# Alternating Copolymerization of Ethylphenylketene with Benzaldehyde: Solvent- and Additive-Controlled Stereospecific Formation of Polyester

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ABSTRACT: Copolymerization of ethylphenylketene with benzaldehyde by butyllithium proceeded in a perfect 1:1 alternating manner to afford the corresponding polyester, of which the repeating unit has two adjacent chiral centers. The relative stereochemistry between these two chiral centers was controlled by solvents (tetrahydrofuran or toluene) and additives such as (−)-sparteine or diethylzinc, and the resulting diastereoselectivity, *erythro*-configuration:*threo*-configuration, was controlled in a range of 80:20 to 12:88. These diastereomeric ratios were determined by HPLC analysis of the diols, which were obtained by reductive degradation of the polyester with maintaining the configuration of the repeating unit. The more polar diol was converted to the corresponding cyclic carbonate, and a single crystal of it was successfully analyzed by X-ray crystallography to determine its configuration as a *threo* one. The *threo*-rich polymer was less soluble, more thermally degradable, and denser than the *erythro*-rich polymer.

## Introduction

Stereoregularity is one of the most important structural parameters to determine properties of polymers, such as thermal property, solubility, and so on. Stereoselective syntheses of polymers have been achieved by polymerization of optically active monomers and by stereoselective polymerization of prochiral or racemic monomers.[1−3] Addition of Lewis base or Lewis acid to anionic polymerization systems has been extensively investigated, expecting that these additives would coordinate with the propagating species or monomers to control their reactivities and to induce stereoselectivity. For example, some anionic polymerizations of achiral vinyl monomers in the presence of homochiral diamines afforded optically active polymers with helical conformations.[4] Addition of Lewis acids also effectively controls the stereoregularity of the polymers in anionic polymerizations of vinyl monomers.[5]

We previously reported the living anionic alternating copolymerizations of ethylphenylketene (EPK) with aromatic aldehydes using *n*-butyllithium as an initiator.[6] The resulting polyesters have two adjacent chiral centers in the repeat unit; however, the relative stereochemistry between them was not clarified. In this study, we report the method for determining the stereochemistry and its control by choosing appropriate solvents and additives. The influence of stereochemistry on the physical properties of the polymers (solubility, thermal property, and density) is also discussed.

## Experimental Section

**Materials and Instruments.** EPK was synthesized according to the reported procedure[7] and was distilled prior to use under reduced pressure. Benzaldehyde (BA, Kanto Chemical, Co., 98.0%) was dried and distilled from $CaH_2$ prior to use. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl prior to use. *n*-BuLi was purchased as a hexane solution (1.52 M) from Kanto Chemical Co. (−)-Sparteine (Ardrich Chemical Co., 99.0%) was dried and distilled from $CaH_2$. Diethylzinc was purchased as a hexane solution (1.00 M) from Kanto Chemical Co.

$^1$H NMR spectra were recorded with a JEOL Lambda-300 spectrometer with tetramethylsilane (TMS) as an internal standard; the $\delta$ and $J$ values are given in ppm and Hz, respectively. IR spectra were recorded with a Jasco FT-IR-5300 spectrometer, and the values are given in cm$^{-1}$. Number-average molecular weights ($M_n$) and molecular weight distributions ($M_w/M_n$) were estimated by size exclusion chromatography (SEC) on a Tosoh HLC 8120 system equipped with two consecutive polystyrene gel columns (Tosoh TSK gels G-2500HXL ($M_n$ < 400 000) and G4000HXL ($M_n$ < 20 000) and ultraviolet and refractive index detectors using tetrahydrofuran (THF) as an eluent, with a flow rate of 1.0 mL/min by polystyrene calibration at 40 °C. X-ray crystallographic analysis was carried out by a Rigaku AFC5R diffractometer at 23 °C using the $\omega-2\theta$ scan method. The structure was solved by direct methods (SIR97) and expanded using Fourier techniques (DIRDIF94). $R = 0.058$, $Rw = 0.042$. Diastereoselectivity was determined by HPLC with a JASCO Finepak SIL-5 column ($SiO_2$, eluent: hexane/2-propanol (volume ratio 95.5/4.5); 1.0 mL/min). Specific optical rotations were measured by a JASCO DIP-1000 digital polarimeter using a sodium lamp as a light source at 25 °C. Thermogravimetric (TG) analysis was carried out on a Tosoh Instruments TG/DTA 6200 at a heating rate of 10 °C/min under a nitrogen atmosphere. The densities were measured by density gradient tubes at 25 °C with a Shibayama Kagaku Seisakusho model A.

**Copolymerization of EPK with BA.** *Typical procedure*: *n*-BuLi (1.50 M in hexane, 0.267 mL, 0.400 mmol) was added to a THF solution (1 mL) of (−)-sparteine (0.092 mL, 0.400 mmol) at room temperature. This solution (0.125 mL, *n*-BuLi content = 0.05 mmol) was added to a THF solution (10 mL) of EPK (440 mg, 3.00 mmol) and BA (0.326 mL, 3.20 mmol) at −40 °C, and the mixture was stirred for 10 min at the same temperature. The reaction was quenched by addition of MeOH (1 mL). The mixture was poured into MeOH (100 mL), and the resulting precipitate was collected by filtration with suction and dried under vacuum to obtain **1** (744 mg, 98%) as a white

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**Table 1. Anionic Copolymerizations of Ethylphenylketene (EPK) with Benzaldehyde (BA) under Various Conditions**[a]

| entry | additive (amount/equiv) | solvent | temp/°C | time | yield/%[b] | $M_n$ ($M_w/M_n$)[d] | *erythro*/*threo*[f] |
|---|---|---|---|---|---|---|---|
| 1 | none | THF | 0 | 10 min | quant | 10800 (1.81) | 80/20 |
| 2 | none | THF | −40 | 10 min | quant | 12600 (2.31) | 67/33 |
| 3 | (−)-sparteine (1) | THF | −40 | 10 min | 98[c] | 13200 (2.31) | 67/33 |
| 4 | (−)-sparteine (30) | THF | −40 | 10 min | 96[c] | 24900 (4.55) | 69/31 |
| 5 | $Et_2Zn$ (30) | THF | −40 | 30 min | quant | 6900 (1.20)[e] | 23/77 |
| 6 | $Et_2Zn$ (70) | THF | −40 | 30 min | quant | 4100 (1.22)[e] | 12/88 |
| 7 | none | toluene | −40 | 3 h | 97 | 6400 (1.99)[e] | 28/72 |
| 8 | none | toluene | −78 | 108 h | 35 | 8000 (1.84)[e] | 31/69 |
| 9 | (−)-sparteine (1) | toluene | −78 | 30 min | 97[c] | 3900 (1.85) | 16/84 |
| 10 | $Et_2Zn$ (30) | toluene | −40 | 12 h | quant | 6400 (3.81)[e] | 29/71 |

[a] Polymerization conditions: $[n\text{-BuLi}]_0 = 0.005$ M; $[\text{EPK}]_0/[n\text{-BuLi}]_0 = 60$. [b] MeOH-insoluble parts. [c] $[\alpha]^{25}_D = 0$ ($c$ = 1.0, $CHCl_3$). [d] Estimated by SEC analysis (eluent: THF, polystyrene standards) of the crude products. [e] THF-soluble parts. [f] Determined by HPLC analysis ($SiO_2$, eluent:hexane/2-propanol (volume ratio 95.5/4.5) after reductive degradation.

powder. SEC analysis of the formed polymer was carried out to estimated the number-average molecular weight ($M_n$) and the molecular weight distribution ($M_w/M_n$) ($M_n$ = 13 200, $M_w/M_n$ = 2.31).

*Typical data*: $^1$H NMR ($CDCl_3$): $\delta$ 0.20−2.50 (5H, br, m), 5.50−7.50 (11H, br, m). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.70; H, 6.19.

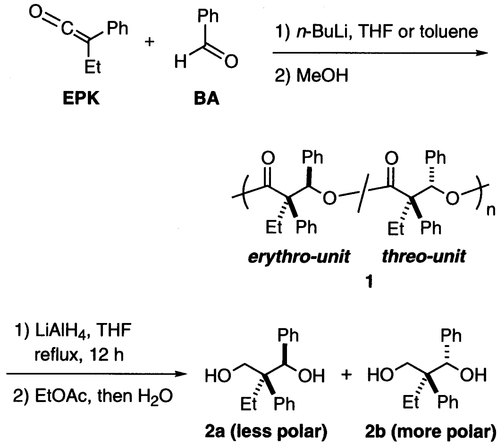
**Reductive Degradation of the Obtained Polymer.** The polymer **1** (320 mg, 1.27 mmol calculated as a repeat unit) and lithium aluminum hydride (160 mg, 4.17 mmol) were added to THF (6 mL). After stirring with refluxing for 12 h, ethyl acetate (2.0 mL) was carefully added to the mixture, and then water (8.0 mL) was added. The resulting mixture was extracted with ether (10 mL × 6), and the combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to give a mixture containing *erythro*-2-ethyl-2-phenyl-1-phenylpropanediol (**2a**) and its *threo*-diastereomer (**2b**). The ratio between **2a** and **2b** was determined by HPLC analysis of the crude mixture. Diols **2a** and **2b** were isolated by preparative thin-layer chromatography (PTLC, $SiO_2$, eluent; ethyl acetate−hexane (v/v = 1/3).

**2a**: $R_f$ = 0.3 ($SiO_2$, eluent: ethyl acetate−hexane (v/v = 1/3)). IR (NaCl): 3370. $^1$H NMR ($CDCl_3$): $\delta$ 0.56 (3H, t, $J$ = 7.3), 1.57 (2H, q, $J$ = 7.3), 3.19 (1H, s), 3.51 (1H, s), 3.79 (1H, d, $J$ = 11.4), 4.19 (1H, d, $J$ = 11.4), 5.06 (1H, s), 7.00−7.32 (10H, m). $^{13}$C NMR ($CDCl_3$): $\delta$ 8.10, 24.34, 50.04, 66.05, 82.85, 126.53, 127.20, 127.61, 127.67, 127.87, 128.31, 140.27, 141.01. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.90; H, 7.66.

**2b**: $R_f$ = 0.2 ($SiO_2$, eluent: ethyl acetate−hexane (v/v = 1/3)). IR (NaCl): 3370. $^1$H NMR ($CDCl_3$): $\delta$ 0.73 (3H, t, $J$ = 7.3), 1.88 (1H, m, $J$ = 7.3), 2.44 (1H, m, $J$ = 7.3), 3.77 (1H, s), 4.19 (1H, s), 3.82 (1H, d, $J$ = 10.6), 4.25 (1H, d, $J$ = 10.6), 4.89 (1H, s), 6.61−7.30 (10H, m). $^{13}$C NMR ($CDCl_3$): $\delta$ 8.22, 24.78, 49.54, 63.00, 82.50, 126.39, 127.14, 127.21, 127.26, 127.43, 127.93, 140.18, 140.78. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.57; H, 8.01.

**Preparation of 2-Ethyl-2-phenyl-1-phenyl Carbonate (3).** Ethyl chloroformate (132 mg, 1.22 mmol) and triethylamine (0.170 mL, 1.22 mmol) were added to a THF solution (1.4 mL) of *threo*-2-ethyl-2-phenyl-1-phenylpropanediol (157 mg, 0.61 mmol) at room temperature, and the mixture was stirred for 12 h at the same temperature. The resulting white precipitate was filtered, and the filtrate was concentrated under reduced pressure. The residue was recrystallized from ethyl acetate−hexane (v/v = 2/1) to give 2-ethyl-2-phenyl-1-phenyl carbonate, **3** (60 mg, 33% yield), as colorless crystals; mp 147.0−148.0 °C. $^1$H NMR ($CDCl_3$): $\delta$ 0.68 (3H, t, $J$ = 7.3), 1.83 (1H, m, $J$ = 7.3), 2.07 (1H, m, $J$ = 7.3), 4.59 (1H, d, $J$ = 11.2), 4.95 (1H, d, $J$ = 11.2), 5.49 (1H, s), 6.68−7.33 (10H, m). $^{13}$C NMR ($CDCl_3$): $\delta$ 8.90, 28.24, 43.31, 74.88, 86.63, 126.45, 127.27, 127.52, 127.97, 128.13, 128.29, 140.20, 140.84, 151.50. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.33; H, 6.34. Crystal data: $C_{18}H_{18}O_3$, $M$ = 282.34, orthorhombic; *Pbca*; $a$ = 17.514(3), $b$ = 18.493(4), $c$ = 9.366(4) Å, $V$ = 3034(1) Å$^3$, $D_{calcd}$ = 1.236 g/cm$^{-3}$, $Z$ = 8.

**Scheme 1**

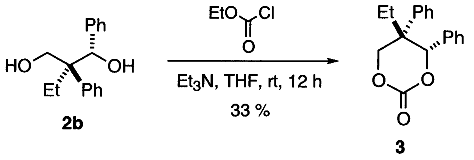


## Results and Discussion

**Determination of Relative Stereochemistry of Polymer Chain.** First, EPK and BA were copolymerized anionically in THF (Scheme 1, Table 1, entry 2). When $n$-BuLi was added to a THF solution of EPK and BA at −40 °C, the characteristic yellow color of EPK disappeared within 5 min, indicating its complete consumption. SEC analysis of the resulting mixture indicated that the corresponding polymer formed, whose number-average molecular weight ($M_n$) and molecular weight distribution ($M_w/M_n$, MWD) were estimated to be 12 600 and 2.31, respectively. The obtained polymer was soluble in THF and $CHCl_3$ and was insoluble in MeOH. The structure of the resulting polymer was confirmed to be polyester **1** by its strong IR absorption at 1737 cm$^{-1}$.[6,8] Treatment of the polymer with lithium aluminum hydride in refluxing THF resulted in reductive degradation of the ester linkage to give the corresponding diol, 2-ethyl-2-phenyl-1-phenylpropanediol (**2**) in 92% yield, as expected from the ideal polyester structure formed by alternating copolymerization (Scheme 1). The diol was obtained as a diastereomeric mixture, whose ratio was determined to be 69:31 (less polar diol **2a**[9]:more polar one **2b**[9]) by HPLC analysis.

When copolymerization was carried out in toluene at −40 °C, the polymerization was considerably slow, and it took 3 h until the yellow color of EPK disappeared (Table 1, entry 7). This suppression of polymerization rate would be due to strong coordination between the propagating end and its counter lithium cation in nonpolar toluene. In contrast to the polymer obtained by polymerization in THF, the obtained polymer was less soluble in THF and the polymerization mixture became a gel. Treatment of the resulting polymer with

**Scheme 2**



lithium aluminum hydride afforded the corresponding diol as a diastereomeric mixture quantitatively. In this case, more polar diastereomer preferentially formed (less polar diol **2a**:more polar one **2b** = 31:69), opposite to the polymerization in THF. Consequently, the differences of the solubilities between the obtained polymers would be correlated to their different stereochemistry on the main chain.

The more polar diol **2b** was converted into the corresponding cyclic carbonate **3** (Scheme 2), and its single crystal, obtained by recrystallization from ethyl acetate−hexane, was analyzed by X-ray crystallography. As shown in the ORTEP drawing of **3**, its two phenyl groups are oriented in a *cis*-configuration (Figure 1). The relative configuration of diols **2a** and **2b** are therefore *erythro* and *threo*, respectively.

**Effects of Solvent and Additive on Stereoselectivity.** The effects of solvent and additive on the diastereoselectivity in anionic copolymerizations of EPK with BA using *n*-BuLi as the initiator were examined. Toluene and THF were used as examples of a nonpolar solvent and polar solvent, respectively. As additives, (−)-sparteine and diethylzinc were employed as a donating ligand and a Lewis acid, respectively, because these have been frequently applied to the various stereoselective polymerizations described in the Introduction. The results and conditions are shown in Table 1. The diastereoselectivity was determined by HPLC analysis of the diol **2**, obtained by reductive degradation of the polymer. The diastereoselectivity was highly dependent on the solvents and the additives. In all cases, except for entry 8, the resulting polyester was obtained almost quantitatively.

As described above, when the polymerization was carried out in the absence of additives in THF at −40 °C, *erythro*-rich polymer was obtained (Table 1, entry 2). *Erythro*-selectivity was increased to 80% by raising the polymerization temperature to 0 °C (entry 1). Addition of (−)-sparteine to the polymerization system changed the stereoselectivity only slightly (entries 3 and 4). By adding $Et_2Zn$ (30 equiv to *n*-BuLi) to the system in THF, the diastereoselectivity was inverted from *erythro*-selectivity to *threo*-selectivity (entry 5) and was further enhanced by increasing the amount of $Et_2Zn$ to 70 equiv (entry 6). There was no polymerization in the presence of only $Et_2Zn$ (0.5 equiv to EPK) in THF at −40 °C.

When the polymerization was carried out in toluene, *threo*-selectivity was induced (entries 7 and 8). *Threo*-selectivity was further enhanced by adding a stoichiometric amount of (−)-sparteine (entry 9). Addition of $Et_2Zn$ did not affect the stereoselectivity (entry 10). This tendency in additive effects is opposite to that observed in THF, where addition of (−)-sparteine is effective while that of $Et_2Zn$ is not. Although specific optical rotations of the polymers obtained in the presence of (−)-sparteine (entries 3, 4, and 9) were measured, all measured values were 0°, indicating that the structure of (−)-sparteine cannot induce chirality in the present copolymerization system. The *erythro*-rich polymers (entires 1−4) were soluble in benzene, chloroform, THF, and *N*,*N*-dimethylformamide and were insoluble in MeOH, while *threo*-rich polymers (entries 5−10) were less soluble or insoluble in common organic solvents. Thus, the polymers having a wide range of stereochemistry (ranging from *erythro*:*threo* = 80:20 to *erythro*:*threo* = 16:84) were successfully obtained by the judicious selection of the solvents and the additives.

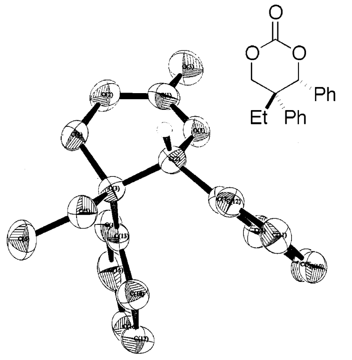


**Figure 1.** ORTEP drawing of **3**.

**Plausible Mechanism for the Diastereoselectivity.** The step forming the two adjacent chiral centers in the alternating copolymerization is an aldol-type reaction of the terminal enolate with BA. As depicted in Scheme 3, there are three plausible models that can explain the stereochemical outcome.

Model (a) involves an equilibrium between substrates and adducts, which generally occurs with aldol reactions of lithium enolates with aldehyde in polar solvent.[10] In this case, stereoselectivity is determined mainly by the thermodynamic stability of the corresponding adduct. The adduct **4**, depicted in Scheme 3a, has a thermodynamically favorable "*erythro*"-configuration, in which two phenyl groups can be oriented at the equatrial position in the cyclic complex. If the adduct has a *threo*-configuration, one of the phenyl groups would be located at the thermodynamically disfavored axial position and therefore would be dissociated into enolate and aldehyde. These consideration based on thermodynamic control of stereochemistry was supported by the above result that *erythro*-selectivity was increased by raising the polymerization temperature (Table 1, entries 1 and 2). Thermogravimetric analyses of the obtained polymers also supported the assumption that the *eythro*-configuration is more thermodynamically favored (vide infra).

Model (b) explains the *threo*-selectivity of the polymerization in the presence of $Et_2Zn$. The transition state could be acyclic, which is often used to explain the *threo*-selectivity in Lewis acid-promoted aldol reactions.[10,11] The most favorable transition state is **5**, in which two double bonds are oriented antiperiplanar to minimize dipole−dipole interaction and the two bulky phenyl groups are also oriented antiperiplanar to minimize steric repulsion.

Model (c) explains the *threo*-selectivity in the polymerization in toluene. This model involves selective formation of (*Z*)-enolate by reaction of terminal alkoxide with ketene, and aldol reaction of enolate with aldehyde via a six-membered cyclic transition state, which is widely used to explain the *threo*-selectivity in reactions of metal enolates with carbonyl compounds.[10,11] The (*Z*)-configurated propagating enolate would be formed by preferential attack of the propagating end to EPK from the *opposite* side of the bulky Ph substituent. In the six-

**Scheme 3**

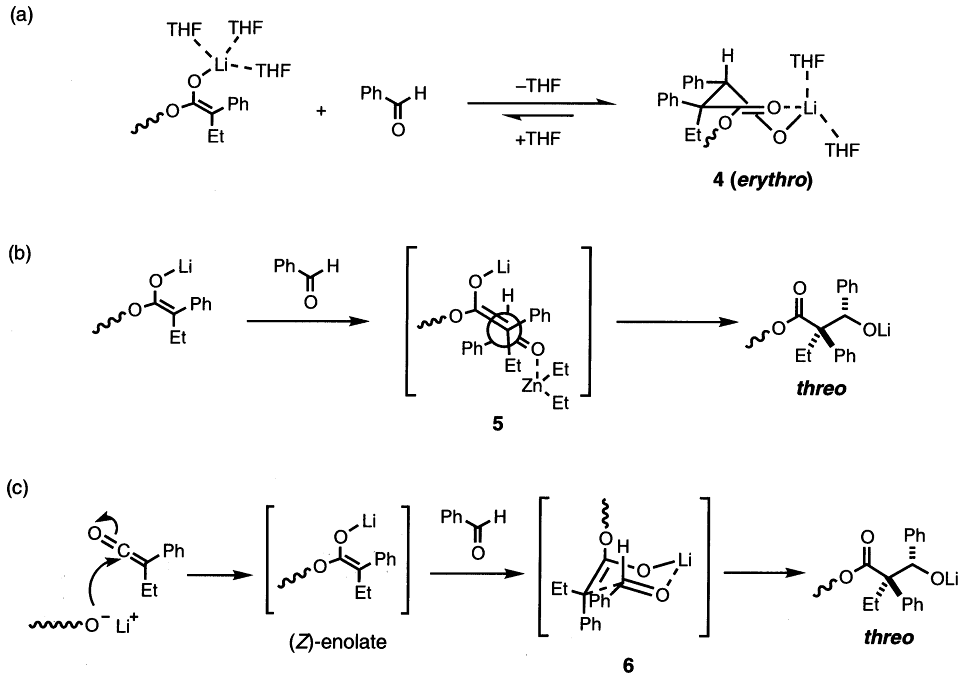


**Table 2. Wavenumber of IR Absorption Corresponding to Ester Moiety of the Polymers**

| entry | erythro/threo | $\bar{\nu}$(C=O) (cm$^{-1}$) | $\bar{\nu}$(C−O) (cm$^{-1}$) |
|---|---|---|---|
| 1 | 80/20 | 1740.0 | 1207.7 |
| 2 | 61/39 | 1738.8 | 1208.1 |
| 3 | 40/60 | 1737.4 | 1208.4 |
| 4 | 16/84 | 1736.7 | 1208.8 |

**Table 3. Thermogravimetric Analysis of the Polymers**

| entry | erythro/threo | $M_n$ ($M_w/M_n$) | $T_{d5}$ [a] | $T_{d90}$ [b] |
|---|---|---|---|---|
| 1 | 28/72 | 6400 (1.99) | 240 | 321 |
| 2 | 40/60 | 8200 (2.89) | 242 | 339 |
| 3 | 67/33 | 12600 (2.31) | 254 | 307 |
| 4 | 80/20 | 10800 (1.81) | 256 | 315 |

[a] Temperature with 5% weight loss. [b] Temperature with 90% weight loss.

membered cyclic transition state **6**, the Ph substituent of BA is oriented at the equatrial position in order to avoid 1,3-diaxial repulsion.

**IR Analysis of the Polymers.** As described above, polyesters with a wide range of stereochemistry were obtained. In general, the structure of polyesters is characterized by IR absorption of the carbonyl group.[12] The wavenumber of the IR absorption of these esters depended on the stereochemistry of the polymer. As shown in Table 2, with increasing of the *threo*-unit content, the carbonyl C=O stretching vibration shifted toward lower wavenumbers, while the main-chain C−O stretching vibration shifted toward higher wavenumbers. Because the shifts are linear to the ratio between the diastereomeric units, IR analysis of the polymer would be also useful in evaluating the stereochemistry.

**Properties of the Polymers.** The thermal properties of the polymers with different stereochemistries were evaluated by thermogravimetry (TG) (Table 3). The weight loss of *threo*-rich polymers started at lower temperatures (temperature at 5% weight loss, $T_{d5} \sim 240$ °C, entries 1 and 2) than those of the *erythro*-rich polymers ($T_{d5} \sim 256$ °C, entries 3 and 4), indicating that the former is less stable than the latter.

Furthermore, the stereochemistry of the repeat unit had remarkable effects on the packing of the polymer in the solid state. The densities of the polymers were measured by a density gradient tube method at 23.5 °C. As shown in Figure 2, the density of the polymer decreased linearly with *threo*-unit content in the polymer chain.

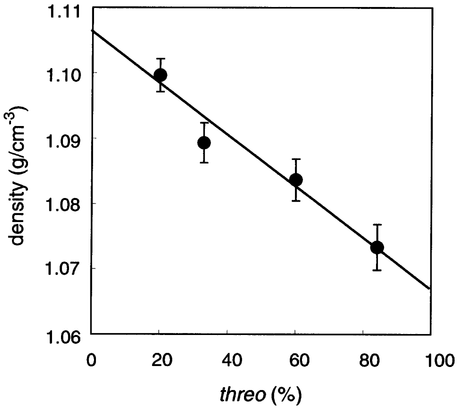


**Figure 2.** Density vs *threo* content of the polymer.

## Summary

We demonstrated the stereospecific synthesis of polyester by anionic alternating copolymerization of EPK with BA using *n*-BuLi as the initiator. The relative stereochemistry between two adjacent chiral centers in the repeat unit formed by alternating copolymerization was successfully controlled by choosing the solvents and the additives, providing polyesters with a wide range of stereochemistries. The polyesters were reductively degraded into the corresponding diols, which were converted into cyclic carbonates to determine their stereochemistry by X-ray crystallography. The relative stereochemistry of the repeat unit remarkably affected the physical properties of the polymers such as solubility, thermal property, and density. Our next challenge will be to accomplish enantioselective copolymerization, which is now under investigation.

**Acknowledgment.** We express sincere thanks to Dr. Daisuke Takeuchi (Chemical Resources Laboratory, Tokyo Institute of Technology) for X-ray crystallographic analysis.

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