Macromolecules

Volume 32, Number 3 February 9, 1999

Optically Active Polymer Synthesis by Diels−Alder Polymerization with Chirally Modified Lewis Acid Catalyst

Koichi Kamahori, Shoichi Tada, Koichi Ito, and Shinichi Itsuno*

Department of Materials Science, Toyohashi University of Technology, Toyohashi 441-8580, Japan

Received September 29, 1998; Revised Manuscript Received November 23, 1998

ABSTRACT: A series of copolymers have been synthesized by Diels−Alder polymerization of bisdienophile monomer with bisdiene monomer. Bismaleimides (**1**) and bis(α,*β*-unsaturated ester)s (**4**) were prepared and used as bisdienophile monomer. Furfuryl and butadienyl moieties were chosen as the diene part of the bisdiene monomers (**2**, **5**). Repetitive Diels−Alder reactions between these monomers in the presence of Lewis acid catalyst yielded alternative Diels−Alder polymers (**6**, **12**, **13**, **15**). On the basis of these results, asymmetric Diels−Alder polymerization was investigated. The use of enantiopure Lewis acid catalysts (**7**−**10**) in the Diels−Alder polymerization of above monomers resulted in the formation of optically active polymers having the asymmetric carbons in their main chain.

Introduction

Chiral synthetic polymers are of special interest due to their applications to chromatographic supports, polymeric reagents, and catalysts.[1] In particular, the synthesis of optically active polymers with chirality in the main chain is currently attracting much attention.[2] Asymmetric synthesis polymerization[1] of prochiral monomers is one of the ways available for synthesizing such optically active polymers.[3,4] After Natta et al.[5] reported the asymmetric anionic polymerization of methyl sorbate as the first example of asymmetric synthesis polymerization, a number of experiments on the induction of configurational main-chain chirality during polymerization have been demonstrated.[3] The following are the recent successful approaches to the chiral synthetic polymers by asymmetric synthesis polymerization; asymmetric alternating copolymerization of α-olefins with carbon monoxide,[6] asymmetric polyaddition of 1,3-dimercaptobenzene to dibenzylidene acetone,[7] asymmetric cyclopolymerization of dienes with a chiral catalyst,[8] and asymmetric anionic polymerization of achiral N-substituted maleimide.[9−11]

Considerable attention has been focused on the catalytic asymmetric C−C bond formation reactions.[12] Recently, highly efficient methodologies and catalysts have been developed to synthesize various kinds of optically active compounds. Some of them can be applied to chiral polymer synthesis. For instance, Lewis acid-mediated additions of dienes to electron-deficient dienophiles has proven to be a powerful method for the preparation of many different types of cyclic ring systems. The enantioselective Diels−Alder reaction between dienophile and diene with a chirally modified Lewis acid catalyst[13] is one of the most important carbon−carbon bond formation reactions to create a chiral cyclic structure. The general methodology disclosed by Koga and co-workers[14] as early as 1979 is still in use for this chemistry. After Koga's catalyst, various chiral Lewis acid catalysts have been developed for Diels−Alder reaction. This asymmetric C−C bond formation reaction is applicable to the synthesis of optically active polymers if the same reaction occurs between bisdiene and bisdienophile. Although such repetitive Diels−Alder reactions have been used to synthesize polymers from a wide variety of bisdiene and bisdienophilic compounds,[15] optically active polymers have not been obtained by the asymmetric Diels−Alder polymerization. Most Diels−Alder polymerizations were achieved by thermal polymerizations without catalyst.[16] Highly reactive monomers such as bistriazolinediones react with bisdiene monomers even at room temperature to give the Diels−Alder polymers in high yield.[17] Lewis acid-catalyzed Diels−Alder polymerization has not been studied. In a preliminary report, we described the possibility of the asymmetric Diels−Alder polymeriza-

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* Corresponding author: Tel and Fax +81-532-44-6813; e-mail itsuno@tutms.tut.ac.jp.

10.1021/ma9815410 CCC: $18.00

tion with a chiral Lewis acid as catalyst and found this polymerization method to be useful for obtaining optically active polymers having configurational main-chain chirality.[18] In this paper we report in full the results of our earlier investigations that show that the asymmetric Diels−Alder polymerizations between bisdienophile and bisdiene monomers represent a convenient method for the synthesis of optically active polymers.

Experimental Section

General. All reactions were carried out under an atmosphere of nitrogen. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and was freshly distilled just before use. Dichloromethane and hexamethylphosphoramide (HMPA) were distilled from calcium hydride. Benzene was distilled from calcium hydride after being washed successively with concentrated H_2SO_4, water, aqueous 1 N NaOH, and water. Toluene solution of chloroprene was a gift from the Denkikagaku Kogyo Co. All other commercial chemicals were used without further purification. 2-Phenyl-1,3-butadiene was prepared according to the reported procedure.[19] Both ^{1}H (270 MHz) and ^{13}C (67.8 MHz) NMR spectra were recorded on a Jeol JNM-GX270 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. IR spectra were recorded on a Jeol JIR-7000 FT-IR spectrometer in KBr. Microanalyses were obtained with a Yanaco MT-3 CHN Corder. Melting points were taken on a Yanaco micro melting apparatus and were uncorrected. A precoated silica gel plate (Merck 5554, 60F254) was used for thin-layer chromatography. Silica gel (Wakogel C-200) was used for column chromatography. Optical rotations were taken on a Jasco DIP-140 digital polarimeter with a 10 cm thermostated microcell. Gel-permeation chromatography (GPC) was performed on Tosoh HLC-8020 gel-permeation chromatograph equipped with a UV-8011. The eluent was *N*,*N*′-dimethylformamide (DMF), and flow rate was 1.0 mL min^{-1}. The column used was TSK-Gel G3000HXL. A molecular weight calibration curve was obtained by using standard polystyrene. Thermogravimetric analysis (TGA) was carried out with a Rigaku Thermo Plus 2, TG 8120, at a heating rate of 5 °C/min under Ar.

Preparation of *N*,*N*′-Hexamethylene Bismaleimide (1b).[20] To a suspension of maleic anhydride (5.4 g, 55 mmol) in benzene (150 mL) was added dropwise a solution of hexamethylenediamine (2.9 g, 25 mmol) in benzene (100 mL) at room temperature. After the mixture was stirred for 1 h at the same temperature, $ZnBr_2$ (12.4 g, 55 mmol) and a solution of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (15.8 mL, 75 mmol) in 30 mL of benzene were added successively. The mixture was stirred for 2 h at reflux temperature and then cooled to room temperature. The reaction mixture was poured into 0.5 N HCl (200 mL) and extracted with ethyl acetate (2 × 150 mL). The organic layer was washed with saturated $NaHCO_3$ aqueous solution (2 × 150 mL) and brine (2 × 150 mL) and then dried over Na_2SO_4 and concentrated. The residue was purified by recrystallization with benzene to give 3.8 g (55%) of **1b**, mp 143−144 °C (lit.[20] mp 140−141 °C).

Preparation of Difurfuryl Terephthalate (2a). To a solution of furfuryl alcohol (7.60 mL, 88 mmol) and pyridine (3.23 mL, 80 mmol) in THF (10 mL) was added dropwise a solution of terephthaloyl chloride (5.76 mL, 40 mmol) in THF (15 mL) at 0 °C. The mixture was stirred for 3 h at room temperature, and water was added at 0 °C. After THF was removed by rotary evaporation, the mixture was extracted with ether (2 × 150 mL). The organic layer was washed with brine (2 × 150 mL), dried over $MgSO_4$, and then concentrated. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (5:2) as an eluent to give 5.0 g (38%) of **2a**. IR (KBr, cm^{-1}) 3126, 2947, 1731, 1591, 1498, 1442, 1373, 1281, 1126, 1065, and 1009; ^{1}H NMR ($CDCl_3$) δ 5.23 (s, 4 H), 6.38 (d, $J = 1.96$ Hz, 2 H), 6.47 (d, $J = 1.47$ Hz, 2 H), 7.35 (d, $J = 1.95$ Hz, 2 H), 7.51 (dd, $J = 3.42$ and 3.42 Hz, 2 H), and 7.72 (dd, $J = 3.42$ and 3.42 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 59.2, 106.9, 110.6, 111.0, 129.1, 131.2, 143.4, 149.1, and 167.0. Anal. Calcd for $C_{18}H_{14}O_6$: C, 66.25; H, 4.33. Found: C, 65.94; H, 4.31.

Preparation of α,α′-Difurfuryloxy-*p*-xylene (2b). To a suspension of sodium hydride (NaH 60 wt % in oil, 7.0 g, 150 mmol) in THF (60 mL) was added dropwise a solution of furfuryl alcohol (10.42 mL, 120 mmol) in THF (30 mL) at 0 °C. The mixture was stirred for 2 h at room temperature, and then a solution of α,α′-dichloro-*p*-xylene (8.75 g, 50 mmol) in THF was added dropwise, followed by heating of the mixture to 60 °C and stirring for 24 h. After cooling of the mixture to room temperature, water was added at 0 °C and then THF was removed by rotary evaporation. The mixture was extracted with ether (2 × 150 mL). The organic layer was washed with brine (2 × 150 mL), dried over $MgSO_4$, and then concentrated to afford a crude product. This crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (24:1) as an eluent to give 14.6 g (98%) of **2b** as a colorless crystals: mp 48−49 °C; IR (KBr, cm^{-1}) 3116, 2860, 1731, 1605, 1502, 1410, 1348, 1267, 1225, 1151, and 1093; ^{1}H NMR ($CDCl_3$) δ 4.51 (d, $J = 17.6$ Hz, 4 H), 4.56 (d, $J = 4.4$ Hz, 4 H), and 7.33−7.42 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ −0.3, 63.8, 71.6, 109.4, 110.2, 128.0, 137.4, 142.2, and 151.7. Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08. Found: C, 72.40; H, 6.08.

Preparation of Furfuryl Benzyl Ether (3). To a suspension of sodium hydride (NaH 60 wt % in oil, 9.0 g, 0.23 mol) in THF (150 mL) was added dropwise a solution of furfuryl alcohol (8.7 mL, 0.10 mol) in THF (50 mL) at 0 °C. The mixture was stirred for 2 h at room temperature, and then a solution of benzyl chloride (13.7 mL, 0.12 mol) in THF was added dropwise and the mixture was stirred for 48 h at the same temperature. After water was added at 0 °C, THF was removed by rotary evaporation. The mixture was extracted with ether (3 × 150 mL). The organic layer was washed with brine (2 × 150 mL), dried over $MgSO_4$, and then concentrated to afford a crude product. This crude product was purified by distillation (150 °C/1 mmHg) to give 10.0 g (53%) of **3** as a colorless oil; IR (neat, cm^{-1}) 3034, 2902, 2856, 1724, 1605, 1500, 1454, 1359, 1217, 1147, and 1008; ^{1}H NMR ($CDCl_3$) δ 4.46 (s, 1 H), 4.53 (s, 1 H), 6.32 (d, $J = 0.97$ Hz, 2 H), and 7.25−7.40 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 63.7, 71.7, 109.3, 127.6, 127.8, 128.3, and 142.6.

Preparation of α,α′-Bis(acryloyloxy)-*p*-xylene (4a). To a solution of α,α′-dichloro-*p*-xylene (2.6 g, 15 mmol) and potassium carbonate (10.4 g, 75 mmol) in HMPA (30 mL) was added dropwise a solution of acrylic acid (2.6 g, 36 mmol) in HMPA (10 mL) at 0 °C. After the mixture was stirred for 18 h at 60 °C, 150 mL of water was added, and the mixture was extracted with dichloromethane (2 × 150 mL). The dichloromethane solution was washed with brine (2 × 150 mL), dried over $MgSO_4$, and then concentrated to afford a crude product. This crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (9:1) as an eluent to give 3.3 g (90%) of **4a** as a colorless crystals: mp 76.5−76.8 °C; IR (KBr, cm^{-1}) 1718, 1633, 1520, 1406, 1365, 1298, and 1205; ^{1}H NMR ($CDCl_3$) δ 5.20 (s, 4 H), 5.85 (dd, $J = 1.96$ and 1.46 Hz, 2 H), 6.16 (dd, $J = 10.25$ and 10.25 Hz, 2 H), 6.45 (dd, $J = 1.46$ and 1.46 Hz, 2 H), and 7.39 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 65.9, 128.2, 128.4, 131.1, 136.0, and 165.9. Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 67.33; H, 5.88.

Preparation of α,α′-Bis(methylmaleoyloxy)-*p*-xylene (4b). Bisdienophile monomer (**4b**) was obtained from α,α′-dichloro-*p*-xylene and potassium carbonate and methyl hydrogen maleate[21] under the reaction conditions described for **4a** in 97% yield as a colorless crystals: mp 46.0−47.0 °C; IR (KBr, cm^{-1}) 3055, 2958, 1711, 1639, 1524, 1443, and 1404; ^{1}H NMR ($CDCl_3$) δ 3.69 (s, 6 H), 5.22 (s, 4 H), 6.27 (s, 4 H), and 7.39 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 52.0, 66.5, 128.6, 129.3, 135.4, and 165.4. Anal. Calcd for $C_{18}H_{18}O_8$: C, 59.66; H, 5.01. Found: C, 59.24; H, 4.93.

Preparation of α,α′-Bis(methylfumaroyloxy)-*p*-xylene (4c). Bisdienophile monomer (**4c**) was obtained from α,α′-dichloro-*p*-xylene and potassium carbonate and methyl hydrogen fumarate[21] under the conditions described for **4a** in 79% yield as colorless crystals: mp 124.4−125.5 °C; IR (KBr, cm^{-1})

1714, 1437, 1375, 1313, and 1159; ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 6 H), 5.24 (s, 4 H), 6.90 (s, 4 H), and 7.39 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 52.3, 66.6, 128.6, 133.4, 133.7, 135.6, 164.6, and 165.2. Anal. Calcd for $C_{18}H_{18}O_8$: C, 59.66; H, 5.01. Found: C, 58.90; H, 5.10.

Preparation of α,α′-Bis(3-methylene-4-pentenyloxy)-*p*-xylene (5a). To a solution of isoprene (5 mL, 50 mmol) and trioxane (1.35 g, 15 mmol) in CH_2Cl_2 (100 mL) was added dropwise a diethyl aluminum chloride (47.4 mL, 45 mmol, 0.95 M solution in *n*-hexane) at 0 °C. The mixture was stirred for 12 h at room temperature, and then 10% NaH_2PO_4 aqueous solution (100 mL) and 2 N HCl (100 mL) were poured into the mixture. The resulting mixture was extracted with ether (2 × 100 mL), followed by washing the extract with brine (2 × 100 mL); the product was and then dried over $MgSO_4$ and concentrated. The residue was purified by distillation (60 °C, 1 mmHg) to give 2.7 g (61%) of 3-methylene-4-penten-1-ol (**11**). To a suspension of sodium hydride (NaH 60 wt % in oil, 1.6 g, 40 mmol) in THF (30 mL) was added dropwise a solution of **11** (2.94 g, 30 mmol) in THF (20 mL) at 0 °C. The mixture was stirred for 2 h at room temperature, and then a solution of α,α′-dichloro-*p*-xylene (2.63 g, 15 mmol) in THF was added dropwise. The mixture was heated to 50 °C and stirred for 48 h. After the reaction mixture was cooled to room temperature, water was added at 0 °C and then THF was removed by rotary evaporation. The mixture was extracted with ether (2 × 150 mL). The organic layer was washed with brine (2 × 150 mL), dried over $MgSO_4$, and then concentrated. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (24:1) as an eluent to give 3.75 g (84%) of **5a** as a colorless oil: IR (neat, cm^{-1}) 3089, 2850, 1809, 1593, 1516, 1477, 1456, 1417, 1211, and 1001; ^{1}H NMR ($CDCl_3$) δ 2.55 (t, J = 7.3 and 6.4 Hz, 4 H), 3.61 (t, J = 11.24 and 11.23 Hz, 2 H), and 7.31 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 31.6, 69.0, 72.6, 113.3, 116.9, 127.6, 137.7, 138.7, and 143.0. Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.49; H, 8.87. Found: C, 79.83; H, 8.81.

Preparation of 1,4-Bis(1-methylene-2-propenyl)benzene (5b). To a suspension of Mg powder (3.7 g, 150 mmol) in THF (35 mL) was added dropwise a solution of 1,4-dibromobenzene (5.9 g, 25 mmol) in THF (25 mL), and the resulting mixture was stirred for 12 h at reflux temperature. After the mixture was cooled to room temperature, [Ni(dppp)$_2$Cl$_2$] (0.33 g, 0.6 mmol) was added. At 0 °C, a toluene solution of chloroprene (47% in toluene; 14.0 g, 75 mmol) was added dropwise to the above reaction mixture. The stirring was continued for 24 h at room temperature. The reaction mixture was poured into saturated $NaHCO_3$ aqueous solution (200 mL) and then THF was removed by rotary evaporation. The mixture was extracted with ether (2 × 200 mL). The organic layer was washed with brine (2 × 200 mL), dried over $MgSO_4$, and then concentrated. The residue was purified by column chromatography on silica gel with hexane as an eluent to give 2.0 g (44%) of **5b** as a colorless oil: IR (neat, cm^{-1}) 1578, 1510, 1313, and 1107; ^{1}H NMR ($CDCl_3$) δ 5.21−5.30 (m, 8 H), 6.62 (dd, J = 10.7 and 11.2 Hz, 2 H), and 7.31 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 116.7, 117.1, 128.0, 138.0, 138.9, and 147.9. Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.46; H, 7.71.

Lewis Acid-Catalyzed Diels−Alder Polymerization. A typical example of the polymerization is as follows. All glass vessels were heated in vacuo before use, filled with dry argon, and handled in a stream of dry nitrogen. Into a dichloromethane (4 mL) solution of Et_2AlCl (0.1 mmol) was added a solution of **1a** (0.358 g, 1 mmol) and **2b** (0.298 g, 1 mmol) in dichloromethane. The reaction mixture was stirred at room temperature for 24 h and then poured into hexane to give a white precipitate of the polymer **6**. The precipitate was collected on a glass filter and washed with ether. Yield was 0.303 g (46%). IR (KBr, cm^{-1}) 3466, 2914, 2858, 1776, 1711, 1508, 1379, 1180, and 1088; ^{1}H NMR δ 2.50 (s, 2 H), 3.20−3.40 (m, 4 H), 3.90−4.15 (m, 4 H), 4.40−4.65 (m, 4 H), 5.35 (s, 2 H), 6.55 (br s, 4 H), and 7.00−7.40 (m, 12 H).

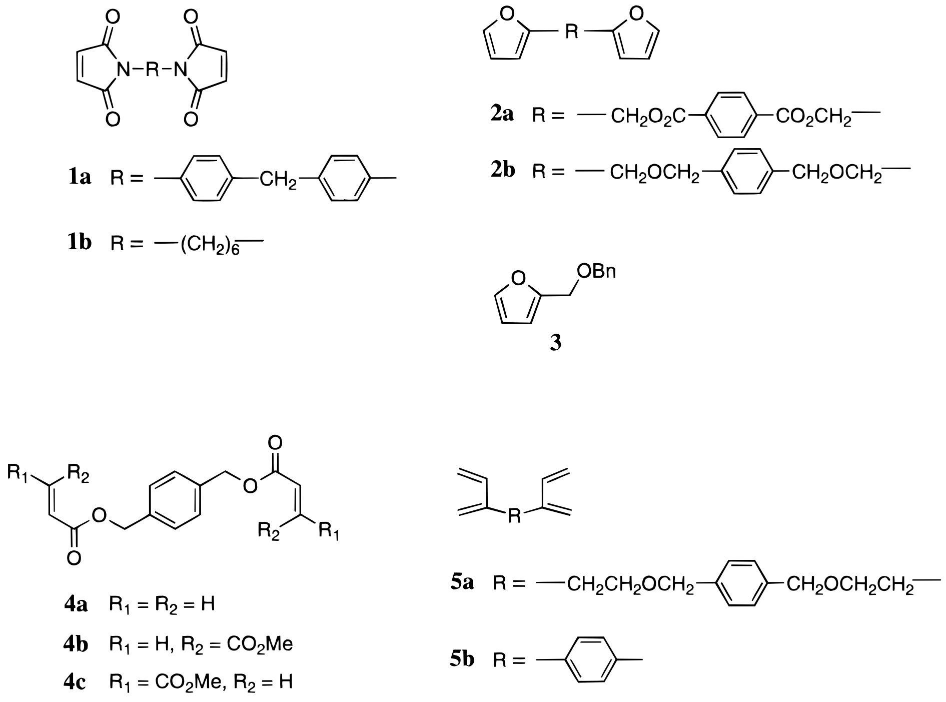
Asymmetric Diels−Alder Polymerization with Chirally Modified Lewis Acid Catalyst. Chirally modified Lewis acid catalyst (**7**) was generated in situ by stirring Et_2AlCl (0.95 M solution in hexane, 0.12 mmol) and (*R*)-(+)-1,1′-bi-2-naphthol (0.034 g, 0.12 mmol) suspended in 2 mL of dichloromethane for 1 h at room temperature. Into the chiral catalyst solution was added a solution of **1a** (0.215 g, 0.6 mmol) and **5b** (0.110 g, 0.6 mmol) at room temperature. The reaction mixture was stirred for 2 h at room temperature and then poured into hexane to give a precipitate of the polymer **15a**. The precipitate was then collected on a glass filter and washed with ether. Purification by reprecipitation into hexanes−ether gave the white powder of **15a**, 0.322 g (99%). $[\Phi]_{589}$ 114° (*c* 1.0, $CHCl_3$); IR (KBr, cm^{-1}) 3466, 3034, 2910, 2848, 1709, 1516, 1387, and 1174; ^{1}H NMR δ 2.00−4.00 (m, 14 H), 6.17 (br s, 2 H), and 7.00−7.18 (m, 12 H). TGA measurement: The 5% weight loss temperature = 428 °C; the 10% weight loss temperature = 456 °C.

Results and Discussion

Bismaleimide **1a** (Chart 1) has been frequently used as a monomer of Diels−Alder polymerization and a cross-linking agent of diene-containing polymers.[16a,16e,16h] For instance, Kuramoto et al.[16h] reported that Diels−Alder polymerization between difurfuryladipate and **1a** under thermal conditions gave poly(ester-imide). Thus the commercially available bismaleimide **1a** was our first choice of bisdienophile monomer for Lewis acid-catalyzed Diels−Alder polymerization. Bisfurfuryl derivatives **2** were prepared and used as bisdiene monomer. However, our early attempts at the Diels−Alder polymerization of **1a** with **2a** containing ester linkages failed to give the polymeric product both in the absence and the presence of Lewis acids such as $BF_3{\cdot}OEt_2$ and Et_2AlCl at room temperature. Ester carbonyls in **2a** may coordinate to the Lewis acid, which would cause insufficient activation of the maleimide moiety. We then prepared furfuryl benzyl ether **3** as a model compound, which was allowed to react with *N*-phenylmaleimide. Although no reaction occurred without Lewis acid at room temperature, this model reaction took place smoothly with 10 mol % Et_2AlCl to afford the corresponding Diels−Alder adduct in 98% isolated yield. This result encouraged us to apply the bisdiene monomer **2b** containing a benzyl ether linkage to the Lewis acid-catalyzed polymerization. No reaction between bisdienophile **1a** with bisdiene **2b** occurred in CH_2Cl_2 at room temperature without catalyst. However, we found that the addition of Et_2AlCl initiated the polymerization to give the corresponding Diels−Alder polymer as a white powder. Number-average molecular weight (M_n) of the obtained polymer 15 000 was calculated from the GPC analysis with a polystyrene standard (Scheme 1 and Table 1, run 1).

On the other hand, asymmetric Diels−Alder reactions with chiral Lewis acid catalysts have been extensively investigated to prepare optically active cyclic compounds.[13] Various chirally modified Lewis acids containing aluminum, boron, titanium, copper, magnesium, and lanthanides have been developed for the catalytic enantioselective Diels−Alder reactions.[13] We then tried to apply such asymmetric Diels−Alder reactions to the formation of optically active polymers. Since we have found that Et_2AlCl was an efficient catalyst for Diels−Alder polymerization of **1a** and **2b**, we have used a chirally modified aluminum chloride (**7**) (Chart 2) readily prepared from Et_2AlCl and (*R*)−(+)-1,1′-bi-2-naphthol, which has been successfully used in the asymmetric Diels−Alder reaction.[22] This chiral catalyst was tested for the asymmetric Diels−Alder polymerization. The desired Diels−Alder polymer **6** was obtained by using 10 mol % **7** in 79% isolated yield. The molar rotation measurement of DMF solution of **6** showed that

Chart 1



Scheme 1

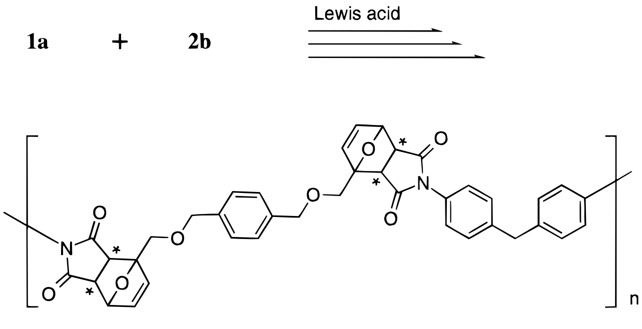


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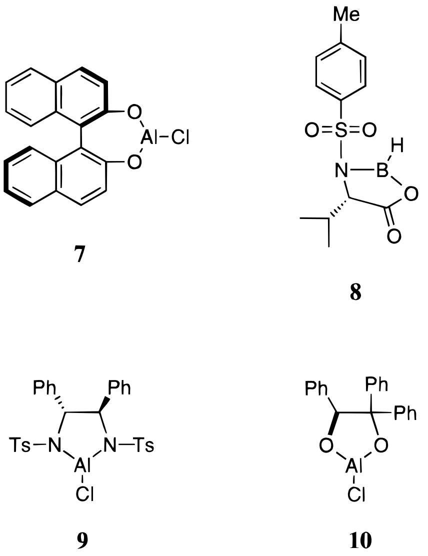
Table 1. Asymmetric Diels–Alder Polymerization of 1a with 2b Using Chiral Lewis Acid[a]

run	Lewis acid	temp (°C)	yield (%)	M_n[b]	M_w/M_n[b]	$[\Phi]_{589}$[c] (deg)
1	Et_2AlCl	rt	46	15 000	1.33	
2	Et_2AlCl	0	44	14 000	1.14	
3	**7**	rt	79	12 000	2.19	−12.0
4	**8**	rt	76	14 000	2.24	−3.00

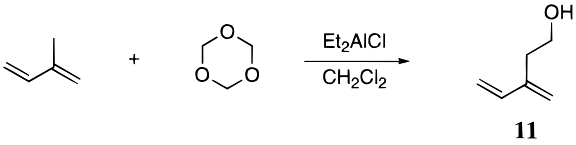
[a] Reaction was carried out with bisdienophile **1a** (1 equiv) and bisdiene **2b** (1 equiv) in the presence of 10 mol % of chirally modified Lewis acid catalyst in CH_2Cl_2 for 24 h. [b] Determined by GPC measurement with polystyrene standard. [c] Measured in DMF, *c* 1.0.

the polymer is optically active, which would be caused from its main-chain chirality induced during asymmetric polymerization reaction (Table 1, run 3). To the best of our knowledge, this is the first example of the asymmetric Diels–Alder polymerization of achiral monomers with a chiral catalyst. We have also used chiral oxazaborolidinone catalyst **8** for asymmetric polymerization of **1a** with **2b**, which showed excellent enantioselectivities in the Diels–Alder reaction between methacrolein and cyclopentadiene.[23,24] Although **8** activated the dienophile sufficiently to yield the Diels–Alder polymer with high molecular weight, the molar rotation observed was lower than that from **7** (Table 1, run 4).

Chart 2



Scheme 2



Butadiene and its derivatives are also well-known dienes used in Diels–Alder reaction. Since we have discovered an efficient synthetic route to the alcohol **11** possessing a butadienyl moiety (Scheme 2), we used this alcohol for the preparation of a novel bisdiene monomer **5a**. We then applied the bisdiene monomer **5a** to Diels–Alder polymerization with **1a** (Scheme 3). The polymerization proceeded smoothly with Et_2AlCl to give the polymer **12** in quantitative yield as shown in Table 2 (run 1). The asymmetric polymerizations were also carried out with 20 mol % of chirally modified Lewis acid catalysts **7**, **9**, and **10**.[25] Optically active polymers

Scheme 3

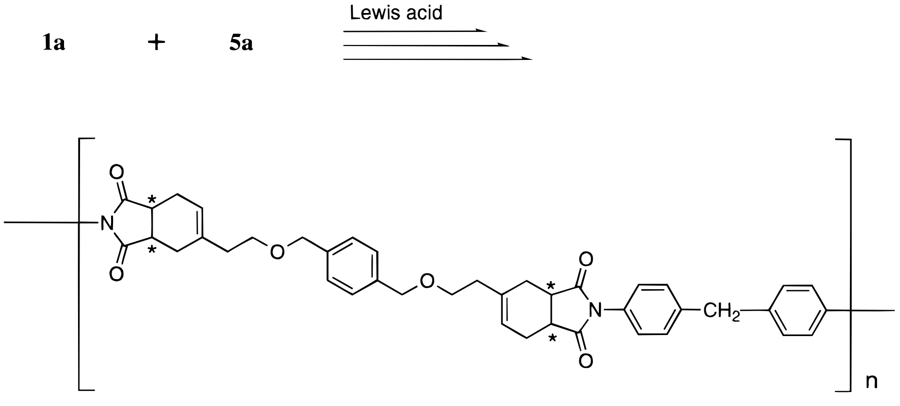


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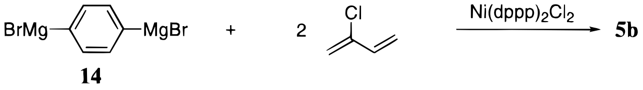
Table 2. Asymmetric Diels−Alder Polymerization of 1a with 5a Using Chiral Lewis Acid[a]

run	Lewis acid	temp (°C)	yield (%)	M_n[b]	M_w/M_n[b]	$[\Phi]_{589}$[c] (deg)
1	Et_2AlCl	rt	99	4100	1.36	
2	**7**	rt	99	4800	1.36	17
3	**7**	−30	88	1700	1.27	19
4	**9**	rt	99	5800	1.26	−35
5	**9**	−30	73	2000	1.23	−13
6	**10**	rt	99	4500	1.28	94
7	**10**	−30	73	2000	1.26	25

[a] Reaction was carried out with bisdienophile **1a** (1 equiv) and bisdiene **5a** (1 equiv) in the presence of 20 mol % of chirally modified Lewis acid catalyst in CH_2Cl_2 for 24 h. [b] Determined by GPC measurement with polystyrene standard. [c] Measured in $CHCl_3$, *c* 1.0.

Scheme 4



Scheme 5

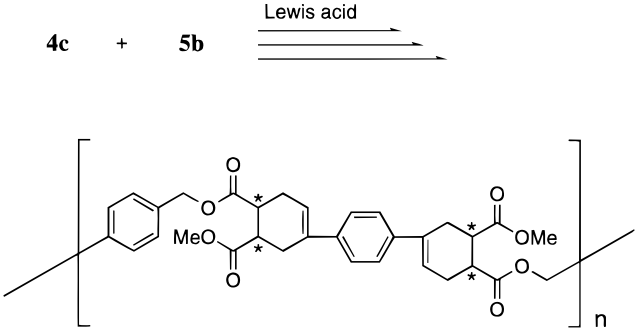


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Table 3. Asymmetric Diels−Alder Polymerization of 4c with 5b Using Chiral Lewis Acid[a]

run	Lewis acid	yield (%)	M_n[b]	M_w/M_n[b]	$[\Phi]_{589}$[c] (deg)
1	**7**	70	2800	1.76	11
2	**8**	66	2700	2.08	42

[a] Reaction was carried out with bisdienophile **4c** (1 equiv) and bisdiene **5b** (1 equiv) in the presence of 100 mol % of chirally modified Lewis acid catalyst in CH_2Cl_2 at room temperature for 24 h. [b] Determined by GPC measurement with polystyrene standard. [c] Measured in $CHCl_3$, *c* 1.0.

were again obtained from the polymerization of **1a** with **5a**. Probably due to somewhat lower reactivity of the diene moiety of **5a**, the molecular weight obtained by this polymerization attained was up to 5800. The lowering the reaction temperature resulted in the decrease of the yield and the degree of polymerization, which may cause the decrease of the molar rotation values of the produced Diels−Alder polymers. In this monomer combination (**1a** and **5a**), the highest molar rotation value was obtained when **10** was used as a chiral catalyst.

Since α,*β*-unsaturated esters are also known to be reactive dienophiles, we have next designed bisdienophile monomers **4a**−**4c** (Chart 1). They were readily prepared in good yield by the reaction between α,α′-dichloro-*p*-xylene with an appropriate α,*β*-unsaturated carboxylic acid in the presence of K_2CO_3 in HMPA.[26] Before polymerization we examined the Diels−Alder reaction of these dienophiles with 2-phenyl-1,3-butadiene in CH_2Cl_2 at room temperature as model reaction. However, in all cases, no reaction occurred without catalyst. Even when Lewis acid was added to the reaction mixture, **4a** was completely recovered after 24 h at room temperature. An excess amount of diene and higher reaction temperature are required to proceed the reaction. Lewis acid-catalyzed reaction of **4b** with 2-phenyl-1,3-butadiene gave the Diels−Alder product contaminated by byproducts. In contrast with the reaction of **4a** or **4b**, the desired Diels−Alder adduct was obtained from **4c** in 90% yield in the presence of 20 mol % Et_2AlCl. On the basis of the model reactions mentioned above, we have then designed a novel bisdiene monomer **5b** having reactive phenylbutadiene structure. The monomer **5b** was prepared by a nickel-catalyzed coupling reaction[19] of di-Grignard reagent **14** with chloroprene (Scheme 4). We examined the asymmetric Diels−Alder polymerization of **4c** with **5b** (Scheme 5 and Table 3). Although no reaction between **4c** and **5b** occurred at room temperature without catalyst, chirally modified Lewis acid catalysts (**7** and **8**) could initiated the polymerization to give optically active Diels−Alder polymers (Table 3, runs 1 and 2). This combination of monomers (**4c** and **5b**) gave polymers having only low molecular weight.

To obtain higher molecular weight polymers in high yield, we have tested various other combinations of dienophiles and dienes. Among many model reactions, we found that 2-phenyl-1,3-butadiene smoothly reacted with *N*-phenylmaleimide in the presence of 10 mol % Et_2AlCl within a few hours to give the corresponding adduct in quantitative yield. Even without catalyst, 89% isolated yield was attained after 14 h. From the above results, **5b** having phenylbutadiene structure and **1a**

Scheme 6

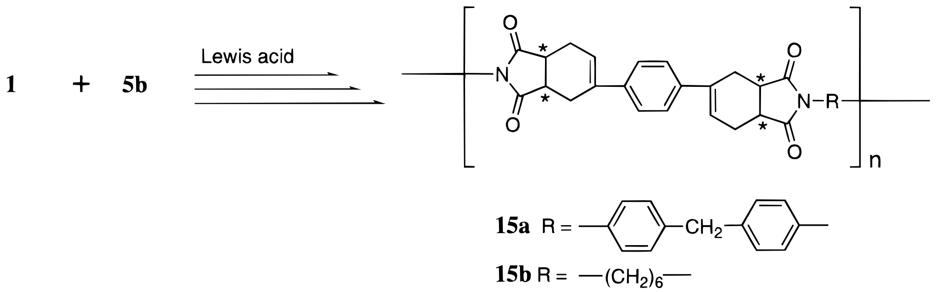

Table 4. Asymmetric Diels–Alder Polymerization of 1 with 5b Using Chiral Lewis Acid[a]

run	bisdieno-phile	Lewis acid	temp (°C)	yield (%)	M_n[b]	M_w/M_n[b]	$[\Phi]_{589}$[c] (deg)
1	**1a**		rt	91	11 300	1.42	
2	**1a**	Et_2AlCl	rt	99	9700	1.44	
3	**1a**	**7**	rt	99	10 800	1.90	114
4	**1a**	**7**	−30	99	9800	1.51	243
5	**1a**	**7**	−78	31	7200	1.20	114
6	**1a**	**7**	−78 to rt	99	10 800	1.84	222
7	**1a**	**9**	rt	99	11 800	2.06	−10
8	**1a**	**9**	−78 to rt	99	12 100	1.85	−14
9	**1a**	**10**	rt	99	13 200	1.74	7.6
10	**1b**	**8**	rt	87	1100	2.36	21
11	**1b**	**7**	rt	82	1500	1.70	184

[a] Reaction was carried out with bisdienophile **1** (1 equiv) and bisdiene **5b** (1 equiv) in the presence of 20 mol % of chirally modified Lewis acid catalyst in CH_2Cl_2. [b] Determined by GPC measurement with polystyrene standard. [c] Measured in $CHCl_3$, *c* 1.0.

having *N*-phenylmaleimide structure were subjected to Diels–Alder polymerization. The polymerization of these monomers proceeded smoothly in CH_2Cl_2 at room temperature without catalyst to give the desired polymer **15a** with high molecular weight in 91% yield (Scheme 6 and Table 4, run 1). Addition of 20 mol % Et_2AlCl as a Lewis acid accelerated the reaction to give the same polymer in quantitative yield within 2 h at room temperature (Table 4, run 2). The asymmetric version of this polymerization was then performed by using 20 mol % chirally modified Lewis acid **7**. Table 4 provides a summary of the typical molar rotation values obtained in the asymmetric polymerization of the monomers together with the yields, molecular weights, and molecular weight distributions. For example, the asymmetric polymerization of **1a** with **5b** using chiral catalyst **7** at room temperature resulted in polymer **15a** with a number-average molecular weight of 10 800 in quantitative yield (run 3), which showed molar optical rotation value $[\Phi]_{589}$ of 114°. When the polymerization was carried out at −30 °C, the chiral polymer having a higher value of molar optical rotation ($[\Phi]_{589}$ 243°) was obtained in quantitative yield (run 4). The lowering of the temperature to −78 °C resulted in decrease of both yield and molar rotation value (run 5). Other chirally modified aluminum chlorides **9** and **10** were prepared and used for the polymerization. Although the optically active polymers were obtained by using **9** or **10** in quantitative yield, molar rotation values were much smaller than those obtained with **7**. Bismaleimide (**1b**) having a hexamethylene chain was also prepared by the reaction of maleic anhydride with hexamethylenediamine in the presence of $ZnBr_2$ and 1,1,1,3,3,3-hexamethyldisilazane.[27] Polymerization of **1b** with **5b** took place to afford the optically active polymer with lower molecular weight (runs 10 and 11).

To understand the thermal stability of the Diels–Alder polymers, thermogravimetric analysis (TGA) of **15a** was performed. TGA data of **15a** showed that the sample started to decompose at about 350 °C. The 5% and 10% weight loss temperatures are 428 and 456 °C, respectively. From this measurement, **15a** is considered to be a class of heat-resistant polymer.

Conclusion

We have shown that Lewis acid-catalyzed repetitive Diels–Alder reactions occurred to give the Diels–Alder polymers in the appropriate combination of bisdienophile and bisdiene monomers. A Lewis acid such as Et_2AlCl catalyzed the Diels–Alder polymerization of bismaleimide **1a** with bisfurfuryl ether **2b** to give poly(imide-ether) **6** having molecular weight of 15 000. This study further demonstrated that chirally modified Lewis acid also catalyzed repetitive Diels–Alder reactions to afford optically active polymers having main-chain chirality. In the presence of chiral Lewis acid **7**, Diels–Alder polymerization of **1a** with **5b** yielded optically active polymer **15a**. The possibility of using other highly enantioselective catalytic C–C bond-forming reactions give this methodology high potential for other asymmetric polymerizations. Such possibilities are currently being explored.

Acknowledgment. We thank Professor Tsutomu Takeichi at Toyohashi University of Technology for use of his TGA instrument. This research was supported by a Grant-in-Aid for Scientific Research in Priority Areas from the Ministry of Education, Science, and Culture, Japan, and The Tatematsu Foundation.

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MA9815410