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Asymmetric Anionic Ring-Opening Polymerization of Octadecyl α-Lipoate with *n*-Butyllithium in the Presence of (–)-Sparteine

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Synopsis

The anionic ring-opening polymerization of octadecyl α-lipoate (ODLPA) with *n*-butyllithium (*n*-BuLi) in the presence or the absence of (–)-sparteine (Sp) was investigated. The polymerization of ODLPA was induced even in the absence of Sp to give high molecular weight linear polymers. The polymer yield in the presence of (–)-Sp was higher than that in the absence of (–)-Sp, which is related to the complex formation between *n*-BuLi and (–)-Sp. The polymer obtained in the presence of (–)-Sp has an optical active, but the polymer obtained in the absence of (–)-Sp did not show any optical active. Moreover, the unreacted ODLPA recovered after polymerization in the presence of Sp shows optical rotation having opposite signal to the polymer. Thus, it is clear that the asymmetric anionic ring-opening polymerization of ODLPA was induced with *n*-BuLi in combination with (–)-Sp.

KEYWORDS: Asymmetric polymerization, Ring-opening polymerization, Cyclic disulfide, Octadecyl α-lipoate, Spartein, *n*-Butyllithium

1. Introduction

In a field of asymmetric polymerizations, many optical active polymers bearing interesting physical properties have been synthesized. Among asymmetric polymerization, enantiomer-selective polymerization is defined as that either one of *R*-form or *S*-form from racemic monomer polymerizes preferentially with optical active catalysts.[1–4] Concerning the enantiomer-selective polymerization of vinyl monomers, the polymerization of methacrylic acid esters has been investigated in detail. The polymer of methacrylic acid esters shows high optical selectivity. In the polymerization of racemic methacrylic acid esters with Grignard reagents in the presence of (–)-spartein (Sp), (*S*)-form of the monomer polymerizes preferentially to give an isotactic polymer bearing optical purity of up to 93%.[4]

Such polymerizations were also reported in the ring-opening polymerization of cyclic monomers such as epoxide,[5] episulfide,[6] and *N*-carboxylic acid anhydride.[7] On the other hand, we have been investigated the thermal polymerization of cyclic disulfides to elucidate unique characters of the polymer obtained from thermal polymerization of the cyclic disulfides.[8,9] An anionic polymerization of cyclic disulfides such as 1,2-dithiane and 1,2-dithiacyclooctane was reported to give polymers.[10] Although lipoic acid (LPA) has an asymmetric carbon in the ring, it is not a suitable monomer for anionic ring-opening polymerization because of containing carboxyl acid group in the side chain. However, its ester is able to polymerize with anionic catalyst. The enantiomer-selective anionic ring-opening polymerization of alkyl α-lipoate was not found in the literatures. Thus, we selected octadecyl α-lipoate (ODLPA) for this purpose.

In this article, we report on the asymmetrical anionic ring-opening polymerization of ODLPA synthesized from octadecyl alcohol with α-lipoic acid by *n*-BuLi in the presence or the absence of (–)-Sp as a complex agent.

2. Experimental

2.1 Materials

Commercially available *RS*-α-LPA, 1,1'-carbonyl-diimidazole, 1-octadecanol and (–)-Sp ($[\alpha]_D = -13.8°$ at 20°C in benzene) were used as received. Other reagents were used after purification by conventional methods. ODLPA was synthesis according to the following procedure. After *RS*-α-LPA (3g) was dissolved in

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chloroform, 1,1'-carbonyl-diimidazole (3g) was added slowly to the solution with stirring. Then, 1-octadecanol (11.8g) was added to the solution under stirring for 30 min at 0°C, and the reaction was carried out at 25°C. After the reaction, the products were passed through a silica gel column to isolate ODLPA. The isolated yield of ODLPA (mp: 33°C) was 72%, and used as monomer after recrystallization from ether. The structure of the product was confirmed by ^{1}H-NMR spectroscopic analysis: ^{1}H–NMR ($CDCl_3$): δ 0.86~0.89 (t, 3H), 1.26~1.31 (m, 32H), 1.45~1.47 (m, 2H), 1.59~1.71 (m, 4H), 1.88~1.93 (m, 1H), 2.29~2.33 (t, 2H), 2.45~2.47 (m, 1H), 3.10~3.18 (m, 2H), 3.56 (m, 1H), 4.04~4.07 (t, 2H).

2.2 Polymerization Procedure

Polymerization was carried out in a sealed tube. After the required amounts of reagents were introduced in the tube, polymerization was carried out for a given time at constant temperature. After the polymerization, the contents of the tube were poured into an excess of acetone to precipitate the polymer formed. The polymer was then dried under high vacuum; polymer yield was determined by a gravimetric method. When (–)-Sp was used as additive, the required amount of (–)-Sp was added to diluted *n*-BuLi solution. After 5 minutes, monomer was added to start the polymerization.

2.3 Polymer Characterization

The number average molecular weight of the polymer (M_n) and, the dispersity (M_w/M_n) were determined by GPC at 38°C in THF as an eluent. CCPD RE-8000 series was used for GPC measurement. It calibrated with the standard polystyrene. The structures of monomer and polymer were estimated by NMR spectra of them. Measurement was carried out in $CDCl_3$ at room temperature using JEOL α-400NMR spectroscopy. TMS is used as an internal standard. DIP-360 (JASCO) was used to measure an optical rotation.

3. Results and Discussion

An anionic polymerization of ODLPA with *n*-BuLi in the presence or absence of Sp was carried out, and the results are summarized in Table 1. The anionic polymerization at 0°C and −30°C proceeded to give solid polymers. The ^{1}H-NMR spectrum of the polymer obtained is shown in Fig. 1, in which the monomer is also shown to comparison. In the ^{1}H-NMR spectrum of the polymer, the peaks of a, b, c, and d based on ODLPA monomer shifted after polymerization as indicated in Fig. 1. This suggests that the polymerization proceeded through a cleavage of disulfide bond of ODLPA. Moreover, as shown in Fig. 2, the resulting polymer was presumed to be a linear from the signals appeared at about 1.4 and 2.5 ppm due to the presence of SH proton at the chain end.

Table 1. Polymerization of ODLPA with *n*-BuLi in toluene for 3h. [a)]

[Sp] / [*n*-BuLi]	Temp. (°C)	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n	$[\alpha]_D$ [b)]
0	0	7.4	1.2	1.2	0
0	–30	3.1	1.8	1.2	0
1.5	0	12.9	1.8	1.3	+4.3 [c)]
1.5	–30	5.6	2.0	1.2	+3.6

a) [*n*-BuLi] = 2.0×10^{-2} mol/L , [ODLPA] = 1.0 mol/L.
b) Measured in benzene at 20°C; *l* = 10 cm.
c) Optical rotation of unreacted ODLPA was $[\alpha]_D$ = –3.8°

In the polymerization of ODLPA, the polymer yields obtained in the presence of (–)-Sp were higher than that obtained in the absence of (–)-Sp regardless of reaction temperature. Since (–)-Sp is one of the *tert*-diamine, (–)-Sp is known to be able to complex with *n*-BuLi to increase an activity for the anionic polymerization.[4)]

To confirm the asymmetric enantiomer-selective polymerization of ODLPA with *n*-BuLi/(–)-Sp catalyst, optical rotation of the polymer and the unreacted ODLPA after the polymerization in the presence of (–)-Sp was measured. The polymer obtained in the presence of (–)-Sp showed optical rotation of $[\alpha]_D$= +4.3° at 20°C, but the polymer obtained in the absence of (–)-Sp did not show any optical rotation. The results demonstrated that either one of the *R* form or the *S* form polymerizes preferentially in the polymerization of ODLPA with *n*-BuLi/(–)-Sp catalyst.

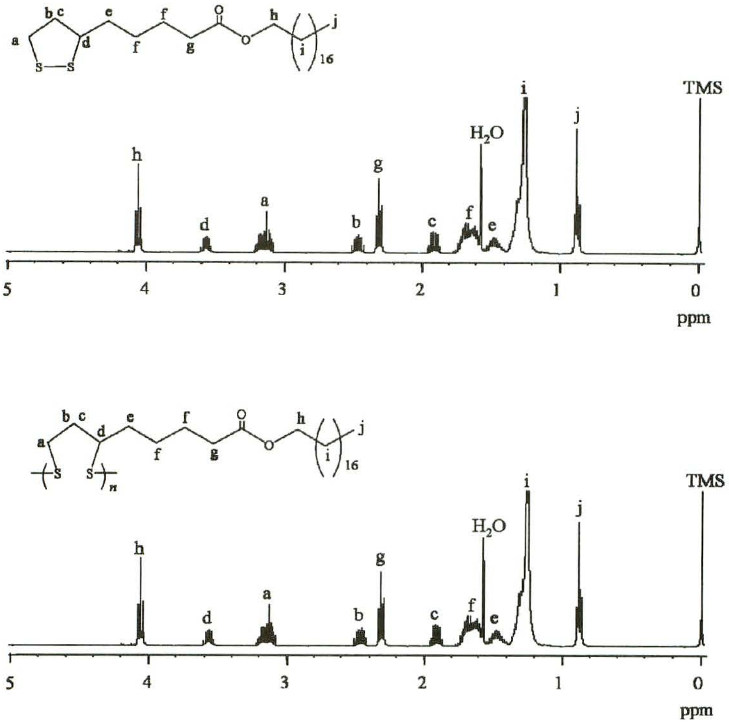


Fig. 1. ^{1}H–NMR spectra of ODLPA and poly(ODLPA)

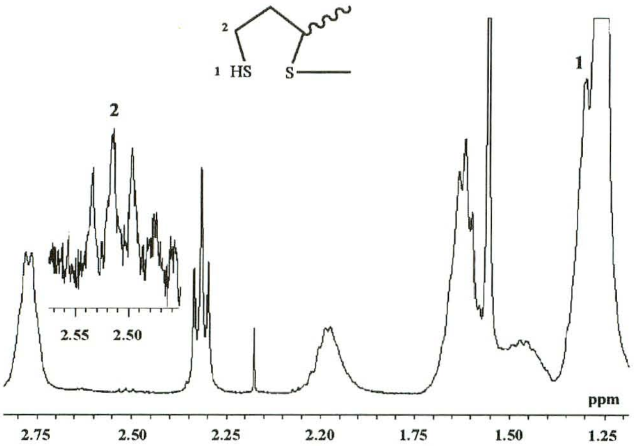
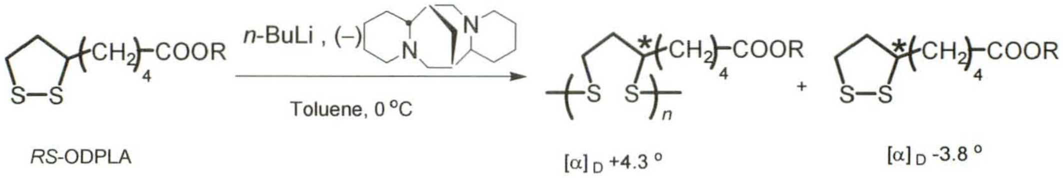


Fig. 2. ^{1}H–NMR spectrum of the chain end poly(ODLPA)

If the polymerization of ODLPA with *n*-BuLi/(–)-Sp catalyst proceeds with an enantiomer-selective mechanism, the value of optical rotation of the unreacted monomer and the polymer will be an opposite signal. To elucidate this point, (–)-Sp was completely removed by recrystallization of the unreacted ODLPA after the polymerization, and optical rotation was measured. As a result, optical rotation of the unreacted ODLPA showed a minus ([α]$_D$ = –3.8°). The polymer obtained with *n*-BuLi/(–)-Sp catalyst showed (+) optical rotation, and the unreacted ODLPA shows optical rotation of minus. Thus, it is clear that the asymmetrical enantiomer-selective polymerization of ODLPA was induced with *n*-BuLi/(–)-Sp catalyst as shown in Scheme 1.



Scheme 1. Polymerization of ODLPA with *n*-BuLi/(–)-Sp catalyst

The effect of polymerization solvent on the polymerization of ODLPA with *n*-BuLi in the presence of (–)-Sp was examined. The results are shown in Table 2. The activity for the polymerization activity in THF decreased in comparison with that the toluene is used. When THF is use as a polar solvent, free propagating species is formed, leading to unfavorable asymmetrical space at the end of propagating chain end.

Table 2. Polymerization of ODLPA with *n*-BuLi/ (–)-Sp at 0°C for 3h

Solvent	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n	[α]$_D$
THF	1.4	13.5	2.7	0
Toluene	12.9	1.8	1.3	+4.3

[ODLPA] = 1.0 mol/L, [*n*-BuLi] = 2.0 × 10^{-2} mol/L, [(–)-Sp]/[*n*-BuLi] = 1.5

In conclusion, the anionic ring-opening polymerization of ODLPA with *n*-BuLi proceeded to give polymers. In the presence of (–)-Sp, asymmetric polymerization was induced to give optical active polymer.

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