

Polyesters Containing Chiral Imidazolidinone Salts in Polymer Main Chain: Heterogeneous Organocatalysts for Asymmetric Diels–Alder Reaction

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Abstract: Novel main-chain polyesters functionalized with chiral imidazolidinone salts were successfully synthesized. Polycondensation of a chiral imidazolidinone dimer bearing two hydroxyphenyl groups with selected achiral dicarboxylic acid chlorides followed by the addition of an acid afforded polyesters with chiral imidazolidinone salts incorporated into the polymer main chain. Main-chain ionic polyesters functionalized with chiral imidazolidinone salts in the polymer main chain were synthesized by the neutralization polymerization of a chiral imidazolidinone dimer with selected aromatic disulfonic acids. These polyesters were used as heterogeneous organocatalysts in the asymmetric Diels-Alder reaction of trans-cinnamaldehyde and 1,3-cyclopentadiene. By optimizing the polymer main-chain structure, enantioselectivity of up to 97% was achieved, which is higher than that attained using the corresponding monomeric and dimeric chiral imidazolidinone salts. These heterogeneous organocatalysts were easily recovered from the reaction mixture and reused several times without significant loss of the enantioselectivity.

Keywords: asymmetric catalysis • Diels-Alder reaction heterogeneous catalysis • organocatalysis • polymers

Introduction

Organocatalysis has been a rapidly growing area of research over the last decade with the penetration of the concept of green chemistry. Chiral organocatalysis is highly effective for the synthesis of optically active compounds for medical and pharmaceutical applications.^[11] With the development of chiral organocatalyst design and its application to asymmetric reactions, high yields and enantioselectivities have been reported for various asymmetric reactions using chiral organocatalysts.

Chiral imidazolidinones and their salts developed by D.W.D. MacMillan and coworkers are one of the most important classes of chiral organocatalysts; this family of organocatalysts can be applied to various asymmetric reactions.^[2] Chiral imidazolidinone organocatalysts have advantages over conventional

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organometallic catalysts such as being metal free, exhibiting higher stability against oxygen or moisture, and permitting ease of operation. However, chiral imidazolidinone organocatalysis, as well as most conventional organocatalysis, requires relatively high amounts of catalyst loading (5 to 20 mol%) to facilitate an asymmetric reaction at a reasonable reaction rate. In the isolation of a product and separation of a chiral organocatalyst from a reaction mixture, burdensome purification methods such as silica gel column chromatography are required. Therefore, chiral imidazolidinone is generally not reused.

To overcome these issues, immobilization of a chiral organocatalyst onto a polymer is a potential solution.^[3] Several studies on the immobilization of chiral imidazolidinone salts onto polymer side chains or chain ends have been reported.^[4] We have also developed some polymeric chiral imidazolidinone salts. Ionically polymer-supported chiral imidazolidinone salts have been successfully prepared by the ion-exchange reaction of a chiral imidazolidinone salt with a sulfonated polymer, in which the chiral imidazolidinone salts were immobilized at the polymer pendants.^[5] The non-covalent immobilization method has also widely used for the immobilization of been chiral organocatalysts.[6]

Recently, we developed polymers incorporating a chiral organocatalyst into the polymer main chain.[7-9] Polyether incorporating chiral imidazolidinone into the polymer main chain has been prepared by the Williamson reaction of a bisphenoltype chiral imidazolidinone monomer with an achiral dihalide, followed by the addition of an acid.^[7] Furthermore, a unique ionic polyether incorporating chiral imidazolidinone salts into the polymer main chain has been successfully synthesized by the neutralization reaction of a chiral imidazolidinone dimer with an achiral disulfonic acid.^[8] Various types of main-chain chiral polyethers can be readily prepared because these building blocks involve various simple amino acids, dihalides, and disulfonic acids. Appropriate tuning of the polymer main-chain structure resulted in high to excellent enantioselectivity in the asymmetric Diels-Alder reaction of trans-cinnamaldehyde and 1,3-cyclopentadiene.

In this article, we focused on polyester as a repeating unit of the polymer main chain. Polyester is a common synthetic polymer that is widely used in fibers, films, and beverage containers.^[10] It is an excellent plastic in terms of heat resistance, impact resistance, gas barrier properties (resistance to gas permeation), chemical resistance, and abrasion resistance, making polyester a promising polymeric chiral catalyst for further industrial application. Polyesters with chirality in the polymer main chain have mainly been applied as functional materials with liquid crystallinity or biodegradability.^[11] However, little attention has been paid to their application as support polymers for heterogeneous asymmetric catalysis. Only a few examples have been reported for these applications.^[12]



Figure 1. Polyesters containing chiral imidazolidinone salts in polymer main chain.

the development of a polyester-supported chiral For imidazolidinone organocatalyst, we designed two types of novel main-chain polyesters functionalized with chiral imidazolidinone salts in the main chain 1 and 2 (Figure 1). These chiral polyesters were used as heterogeneous polymeric chiral organocatalysts in the asymmetric Diels-Alder reaction of transcinnamaldehyde and 1,3-cyclopentadiene. The effects of dicarboxylate, counteranions, and disulfonate of the chiral polyester on the reactivity and stereoselectivity were investigated in detail. The substrate generality and reusability of these chiral polyesters were also tested in the same reaction. To the best of our knowledge, this is the first report on the asymmetric organocatalytic application of main-chain chiral polyester.

Results and Discussion

Synthesis of main-chain chiral polyester functionalized with chiral imidazolidinone salt (1)



Scheme 1. Synthesis of chiral polyesters 1.

Polyesters incorporating chiral imidazolidinone salts into the polymer main chain **1** were synthesized by the polycondensation of a chiral imidazolidinone bearing two hydroxyphenyl groups **4** with a few achiral dicarboxylic acid chlorides **5**, followed by the addition of an acid, as illustrated in Scheme 1. First, **4** was synthesized from (*S*)-tyrosine **3** according to the process described in our previous report.^[7]

Polyester is generally prepared using polymerization methods such as alcoholic transesterification, azeotrope esterification, ring-opening polymerization, and enzymatic synthesis. Among these methods, we chose the polycondensation of a dicarboxylic acid dihalide with a diol because this approach is general and affords polyester in good yield and with high molecular weight. In addition, the polymerization procedure is simple: the addition of a diol to an equimolar amount of a dicarboxylic acid dihalide in the presence of a base. First, we performed the polycondensation of 4 and 5 in the presence of a catalytic amount of benzyltributylammonium chloride in 1.0 M NaOH and CH₂Cl₂ biphasic solution.^[13] We confirmed that only the ester formation occurred and the secondary amines in 4 remained intact under these polymerization conditions. Precipitates were observed as soon as the CH₂Cl₂ solution of 5 was added to the NaOH aqueous solution of 4. Various types of dicarboxylic acid dihalides including aromatic, unsaturated aliphatic, and saturated aliphatic dicarboxylic acid dichlorides were used to prepare chiral polyester 6. In all the cases, the polycondensation occurred smoothly to afford 1 in high yield under these experimental conditions (Table 1). When the polycondensation of 4 and dicarboxylic acid was used instead of 5 in the presence of Sc(OTf)₃,^[14] no polymer was obtained.

ntry	5	Chiral polyester 6	Yield [%]
1	5a	6a	99
2	5b	6b	86
3	5c	6c	98
4	5d	6d	80
5	5e	6e	90
6	5f	6f	84

Interestingly, the solubility of **6** was quite different from that of main-chain chiral polymers we have previously synthesized. Regardless of the difference in the spacer structure derived from **5**, the resulting polyesters were completely insoluble in common solvents such as hexanes, CH_2Cl_2 , ethyl acetate, methanol, and H_2O and very slightly soluble only in *N*,*N*-dimethylformamide (DMF), most likely because of the rigid ester repeating unit in the polymer main chain.

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The slightly soluble part in DMF was barely able to be analyzed by sizeexclusion chromatography (SEC). Table 1 summarizes these number- and weight-averaged molecular weights and molecular weight distributions. These SEC traces were monomodal, and their number-averaged molecular weights were sufficiently high $(M_n > 7,000)$ (see Table S1 in the supporting information). Figure 2a presents a Fourier-transform infrared (FT-IR) spectroscopy spectrum of a chiral polyester functionalized with chiral imidazolidinone 6a. The absorption peaks at 1739 and 1263 cm^{−1} are assigned to stretching vibrations of C=O and C-O bonds for the polvester, respectively. In addition, the absorption peaks at 1640 and 1167 cm^{−1} are assigned to stretching vibrations of C=O and C-N bonds for

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the imidazolidinone, respectively. In contrast, a good liquid ¹H NMR spectrum was not obtained because of the low solubility of the chiral polyester 6 in common deuterated solvents (CDCl₃, dimethylsulfoxide (DMSO- d_6), and D₂O). Alternatively, solid state ¹³C NMR spectrum was measured. The signal ranging from 165 to 175 ppm assigned to ester carbon was obviously observed. These results indicate that the polycondensation of 4 and 5 proceeded smoothly and that the imidazolidinone moiety was incorporated into the polyester. The treatment of the main-chain polyester of chiral imidazolidinone 6 with an acid yielded a mainchain polyester with chiral imidazolidinone salt moiety 1 (Scheme 1). For example, the reaction of 6a with ptoluenesulfonic acid yielded 1a-OTs. The imidazolidinone salt structure was confirmed by FT-IR spectroscopy, as shown in Figure 2b. The broad absorption peaks in the range from 2800 to 2200 cm⁻¹ are assigned to stretching vibrations of N-H for the imidazolidinone salt. In addition, the absorption peaks at 2940, 1164, 810, 679, and 563 cm⁻¹ are assigned to the ptoluenesulfonate.





Scheme 2. Synthesis of ionic chiral polyesters 2.

Synthesis of ionic main-chain polyester functionalized with chiral imidazolidinone salt (2)

lonic polyesters incorporating chiral imidazolidinone salts into the polymer main chain **2** were prepared by the neutralization polymerization of a chiral imidazolidinone dimer **8** with selected aromatic disulfonic acids **9**, as illustrated in Scheme 2. Chiral imidazolidinone with a hydroxyphenyl group **7** was synthesized from (*S*)-phenylalanine using a synthetic procedure similar to that of **4**. Dimerization of **7** was performed by esterification with dicarboxylic acid dichloride **5**. Chiral imidazolidinone dimers with different dicarboxylate spacers **8** were obtained with moderate to high yield.

Table 2. Characterization of ionic main-chain chiral polyesters 2.

Entry	8	9	lonic chiral polyester 2	Yield [%]	<i>M</i> n ^[a]	$M_{\rm w}^{\rm [a]}$	<i>M</i> w/ <i>M</i> n [a]
1	8a	9A	2aA	73	5,000	11,000	2.2
2	8b	9A	2bA	93	4,500	6,200	1.4
3	8c	9A	2cA	76	4,400	5,500	1.2
4	8d	9A	2dA	74	5,000	7,900	1.6
5	8e	9A	2eA	95	4,800	9,700	2.0
6	8f	9A	2fA	77	4,900	8,300	1.7
7	8e	9B	2eB	90	4,200	5,100	1.2
8	8e	9C	2eC	75	4,300	9,900	2.3
9	8e	9D	2eD	77	6,200	14,400	2.3
10	8e	9E	2eE	84	4,700	6,900	1.5

[a] Determined by SEC using DMF as an eluent at a flow rate of 1.0 mL min⁻¹ at 40 $^{\circ}$ C (polystyrene standards).



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Figure 3. ¹H NMR spectrum of ionic chiral polyester 2eA.

Polymerization was conducted by adding an aqueous solution of disulfonic acid ${\bm 9}$ to a CH_2CI_2 solution of chiral imidazolidinone dimer 8 at room temperature. The successive intermolecular neutralization reaction between 8 and 9 proceeded smoothly to afford ionic chiral polyester 2. During the neutralization polymerization, polymers were gradually precipitated in the solution because these polymers were soluble neither in CH₂Cl₂ nor in H₂O. Chiral imidazolidinone dimers 8 and disulfonic acids 9 were used to prepare various types of polyesters 2. We prepared ionic chiral polyesters with selected aromatic disulfonate spacers because a similar ionic polymeric chiral imidazolidinone salt with naphthalenedisulfonate exhibited high catalytic performance in the following Diels-Alder reaction.^[8] Table 2 summarizes the isolated yield, number- and weightaveraged molecular weights, and molecular weight distribution of chiral polyester 2. Unlike the chiral polyesters 1, the ionic chiral polyesters 2 were highly soluble in DMF and DMSO; therefore, their molecular weights and molecular weight distribution were easily measured using SEC. The numberaveraged molecular weights determined by SEC ranged between 4.2 and 6.2 kg/mol.

Figure 3 presents a ¹H NMR spectrum of ionic chiral polyester functionalized with chiral imidazolidinone salts **2eA** in DMSO- d_6 . Both signals assigned to imidazolidinone and disulfonate moieties were observed with a 1:1 ratio. These results clearly indicate that the neutralization polymerization of **8** and **9** proceeded smoothly to afford unique ionic main-chain chiral polyesters incorporating chiral imidazolidinone salt into the polymer main chain **2**. Asymmetric Diels-Alder reaction using model chiral imidazolidinone salt



Figure 4. Monomeric and dimeric chiral imidazolidinone salts.

To evaluate the catalytic activity of these chiral imidazolidinone salt polyesters and their monomeric counterparts, the asymmetric Diels–Alder reaction of *trans*-cinnamaldehyde **12** and 1,3-cyclopentadiene **13** was investigated. Initially, the catalytic activity of the model chiral imidazolidinone salts in the Diels–Alder reaction was examined (Table 3). The reaction was conducted with 10 mol% chiral imidazolidinone salt in a $CH_3OH:H_2O$ (95:5, *v/v*) mixed solvent at 25 °C for 24 h. The

reaction catalyzed by the original chiral imidazolidinone hydrochloride 10-CI (Figure 4) afforded bicycle[2.2.1]heptene derivatives 14 in quantitative yield with 93% ee for exo and endo isomers (entry 1).^[2g] The chiral imidazolidinone ptoluenesulfonate 10-OTs and two hydroxyphenyl-functionalized chiral imidazolidinone p-toluenesulfonate 4-OTs exhibited similar enantioselectivity for the endo isomer to 10-Cl and somewhat lower enantioselectivity for the exo isomer (entries 2-3). The chiral imidazolidinone salt functionalized with two benzoyloxy moieties 11-OTf (Figure 4) as a substructure for the repeating unit of chiral polyester 1 exhibited comparable enantioselectivity to 10-OTs (entry 4). These monomeric and dimeric chiral imidazolidinone salts exhibited similar reactivity and enantioselectivity for endo isomers.

has a significant effect on the catalytic activity.^[5a,15] 1a-OTs exhibited good affinity to CH₂Cl₂ and CH₃CN but not to CH₃OH and H₂O. When H₂O or CH₃OH was used for the reaction, significant reductions of both the yield and enantiomeric excess of these adducts were observed (entries 1-2). The catalytic activity in CH₃CN or CH₂Cl₂ was also comparable to those in H₂O or CH₃OH (entries 3–4). The CH₃OH–H₂O (95:5, v/v) mixed solvent used in the Diels-Alder reaction by the model chiral imidazolidinone salt gave the desired adducts quantitatively with high enantioselectivity (entry 5). The acceleration of the reaction rate in the conventional Diels-Alder reaction with the addition of H₂O has been reported.^[16] Similarly, the presence of H₂O in the Diels-Alder reaction catalyzed by the chiral imidazolidinone salt enhanced the reactivity.^[17] Based on these results, we chose the CH₃OH-H₂O mixed solvent as a suitable reaction solvent for the reaction catalyzed by the chiral imidazolidinone polyester.



[a] Reaction conducted with 10 mol% of catalyst in CH₃OH:H₂O (95:5) at 25 °C for 24 h. [b] Isolated yield. [c] Determined by ¹H NMR. [d] Determined by GC (CHIRALDEX β -PH). [e] See ref 2g. [f] See ref 5a. [g] See ref 7.

Table 5. Asymmetric Diels–Alder reaction using chiral imidazolidinone salt polyester $1^{\rm [a]}$

Entry	Chiral	14				
4	nidazolidinone salt polyester	Yield [%] ^[b]	exo/endo ^[c]	ee (<i>exo</i>) (%) ^[d]	ee (<i>endo</i>) (%) ^[d]	
1	1a-OTf	99	54/46	81	90	
2	1b-OTf	99	56/44	88	93	
3	1c-OTf	42	55/45	79	77	
4	1d-OTf	81	55/45	78	84	
5	1e-OTf	56	55/45	69	75	
6	1f-OTf	88	56/44	83	88	
7	1a-BF₄	99	53/47	89	89	
8	1a-OMs	99	56/44	92	93	
9	1a-OTs	99	56/44	91	94	
10	1a-Cl	94	56/44	87	91	
11 ^[e]	1a-OTs	87	54/46	92	96	
12 ^[e]	1b-OTs	99	53/47	91	95	

Asymmetric Diels–Alder reaction using chiral imidazolidinone salt polyester 1

Table 4. Solvent screening in asymmetric Diels–Alder reaction using chiral imidazolidinone salt polyester ${\bf 1a-OTs}^{[a]}$

Entry	Solvent	14				
,		Yield [%] ^[b]	exo/ endo ^[c]	ee (<i>exo</i>) (%) ^[d]	ee (<i>endo</i>) (%) ^[d]	
1	H ₂ O	58	52/48	68	73	
2	CH₃OH	49	56/44	75	77	
3	CH₃CN	41	58/42	59	56	
4	CH ₂ Cl ₂	43	58/42	55	58	
5	$CH_3OH:H_2O = 95:5$	99	56/44	91	94	

[a] Reaction conducted with 10 mol% of **1a-OTs** at 25 °C for 24 h. [b] Isolated yield. [c] Determined by ¹H NMR. [d] Determined by GC (CHIRALDEX β -PH).

Next, the solvent effect was briefly examined using a polyester functionalized with chiral imidazolidinone *p*-toluenesulfonate **1a-OTs** in the same asymmetric Diels–Alder reaction (Table 4). The affinity of a polymeric catalyst for a reaction solvent generally

[a] Reaction conducted with 10 mol% of catalyst in CH₃OH:H₂O (95:5) at 25 °C for 24 h. [b] Isolated yield. [c] Determined by ¹H NMR. [d] Determined by GC (CHIRALDEX β -PH). [e] Reaction conducted at 0 °C for 72 h.

Table 5 summarizes the reaction catalyzed by the polyester functionalized with chiral imidazolidinone salt 1. The effect of the dicarboxylate spacer on the catalytic activity was investigated in detail. The chiral imidazolidinone trifluoromethanesulfonate polyester with the saturated aliphatic (butylene) spacer 1a-OTf produced Diels-Alder adducts 14 in quantitative yield but somewhat lower ee for exo and endo isomers than those obtained using the corresponding model chiral imidazolidinone salts (entry 1). The chiral imidazolidinone salt polyester with the longer aliphatic (octylene) spacer 1b-OTf exhibited comparable enantioselectivity as these model catalysts (entry 2). Other polymeric chiral imidazolidinone salts with an unsaturated aliphatic spacer 1c-OTf and aromatic spacer 1d-OTf, 1e-OTf, 1f-OTf exhibited lower reactivity and moderate enantioselectivity (entries 3-6). These results clearly indicate that the dicarboxylate spacer structure introduced into the polymer main chain affected the catalytic activity. The reason why 1b-OTf exhibited similar catalytic activity as the corresponding model chiral imidazolidinone salt has not been clarified. We suppose that the rigidity of the main-chain structure of the polymer due to the ester bond is relaxed by introducing a flexible spacer such as octylene, which leads to a conformation of the chiral imidazolidinone moiety suitable for the asymmetric Diels–Alder reaction.

Next, we investigated the effect of the counteranion of **1a** in the reaction (Table 5). Chiral imidazolidinone salts with methanesulfonate **1a-OMs**, *p*-toluenesulfonate **1a-OTs**, and hydrochloride **1a-CI** exhibited higher enantioselectivities than that with trifluoromethanesulfonate **1a-OTf** (entries 8–10). Among them, the polyester with *p*-toluenesulfonate **1a-OTs** exhibited the highest enantioselectivity for the *endo* isomer (entry 9). Reducing the reaction temperature to 0 °C increased the enantioselectivity for both diastereomers of **14** (entries 11–12). Based on these results, the counteranion and reaction temperature were observed to affect the enantioselectivity to a certain extent.

Asymmetric Diels–Alder reaction using chiral imidazolidinone salt polyester 2

Table 6. Asymmetric Diels-Alder reaction using chiral imidazolidinone salt polyester $\mathbf{2}^{[a]}$

Entry	Chiral			14		
	imidazolidinone salt polyester	Yield [%] ^[b]	exo/endo ^[c]	ee (<i>exo</i>) (%) ^[d]	ee (<i>endo</i>) (%) ^[d]	
1	7-OTs	88	56/44	84	86	
2	8e-OTs	99	60/40	92	97	
3	2aA	37	52/44	75	72	
4	2bA	99	56/44	92	97	
5	2cA	49	54/46	73	71	
6	2dA	99	58/42	91	97	
7	2eA	99	56/44	94	97	
8	2fA	99	55/45	94	97	
9	2eB	96	56/44	91	94	
10	2eC	85	55/45	88	90	
11	2eD	47	53/47	81	76	
12	2eE	59	54/46	84	80	
13	2eA ^[e]	98	56/44	94	97	
14 ^[f]	2eA	99	56/44	94	97	
15 ^[g]	2eA	78	55/45	94	97	

[a] Reaction conducted with 10 mol% of catalyst in CH₃OH:H₂O (95:5) at 25 °C for 24 h. The catalyst amount is based on the repeating unit of **2**. [b] Isolated yield. [c] Determined by ¹H NMR. [d] Determined by GC (CHIRALDEX β -PH). [e] Prewashed with CH₃OH:H₂O (95:5). [f] Reaction conducted for 12 h. [g] Reaction conducted at 0 °C for 48 h.

The catalytic activity of ionic polyester **2** and the corresponding monomeric and dimeric chiral imidazolidinone salts were also examined in the Diels–Alder reaction. The reaction using model chiral imidazolidinone *p*-toluenesulfonate with a hydroxyphenyl group **7-OTs** afforded **14** in 88% yield with 84% ee (*exo*) and 86% ee (*endo*) (Table 6, entry 1). The dimer of chiral imidazolidinone *p*-toluenesulfonate with butylene spacer **8e-OTs**

afforded a quantitative yield and high enantioselectivity (97% ee for endo isomer) (entry 2). Encouraged by these results, we investigated the catalytic activity of ionic polyester 2 in the same reaction. Although 2 was completely insoluble in the CH₃OH-H₂O (95:5, v/v) mixed solvent, it was well dispersed in the reaction mixture. Higher catalytic activity of 2 is expected due to the high surface area. Polymeric ionic chiral imidazolidinone salts with aromatic dicarboxylate spacers 2aA and 2cA exhibited low reactivity and enantioselectivity (Table 6, entries 3 and 5). However, chiral imidazolidinone salt polyesters with a 1,3phenylene spacer 2bA and aliphatic linkers 2dA, 2eA, 2fA exhibited quantitative yield and excellent enantioselectivity in both exo (up to 94% ee) and endo (up to 97% ee) isomers (entries 4 and 6-8). The effect of the disulfonate spacer of 2 was also investigated in the reaction (Table 6). A chiral imidazolidinone salt polyester with naphthalene 1,4-disulfonate 2eB exhibited comparable catalytic activity to that of the original chiral imidazolidinone salt (entry 9). However, the catalytic reactivity and enantioselectivity of the chiral imidazolidinone salt polyester with hindered aromatic disulfonate 2eC, 2eD, and 2eE were lower than those of 2eA (entries 10-12). The catalytic activity of 2eA washed with the reaction solvent before the reaction was comparable to that of 2eA without prewashed with the solvent (entries 7 and 13), indicating that the catalytic site is heterogeneous. The reaction using 2eA was completed within 12 h (entry 14). Reducing the reaction temperature to 0 °C did not enhance the enantioselectivity, whereas the yield dropped to 78% despite the extended reaction time (48 h) (entry 15). Appropriate tuning of the dicarboxylate spacer and disulfonate structure of these ionic polyesters led to a suitable conformation of the polymer main chain. The conformation affected the microenvironment of the catalytic site, which enhanced the catalytic performance in the asymmetric reaction.

Substrate scope and reusability of chiral imidazolidinone salt polyester in asymmetric Diels-Alder reaction

An ionic polyester functionalized with chiral imidazolidinone salt **2eA** was used for asymmetric Diels–Alder reactions of some aldehydes and ketones to verify the substrate generality (Table 7). The reaction between 4-fluorocinnamaldehyde **15** and 1,3-cyclopentadiene **13** afforded these adducts **16** in 93% yield and with 90% ee (*exo*) and 90% ee (*endo*) (entry 1). The reaction between 2-methoxycinnmahyde **17** and **13** produced **18** in quantitative yield and with excellent ee (99% ee for *exo* isomer)(entry 2). The reaction of acrolein **19** and **13** proceeded with moderate enantioselectivity (entry 3). The same polymeric imidazolidinone salt **2eA** was used for the asymmetric Diels–Alder reaction of **19** and 2,3-dimethylbutadiene **21** and exhibited high enantioselectivity (entry 4). Therefore, the novel ionic polyester functionalized with chiral imidazolidinone salt **2eA** has the substrate generality in the reaction.



[a] Reaction conducted with 10 mol% of **2eA** in CH₃OH:H₂O (95:5) at 25 °C for 24 h. The catalyst amount is based on the repeating unit of **2eA**. [b] Isolated yield. [c] Determined by ¹H NMR. [d] Determined by HPLC after reduction of aldehydes (CHIRALCEL OJ-H). [e] ee (%) determined by GC (CHIRALDEX β -PH).

Chiral polyester 1a-OTs was insoluble in general organic solvents such as hexanes, acetone, CH₂Cl₂, ethyl acetate, THF, methanol, DMF, DMSO, and H₂O. Regardless of the heterogeneous system, the Diels-Alder reaction proceeded smoothly, as demonstrated in Table 4 and Table 5. After completion of the Diels-Alder reaction, the polyester was easily separated from the reaction mixture by simple filtration or decantation. The recovered chiral imidazolidinone salt polyester was dried with a vacuum pump at room temperature and used for the next reaction (procedure A, see experimental section). Both the reactivity and enantioselectivity were decreased with the reuse (5th cycle: 93% yield for 72 h, 59% ee for endo isomer). The recovered polymeric catalyst was treated with ptoluenesulfonic acid monohydrate before the next reaction (procedure B, see experimental section), which was effective for the reuse of chiral imidazolidinone salt polyether probably due to the recovery of the counteranion leaching from the polymeric chiral imidazolidinone salt.^[7] slightly inhibited the reduction of the enantioselectivity (5th cycle: 69% ee for endo isomer). The reusability of the ionic polyester functionalized with chiral imidazolidinone salt 2eA was also examined using procedure A (Figure 5). The polymeric catalyst could be reused several times with high enantioselectivity comparable to that of the corresponding model catalyst. To evaluate the catalytic activity in the reuse experiment, the yield at 3 h after starting the each reaction was investigated. The yield tended to decrease slightly with the repeated reaction, but the high reactivity was maintained. The exo/endo selectivity and enantioselectivity were

not changed at all in the reuse (see Table S2 in the supporting information).





Conclusions

We have successfully synthesized covalent and ionic main-chain chiral polyesters functionalized with chiral imidazolidinone salts. These chiral polyesters were used as polymeric chiral organocatalysts in the asymmetric Diels-Alder reaction of transcinnamaldehvde and 1,3-cyclopentadiene. The chiral imidazolidinone salt polyester with 1,4-phenylene spacer exhibited high reactivity and enantioselectivity (94% ee for endo isomer), comparable to those of the corresponding model catalyst. In addition, the chiral imidazolidinone salt ionic polyester with 2,6-naphthalene disulfonate afforded these Diels-Alder adducts with quantitative yield and excellent enantioselectivity of up to 97% ee for the endo isomer, higher than that obtained by the corresponding monomeric chiral imidazolidinone salt. We observed that the dicarboxylate spacer, counteranion, and disulfonate structure affected the catalytic activity in the reaction. The ionic chiral polyester was easily recovered and could be reused several times without significant loss of the enantioselectivity. A study on the influence of the molecular weight of main-chain ionic polymeric chiral catalyst on the catalytic performance is underway.

Experimental Section

General procedure for synthesis of covalent main-chain chiral polyesters 1

A 50-mL round-bottomed flask equipped with a magnetic stirring bar was charged with $4^{[7]}$ (0.340 g, 1.00 mmol), benzyltributylammonium chloride (3.1 mg, 0.01 mmol), and 1 M NaOH aqueous solution (5.0 mL, 5.00 mmol). Then, 5 (1.00 mmol) in 12 mL of CH₂Cl₂ was added dropwise to the mixture at room temperature and the mixture was vigorously

stirred for 3 h. After the solvent was removed by a vacuum pump, the residue was washed with hot water and ethyl acetate. The solid was dried under vacuum to produce **6** as a pale yellow powder.

6a: 99% yield; IR (KBr): v = 1739 (C=O), 1640 (C=O), 1263 (C=O), 1167 (C=N) cm⁻¹; solid state ¹³C NMR: (100 MHz): $\delta = 36.7, 42.8, 50.5, 70.2, 85.8, 89.0, 109.0, 123.7, 130.2, 138.9, 141.5, 145.9, 158.3, 173.2, 187.3; <math>M_n$ (SEC) = 7.2 kg/mol , M_w (SEC) = 18.8 kg/mol, $M_w/M_n = 2.61$.

An acid (0.60 mmol) was added to a suspension of **6** (0.20 mmol) in methanol (2.0 mL). Then, the reaction mixture was stirred at room temperature for 2 h. After the suspension was filtered using a glass filter, the residue was washed with methanol (2 x 5 mL). The solid was dried under vacuum to produce **1** as a white solid, which was used for the following asymmetric reaction without further purification.

General procedure for synthesis of ionic main-chain chiral polyesters 2

A 50-mL round-bottomed flask equipped with a magnetic stirring bar was charged with **9** (0.500 mmol) and 3 mL of H₂O. Then, **8** (0.500 mmol) in 9 mL of CH₂Cl₂ was added to the mixture at room temperature, followed by vigorous stirring for 6 h. After the solvent was removed using a vacuum pump, the residue was washed with CH₂Cl₂ and H₂O. The solid was dried under vacuum to produce **2** as an off-white powder.

2eA: An off-white powder. 95% yield; ¹H NMR (400 MHz, DMSO- d_{6} , $\delta = 2.50$ (DMSO)): $\delta = 1.47$ (s, 6H, CH₃), 1.58 (s, 6H, CH₃), 1.73 (br, 4H, CH₂CH₂), 2,64 (br, 4H, CH₂CO), 2.84 (br, 4H, CH₂CH₂), 2.94–3.00 (m, 2H, CH₂Ph), 3.46 (br, 2H, CH₂N), 4.67 (br, 2H, CH), 7.07 (d, J = 7.9 Hz, 4H, Ar), 7.30–7.38 (m, 14H, Ar, Ph), 7.71 (d, J = 8.2 Hz, 2H, Ar), 7.91 (d, J = 8.5 Hz, 2H, Ar), 8.12 (s, 2H, Ar); ¹³C NMR: (100 MHz, DMSO- d_{6} , $\delta = 39.5$ (DMSO)): $\delta = 23.7$, 24.7, 26.2, 33.2, 33.8, 35.9, 41.3, 57.9, 76.5, 121.7, 123.8, 124.3, 126.6, 128.1, 128.4, 129.3, 129.9, 132.0, 137.5, 145.9, 149.0, 171.7; M_n (SEC) = 4.8 kg/mol, M_w (SEC) = 9.7 kg/mol, $M_w/M_n = 2.00$; $[\alpha]_D^{20} = -47.5$ (c = 0.990 g/dL in DMF).

General procedure for asymmetric Diels–Alder reaction of *trans*-cinnamaldehyde and 1,3-cyclopentadiene catalyzed by main-chain chiral polyester

A 5-mL round-bottom flask equipped with a magnetic stirring bar was charged with trans-cinnamaldehyde 12 (0.264 g, 2.00 mmol), main-chain chiral polyester 1 or 2 (0.20 mmol of catalyst), and 1.0 mL of CH₃OH/H₂O (95/5, v/v) mixed solvent. After three freeze-thaw cycles under liquid nitrogen, the mixture was stirred at room temperature for 10 min. Then, 1,3-cyclopentadiene 13 (0.397 g, 6.00 mmol) was added to the mixture, which was stirred at 25 °C for 24 h. After removing the solvents using a vacuum pump, the residue was extracted with CH₂Cl₂. The solvent of the organic layer was removed with a vacuum pump, and the residue was added to CH2Cl2:H2O:trifluoroacetic acid (2:2:1 mL). After stirring the mixture for 2 h, the mixture was neutralized by saturated NaHCO3 aqueous solution. The mixture was extracted with 5 mL of Et₂O three times, and the organic layer was dried with anhydrous MgSO₄. After removing MgSO₄ by filtration, the solvent of the filtrate was removed with a

vacuum pump, and the residual liquid was purified using silica gel column chromatography (with 1:19 ethyl acetate/hexanes as an eluent). The Diels–Alder adducts **14** were obtained as colorless liquids. The yield and *exo/endo* ratio were determined using ¹H NMR through comparison of the proton signals of the aldehyde. The enantiomeric excess of *exo* and *endo* isomers was determined by GC analysis (Astec CHIRALDEX β -PH; injection temperature of 180 °C, detection temperature of 180 °C, the column temperature was increased from 120 °C to 150 °C with 5 °C/min and then to 180 °C with 1 °C/min; retention time: 26.2 min (*exo*(2*R*)), 26.8 min (*exo*(2*S*)), 27.3 min (*endo*(2*R*)), and 27.7 min (*endo*(2*S*)).

General procedure for reuse of main-chain chiral polyester in the asymmetric Diels-Alder reaction

Procedure A:

The main-chain chiral polyester was isolated from the reaction mixture by simple filtration or decantation. The recovered mainchain chiral polyester was dried with a vacuum pump at room temperature. A 5-mL round-bottom flask equipped with a magnetic stirring bar was charged with **12** (0.264 g, 2.00 mmol), recovered main-chain chiral polyester, and 1.0 mL of CH₃OH/H₂O (95/5, v/v) mixed solvent. After three freeze-thaw cycles under liquid nitrogen, the mixture was stirred at room temperature for 10 min. Then, **13** (0.397 g, 6.00 mmol) was added to the mixture, which was stirred at 25 °C. The reaction was monitored by TLC or ¹H NMR. The procedures of the following work and hydrolysis were the same as those of the first reaction.

Procedure B:

The main-chain chiral polyester was isolated from the reaction mixture by simple filtration or decantation. A methanol solution of *p*-toluenesulfonic acid monohydrate (3 equivalents relative to imidazolidinone) was added to the recovered main-chain chiral polyester at room temperature, and the mixture was stirred for 2 h. The polymer was washed with methanol and dried with a vacuum pump at room temperature. The following procedure was as same as that used for *procedure A*.

Acknowledgements

This work was partially supported by JSPS KAKENHI Grant Number 2475103 and 26105729 (Grant-in-Aid for Scientific Research on Innovative Areas "Advanced Molecular Transformations by Organocatalysts").

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Entry for the Table of Contents

Layout 2:

FULL PAPER



Novel polyesters containing chiral imidazolidinone salts in the main chain were successfully synthesized by polycondensation or neutralization polymerization and applied them as heterogeneous polymeric chiral organocatalysts to the asymmetric Diels-Alder reaction of *trans*-cinnamaldehyde and 1,3-cyclopentadiene. These polymeric catalysts exhibited high enantioselectivity of up to 97% ee for the *endo* isomer.

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Polyesters Containing Chiral Imidazolidinone Salts in Polymer Main chain: Heterogeneous Organocatalysts for Asymmetric Diels-Alder Reaction