

# Asymmetric Diels–Alder polymerization using a chirally modified Lewis acid catalyst

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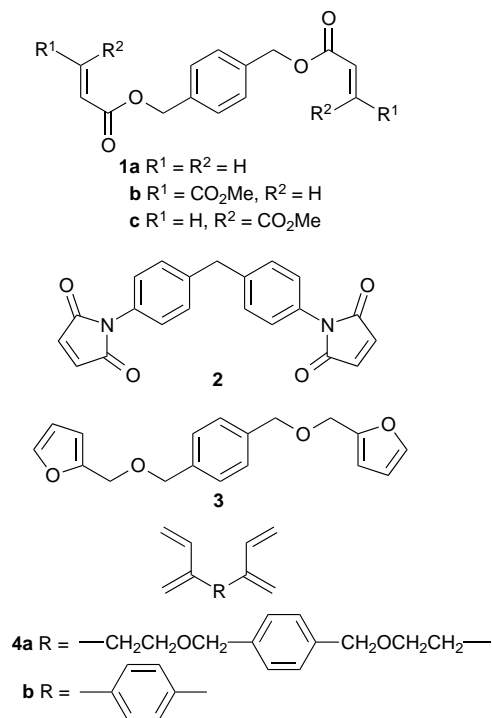
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**The asymmetric Diels–Alder reaction between bisdiene and bisdienophile monomers occurs in the presence of a chirally modified Lewis acid catalyst to give optically active polymers.**

Synthesis of optically active polymers has attracted a great deal of interest and a large number of papers on asymmetric polymerization have been published.<sup>1</sup> An important contribution in this area is the preparation of such polymers having macromolecular asymmetry that originates from the helical structure; these include the polymerization of methacrylates,<sup>2</sup> chloral,<sup>3</sup> isocyanides<sup>4–6</sup> and isocyanates.<sup>7</sup> On the other hand, in the recent remarkable development of catalytic asymmetric synthesis, many useful reactions have been proposed for C–C bond formation with induction of chirality. However, there are only a few reports on asymmetric polymerization based on such enantioselective C–C bond formations using chiral catalysts. For example, some successful asymmetric alternating copolymerizations of  $\alpha$ -olefins with carbon monoxide have been reported only recently.<sup>8,9</sup> Of the excellent asymmetric transformations developed, the enantioselective Diels–Alder reaction is one of the most important C–C bond formation reactions to create a unique chiral cyclic structure. Indeed, recent extensive studies on designing chiral Lewis acids based on boron, aluminium and titanium led to fruitful results in the control of the absolute stereochemistry of various pericyclic reactions, particularly Diels–Alder reactions producing various enantiopure cyclic adducts, key starting materials for synthesis of complex optically active compounds.<sup>10</sup> This impressive stereoselectivity of chiral Lewis acid catalysts in Diels–Alder reactions presents unprecedented opportunities for the molecular design of polymers that are difficult to prepare with other polymerization methods. Asymmetric, Lewis acid catalysed, Diels–Alder polymerization should provide a novel strategy for the synthesis of optically active polymers whose chirality derives from configurational main-chain stereochemistry. Although polymer synthesis *via* repetitive Diels–Alder reactions is well known for the preparation of thermostable polyimides and conjugated polymers with ladder structures,<sup>11–15</sup> to the best of our knowledge, a chiral polymer has not been synthesized by asymmetric Diels–Alder polymerization. Here we report the asymmetric Diels–Alder polymerization between bisdiene and bisdienophile monomers in the presence of a chirally modified Lewis acid catalyst.

We designed several bifunctional monomers.  $\alpha,\beta$ -Unsaturated esters are well known to be important dienophiles in Diels–Alder reactions. Bisdienophile monomers **1** were thus easily prepared from  $\alpha,\alpha'$ -dichloro-*p*-xylene and the appropriate carboxylic acids such as acrylic acid **1a**, monomethyl fumarate **1b** and monomethyl maleate **1c**. *N*-Phenylmaleimide is another reactive dienophile. Useful bisdienophile, 1,1'-(methylenedi-4,1-phenylene)bismaleimide **2** is commercially available, and has often been used as a Diels–Alder monomer.<sup>16,17</sup> Since furyl and butadienyl groups are well known in Diels–Alder chemistry, we designed bisdiene monomers having these structures. Bisdiene **3** and **4a** were prepared from  $\alpha,\alpha'$ -dichloro-*p*-xylene and furfuryl alcohol and 3-methylenepent-4-enol,<sup>†</sup> respectively. The monomer **4b** was also easily

prepared by Ni-catalysed Grignard coupling<sup>18</sup> of the bis-Grignard reagent from 1,4-dibromobenzene with chloroprene. Monomer **4a** contains a flexible methylene chain, compared to the relatively rigid structure available in **4b**, in which the butadienyl group links directly to the benzene ring.

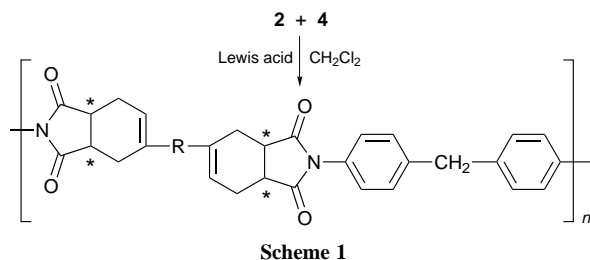


First, we tried to polymerize the bisdienophile **1** with bisdiene monomers. However, we found that the reactivity of **1** is not sufficient to obtain chiral polymers in the presence of Lewis acid catalyst at room temperature. On the other hand, although no reaction between bismaleimide **2** and bisdiene **3** occurred at room temperature in the absence of catalyst, added diethylaluminium chloride (Et<sub>2</sub>AlCl) as Lewis acid interacted with carbonyl oxygen of **2** and the rate of the reaction with **3** was enhanced considerably to give the Diels–Alder polymer smoothly with high molecular weight (Table 1, run 1). Since enantioselective Diels–Alder reactions have been extensively studied by using chiral metal complexes,<sup>10,19,20</sup> and high enantioselectivities were obtained by using chiral aluminium chloride generated *in situ* from Me<sub>3</sub>Al or Et<sub>2</sub>AlCl with chiral diols<sup>21,22</sup> and bis(sulfonamide),<sup>23</sup> we first chose chiral aluminium complex **6** as a catalyst for the asymmetric Diels–Alder polymerization of these monomers. The obtained polymer showed optical activity as shown in Table 1 (run 2). The butadienyl group of **4** also reacted with **2** in the presence of a chiral Lewis acid catalyst to afford optically active polymers in quantitative yield (Scheme 1). Asymmetric polymerization of **4a** and **2** with a chiral Lewis acid gave optically active polymer **5a** having somewhat lower molecular weight. The higher molar optical rotation ([ $\Phi$ ]<sub>D</sub> +94) for the polymer from **4a** was

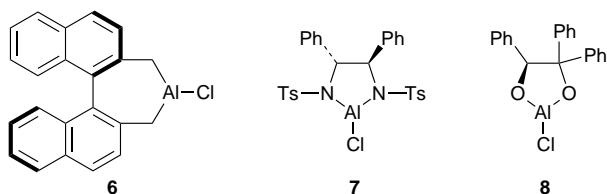
**Table 1** Asymmetric Diels–Alder polymerization between bisdienophile **2** and bisdiene monomers<sup>a</sup>

Run	Lewis acid	Bisdiene monomer	Polymer				
			Yield (%) <sup>b</sup>	$M_n^c$	$M_w/M_n^c$	$[\Phi]_D^d$	$[\Phi]_{435}^d$
1	Et <sub>2</sub> AlCl	<b>3</b>	46	15 000	1.33	—	—
2	<b>6</b>	<b>3</b>	79	12 000	2.19	−12 <sup>e</sup>	—
3	<b>6</b>	<b>4a</b>	99	4 800	1.36	17	—
4	<b>6</b>	<b>4b<sup>f</sup></b>	99	9 800	1.51	243	578
5	<b>6</b>	<b>4b<sup>g</sup></b>	99	10 800	1.90	114	281
6	<b>7</b>	<b>4a</b>	99	5 800	1.26	−35	—
7	<b>7</b>	<b>4b<sup>h</sup></b>	99	12 100	1.85	−14	—
8	<b>8</b>	<b>4a</b>	99	4 500	1.28	94	—
9	<b>8</b>	<b>4b<sup>i</sup></b>	99	13 200	1.74	7.6	—

<sup>a</sup> Reaction was carried out with bisdienophile **2** (1 equiv.) and bisdiene (1 equiv.) in the presence of 20 mol% of Lewis acid catalyst in CH<sub>2</sub>Cl<sub>2</sub> at room temp. for 24 h, unless otherwise noted. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by GPC measurement with polystyrene standard. <sup>d</sup> Measured in CHCl<sub>3</sub>, *c* 1.0. <sup>e</sup> Measured in DMF, *c* 1.0. <sup>f</sup> At −30 °C, 6 h. <sup>g</sup> At room temp., 6 h. <sup>h</sup> At −78 °C, 6 h + room temp., 6 h. <sup>i</sup> At room temp., 6 h.



attained when the catalyst **8** was used (Table 1, run 8). Further, use of sterically more rigid bisdiene monomer **4b** having reactive phenylbutadiene units has proved to exhibit excellent polymerization behavior. The corresponding chiral polymers **5b** were obtained with relatively higher molar optical rotations up to  $[\Phi]_{435} +578$  (Table 1, run 4) by using (*R*)-1,1'-binaphth-2-ol derived Lewis acid catalyst **6**. This is the first example of synthesis of the chiral polymer having a high optical rotation value using asymmetric Diels–Alder polymerization.‡



Another feature of this polymerization is that optically active prepolymers with reactive end groups accessible for further reactions can be readily obtained. Nonstoichiometric Diels–Alder polymerization with a slight excess of one monomer should provide the possibility to synthesize such polymers. For example, when a small excess of monomer **2** was polymerized with **3**, a polymer having reactive maleic double bond end groups was obtained, which acts as a good Michael acceptor for further modification of the chiral polymer.

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## Footnotes

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† This compound was successfully prepared by a new method using the ene reaction of trioxane with isoprene in the presence of Et<sub>2</sub>AlCl in CH<sub>2</sub>Cl<sub>2</sub>.

‡ All polymerizations were performed in CH<sub>2</sub>Cl<sub>2</sub>; replacing the solvent with CHCl<sub>3</sub> or THF gave the polymers with only low optical rotations ( $[\Phi]_D +30$  and  $-5.4$ , respectively).

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