	% Yield[b]	% ee[c]	Config.[d]
1	**1a**	CO_2Me	NMO	30 h	74	30	2*S*, 3*R*
2	**1a**	"	$K_3Fe(CN)_6$	24 h	80	41	2*S*, 3*R*
3	**2a**	"	NMO	60 h	73	45	2*S*, 3*R*
4	**2a**	"	$K_3Fe(CN)_6$	18 h	85	91[f]	2*S*, 3*R*
5	**2a**[e]	"	$K_3Fe(CN)_6$	44 h	80	88	2*S*, 3*R*
6	**2b**	"	NMO	60 h	80	51	2*R*, 3*S*
7	**2b**	"	$K_3Fe(CN)_6$	18 h	84	87	2*R*, 3*S*
8	**2a**	Ph	NMO	20 h	81	70	*R,R*
9	**2a**	"	$K_3Fe(CN)_6$	20 h	80	89	*R,R*
10	**2b**	"	NMO	20 h	80	59	*S,S*
11	**2b**	"	$K_3Fe(CN)_6$	20 h	82	93	*S,S*

[a] The reaction conditions were not optimized: molar ratio of olefin/OsO_4/polymeric alkaloid = 1/0.01/0.25; reaction temperature (10 °C). [b] Isolated yields by column chromatography. [c] % ee was determined by comparison of $[\alpha]_D^{20}$ with literature values.[8,9] [d] Absolute configurations were assigned by comparing the sign of $[\alpha]_D^{20}$ with literature values.[8,9] [e] Reaction was carried out with polymer **2a** which had been used in entry 4 without further addition of OsO_4. [f] This is the highest ee for the heterogeneous ADH of methyl *trans*-cinnamate.

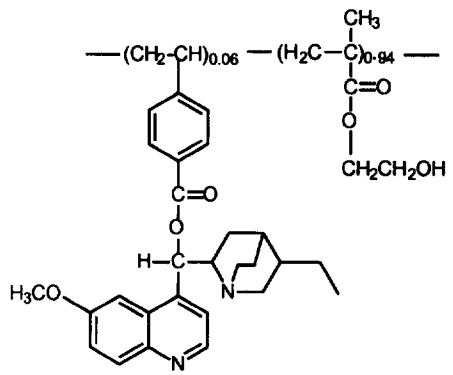
formed a viscous lump which may prevent the penetration of the substrate to the catalytic site. Thus, the substrate will mostly remain outside of the polymer and its concentration near the active site in the polymer matrix will be relatively low. However, in the *t*-BuOH/H_2O-$K_3Fe(CN)_6$ system, the polymeric catalysts swelled well which may provide similar chiral environments to the homogeneous catalytic system. This indicates that the accessibility of the active site in the polymer matrix depends on the compatibility between the polymer support and the liquid reaction medium. It could be imagined that, in a polar solvent, the compatibility would be improved by increasing the polarity of the polymer support.

To test the influence of the polymer backbone polarity on the compatibility with the reaction medium, we prepared copolymers **3** and **4**, [poly(dihydroquinidine 4-vinylbenzoate-*co*-MMA) **3a**, poly(dihydroquinine 4-vinylbenzoate-*co*-MMA) **3b** and poly(dihydroquinidine 4-vinylbenzoate-*co*-HEMA) **4a**], which have a highly polar polymer backbone. The required copolymers **3a, b** and **4a** were easily prepared by copolymerization of DHQD 4-VB or DHQN 4-VB (1 eq.) with methyl methacrylate (MMA, 6

eq.) or 2-hydroxyethyl methacrylate (HEMA, 9 eq.) using AIBN as an initiator in dry benzene at 80 °C, respectively. It should be noted that since commercial HEMA contains ethylene dimethacrylate, the copolymer **4a** was obtained as a lightly cross-linked polymer. The nitrogen analysis of copolymers **3**, **4** confirmed 20.2 and 6.0 mol % incorporation of styryl monomer, respectively. These copolymers are swelled well in both solvents.



3a: poly(DHQD 4-VB-*co*-MMA)
3b: poly(DHQN 4-VB-*co*-MMA)



4a: poly(DHQD 4-VB-*co*-HEMA)

The heterogeneous ADHs were carried out using copolymer **3a, b** and **4a** with the less reactive substrate methyl *trans*-cinnamate and the results are summerized in Table 2. As we expected, all the reactions using new copolymers **3a, b** and **4a** proceeded fast and gave excellent optical yields of the diol in both solvent systems. Especially, for NMO-acetone/H_2O system (entries 1, 4 and 6), the reaction rates and optical yields were dramatically increased by increasing the polarity of the polymer backbone (compare the results using polymer **2a, b** with **3a, b** and **4a**). Even though there was no significant differences, it is also interesting that MMA-copolymers **3a, b** were more effective for the acetone-H_2O solvent system than in *t*-BuOH-H_2O (entry 1 *vs.* entry 2 and entry 4 *vs.* entry 5), while HEMA-copolymer **4a** gave the opposite results (entry 6 *vs.* entry 7). Moreover, OsO_4-polymer **3** complex can be easily filtered from the reaction mixture. However, copolymer **4a** was too highly swelled leading to difficulties in filtration. These results imply that the polarity of polymer backbone affects the compatibility of the polymer support with reaction medium. The importancy of the compatibility of polymer backbone with reaction medium in the heterogeneous asymmetric catalysis was also indicated by Stille *et al.*[10]

It should be noted here (1) the catalytic reactivity and enantioselectivity of the homopolymers **2** and copolymers **3** and **4** exhibited almost the same as those of the monomeric alkaloids, (2) in contrast to the homogeneous system, there were no significant differences between slow addition and one-pot addition of the olefins in the acetone/H_2O-NMO system (all results in NMO system were obtained by one-pot addition of the olefins), and (3) moreover, the enantioselectivities of the polymer-OsO_4 complex were almost retained after reaction but the catalytic activities were decreased which may due to the loss of OsO_4 during the filtration (entry 5 in Table 1 and entries 3 and 8 in Table 2).

Table 2. Heterogeneous catalytic ADH of methyl *trans*-cinnamate using polymeric cinchona alkaloids **3-4**[a]

Entry	Polymers	Secondary oxidant	Reaction time	% Yield[b]	% ee[c]	Config.[d]
1	**3a**	NMO	18 h	80	89	2*S*, 3*R*
2	**3a**	$K_3Fe(CN)_6$	26 h	84	79	2*S*, 3*R*
3	**3a**[e]	$K_3Fe(CN)_6$	34 h	85	80	2*S*, 3*R*
4	**3b**	NMO	18 h	83	89	2*R*, 3*S*
5	**3b**	$K_3Fe(CN)_6$	26 h	80	83	2*R*, 3*S*
6	**4a**	NMO	28 h	87	85	2*S*, 3*R*
7	**4a**	$K_3Fe(CN)_6$	20 h	86	90	2*S*, 3*R*
8	**4a**[e]	$K_3Fe(CN)_6$	29 h	84	88	2*S*, 3*R*

[a] The reaction conditions were not optimized: molar ratio of olefin/OsO_4/polymeric alkaloid = 1/0.01/0.10; reaction temperature (10 °C). [b] Isolated yields by column chromatography. [c] % ee was determined by comparison of $[\alpha]_D^{20}$ with literature value.[8] [d] Absolute configurations were assigned by comparing the sign of $[\alpha]_D^{20}$ with literature value.[8] [e] Reaction was carried out with polymer **3a** or **4a** which had been used in entry 2 or 7 without further addition of OsO_4.

In conclusion, in hetergeneous catalytic ADH reactions, the benzoate type homopolymers **2a, b** showed high enantioselectivities in *t*-BuOH/H_2O solvent using $K_3Fe(CN)_6$ as a secondary oxidant. However, their catalytic efficiency was decreased in acetone/H_2O solvent using NMO as a secondary oxidant which may relate to the accessibility of the active catalytic site. The compatibility of the polymer support with the reaction medium was increased by increasing the polarity of the polymer backbone. Thus, dramatically increased reactivity and enantioselectivity was achieved under both reaction conditions using copolymers **3** and **4** having polar polymer backbones. In addition, the polymer-OsO_4 complex exhibited a promising reusebility, even though the catalytic efficiency of the recovered polymeric catalyst was slightly decreased. Further studies are in progress to improve the binding ability of polymeric alkaloids for OsO_4 and will help shed light on the practical limitation on the large scale ADH reactions.

Experimental

The ^1H NMR and ^{13}C NMR spectra were recorded with a Gemini 300 (300 MHz) Varian spectrometer using TMS as an internal standard. Optical rotations were measured on a AUTOPOL III Rudolph Research Polarimeter. Elemental analyses were performed in the Microanalytical Department in Korea Institut of Science and Technology. Thin Layer chromatography was performed on Merck DC-alufolien with Kieselgel 60F-254. Column chromatography was carried out on silica gel (Silica gel 60, 230-400 mesh ASTM, Merck). All commercially available chemicals were obtained from Aldrich and were used without further purification.

Dihydroquinidine acrylate: To a solution of dihydroquinidine (3 g, 9.19 mmol) and triethyl amine (1.6 ml, 13.78 mmol) in dichloromethane (50 ml) a solution of freshly distilled acryloyl chloride (1.24 g, 13.78 mmol) in dichloromethane (10 ml) at -10 °C was added dropwise. After stirring 20 hrs at room temperature, the reaction mixture was poured into water (100 ml). The separated organic layer was washed with saturated sodium hydrogencarbonate and water, and dried over anhydrous magnesium sulfate. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent ; ethyl acetate : acetone = 1:4) to give the dihydroquinidine acrylate: Yield 3.1 g (88 %); $[\alpha]_D^{23}$ -89.3 (*c* 1.02, $CHCl_3$).

Dihydroquinidine 4-vinylbenzoate: To a solution of dihydroquinidine (7.3 g, 19.9 mmol) and triethyl amine (4.7 ml, 33.6 mmol) in dichloromethane (120 ml) a solution of 4-vinyl benzoyl chloride (5.6 g, 33.6 mmol) in dichloromethane (40 ml) at -10 ℃ was added dropwise. After stirring 20 hrs at room temperature, the reaction mixture poured into water (300 ml). The separated organic layer was washed with saturated sodium hydrogencarbonate and water, and dried over anhydrous magnesium sulfate. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (euent; ethyl acetate : acetone = 1:4) to give the dihydroquinidine 4-vinylbenzoate: Yield 8.4 g (82%); $[\alpha]_D^{23}$ -120.2 (*c* 1.01, $CHCl_3$). Dihydroquinine 4-vinylbenzoate was prepared by same method: Yield 87 %; $[\alpha]_D^{23}$ +161.8 (*c* 1.12, $CHCl_3$).

Preparation of poly(dihydroquinidine acrylate) 1a: A solution of dihydroquinidine acrylate (5.83 g) and azobisisobutyronitrile (45 mg) in dry benzene (100 ml) was refluxed under nitrogen atmosphere. After 48 hrs, the solution was cooled to room temperature and poured into ether. A precipitate was filtered off, washed throughly with ether and dried under vacuo to give 1.2 g (21%) of **1a**; $[\alpha]_D^{23}$ +59.9 (*c* 1.26, $CHCl_3$); Anal Cacld. for $(C_{23}H_{28}N_2O_3)_n$: C, 72.60; H, 7.41; N, 7.36. Found: C, 70.7; H, 7.36; N, 7.39.

Preparation of poly(dihydroquinidine 4-vinylbenzoate) 2a: A solution of dihydroquinidine 4-vinyl benzoate (7.8 g) and azobisisobutyronitrile (53 mg) in dry benzene (80 ml) was refluxed under nitrogen atmosphere. After 48 hrs, the solution was cooled to room temperature and poured into ether. The precipitate was filtered, washed with ethanol and dried to give 6.6 g of polymer **2a** (84%). $[\alpha]_D^{23}$ -114.5 (*c* 1.18, $CHCl_3$); Mw 37364 (THF); Anal Cacld. for $(C_{29}H_{32}N_2O_3)_n$: C, 76.28; H, 7.06; N, 6.13. Found: C, 75.1; H, 7.22; N, 5.96. Poly(dihydroquinine 4-vinylbenzoate) **2b** was prepared by same method: yield; 81 %; $[\alpha]_D^{23}$ +197.2 (*c* 1.21, $CHCl_3$); Anal Cacld. for $(C_{29}H_{32}N_2O_3)_n$: C, 76.28; H, 7.06; N, 6.13. Found: C, 74.7; H, 7.05; N, 6.09.

Copolymerization of dihydroquinidine 4-vinylbenzoate with methyl methacrylate (MMA): A solution of dihydroquinidine 4-vinylbenzoate (10.0 g), MMA (14.95 g) and azobisisobutyronitrile (50 mg) in dry benzene (150 ml) was refluxed under nitrogen atmosphere. After 43 hrs, the solution was concentrated under vacuo and the residue was poured into ethanol. The precipitate was filtered, washed with ethanol and dried to give 19.4 g of copolymer **3a**. The component of coplymer was determined by elemental analysis: Anal. Calcld. for a polymer containing 79.8 mol % of MMA: C, 68.72; H, 7.52; N, 3.29. Found: C, 67.3; H, 7.58; N, 3.29. Poly(dihydroquinine 4-vinylbenzoate-*co*-MMA) **3b** was prepared by same method.

Copolymerization of dihydroquinidine 4-vinylbenzoate with 2-hydroxyethyl methacrylate (HEMA): A solution of dihydroquinidine 4-vinylbenzoate (4.0 g), HEMA (10.25 g) and azobisisobutyronitrile (30 mg) in dry benzene (100 ml) was refluxed under nitrogen atmosphere for 19 hrs. The polymer began to precipitate after stirring for 30 min. The precipitate polymer was filtered, washed twice with 100ml portions of benzene, and dried under vacuo to give 9.0 g of white powder **4a**. The polymer **4a** was insoluble in all organic solvents. The component of coplymer was determined by elemental analysis: Anal. Cacld. for a polymer containing 94 mol % of HEMA: C, 59.16; H, 7.62; N, 1.11. Found: C, 58.5; H, 7.75; N, 1.11.

Typical procedure for the heterogeneous catalytic ADH of olefines:

(a) In acetone/H_2O solvent system using NMO as secondary oxidant (all reactions were carried out at 10 °C): To a magnetically stirred suspension of the alkaloid polymer (0.25 eq. for polymer **1** and **2** and 0.10 eq. for polymer **3** and **4**), NMO (1.5 eq.), and tetraethylammonium acetate (1.2 eq.) in acetone-water (10/1, v/v) was added 1% solution of OsO_4 (0.01 eq.) in distilled water. After stirring for 1 hr, methyl *trans*-cinnamate (1 eq.) was added all at once. The concentration of olefin in the reaction mixture was about 0.3 M. When the reaction was completed, the polymer was filtered out from the reaction mixture. To the filtrate, sodium metabisulfite (1.5 eq.) was added and stirred for 2 hrs at room temperature. Reaction mixture was extracted with ethyl acetate and organic phase was washed with water and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using ethyl acetate : *n*-hexane = 1: 2 as eluent.

(b) In *t*-BuOH/H_2O solvent system using $K_3Fe(CN)_6$ as secondary oxidant (all reactions were carried out at 10 °C): To a well-stirred mixture of the alkaloid polymer (0.25 eq. for polymer **1** and **2** and 0.10 eq. for polymer **3** and **4**), potassium ferricyanide (3.0 eq.), potassium carbonate (3.0 eq.) and methanesulfonamide (1.2 eq.) in *tert*-butanol and water (1/1, v/v) was added 1% OsO_4 solution (0.01 eq.) in distilled water. After stirring for 1 hr, methyl *trans*-cinnamate (1 eq.) was added all at once and the reaction was monitored by TLC. When the reaction was completed, the polymer was filtered out. To the filtrate, sodium sulfite (1.5 eq.) was added and stirred for 2 hrs at room temperature. The following procedures were same as above (a).

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