# Synthesis and Biodegradability of Tartaric Acid-Based Poly(ester-thioether)s via Thiol−Ene Click Polymerization

Ryota Imamura, Kota Oto, Kaho Kataoka, and Akinori Takasu*

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**ABSTRACT:** Using scandium triflate $[Sc(OTf)_3]$ as a catalyst, chemo-selective esterification of tartaric acids by 3-butene-1-ol was performed, and we produced three dialkene monomers: L-di(3-butenyl) tartrate (BTA), D-BTA, and *meso*-BTA. Thiol−ene polyaddition of these dialkenyl tartrates and dithiols including 1,2-ethanedithiol (ED), ethylene bis(thioglycolate) (EBTG), and D,L-dithiothreitol (DTT) proceeded in toluene at 70 °C under nitrogen to give tartrate-containing poly(ester-thioether)s ($M_n$, (4.2−9.0) × $10^3$; molecular weight distribution ($M_w/M_n$), 1.6−2.5). In differential scanning calorimetry, the poly(ester-thioether)s showed single $T_g$s between −25 and −8 °C. In biochemical oxygen demand (BOD) tests using activated sludge, poly(L-BTA-*alt*-EBTG) and poly(L-BTA-*alt*-ED) showed 32 and 8% biodegradability, which is comparable to that of similar L-malate-containing poly(ester-thioether)s (23 and 13% biodegradation, respectively). Notably, we observed enantio and diastereo effects on biodegradation because poly(L-BTA-*alt*-EBTG), poly(D-BTA-*alt*-EBTG), and poly(*meso*-BTA-*alt*- EBTG) showed different degradation behaviors during the biodegradation test (BOD/theoretical oxygen demand (TOD) values after 28 days, 32, 70, and 43%, respectively). Our findings provide insights into the design of biomass-based biodegradable polymers containing chiral centers.
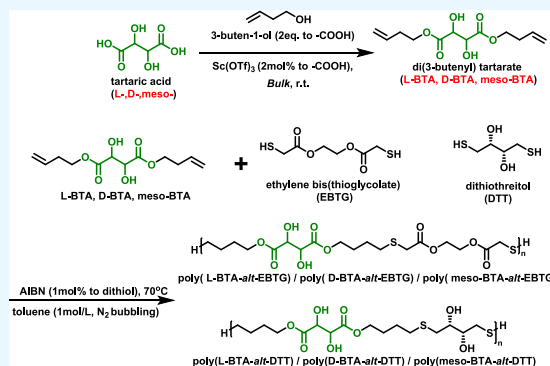
## INTRODUCTION

Biodegradability, as well as fine-tuning of polyesters or polyester-based plastics, is currently an important research subject in polymer chemistry.[1−6] Polyester design based on biorefinery carbon sources is one of the promising approaches toward this goal. Several reports have described carbohydrate-based polymeric materials;[7−16] among them, some polymers show excellent biodegradability, as well as thermal properties[11−16] when 1,4:3,6-dianhydrohexitols are incorporated into the polymer backbone.[13−16] In addition to exploring the biodegradability of these polymers, investigating new synthetic strategies remains one of the most urgent areas of research.

In the past decade, the development of "click chemistry" has become one of the most important procedures for the formation of covalent bonds. Click chemistry enables us to link monomer units via different chemical bonds in contrast to conventional step and chain polymerizations. In particular, the "click" reactions pioneered by Sharpless and co-workers[17] are useful for the preparation of various organic compounds including polymer molecules. The copper-catalyzed "click" reaction[17,18] performs a 1,3-dipolar cycloaddition between azides and alkynes effectively, even at ambient temperatures, and the orthogonality is extremely high. Since its inception, optimized reaction conditions and applications to biomedical substances have been reported for "click" chemistry; however, its application in the academic field of polymer chemistry is still relatively limited.[19−25] We have already reported several

examples using copper-catalyzed alkyne−azide[18] and thiol−ene[26] click polymerizations to afford polyesters consisting of a triazole ring,[27,28] thioether,[29] and ether−sulfone[29] moieties, respectively. As far as we know, however, there have been few reports of biodegradable polymers synthesized by click polymerization, although click polymerizations of biomass-based monomers are already reported.[30−33] In 2021, we also used thiol−ene click polymerization to synthesize L-malic acid-based poly(ester-thiether)s, which had a biodegradability (biochemical oxygen demand (BOD)/theoretical oxygen demand (TOD)) of 13−23%.[34] In this study, the dialkene monomers were derived from chemoselective esterification of L-malic acid by 3-butene-1-ol because we had previously reported chemoselective direct polyesterification of L-malic acid or tartaric acid[35,36] catalyzed by scandium trifluoromethanesulfonate $[Sc(OTf)_3]$.[37,38]

In the present study, we prepared the targeted tartrate-containing poly(ester-thioether)s via thiol−ene click polymerization (Scheme 1) in order to compare with our reported L-

**Scheme 1. Synthetic Scheme for Tartaric Acid-Based Poly(ester-thioether) via Thiol−Ene Click Polymerization**
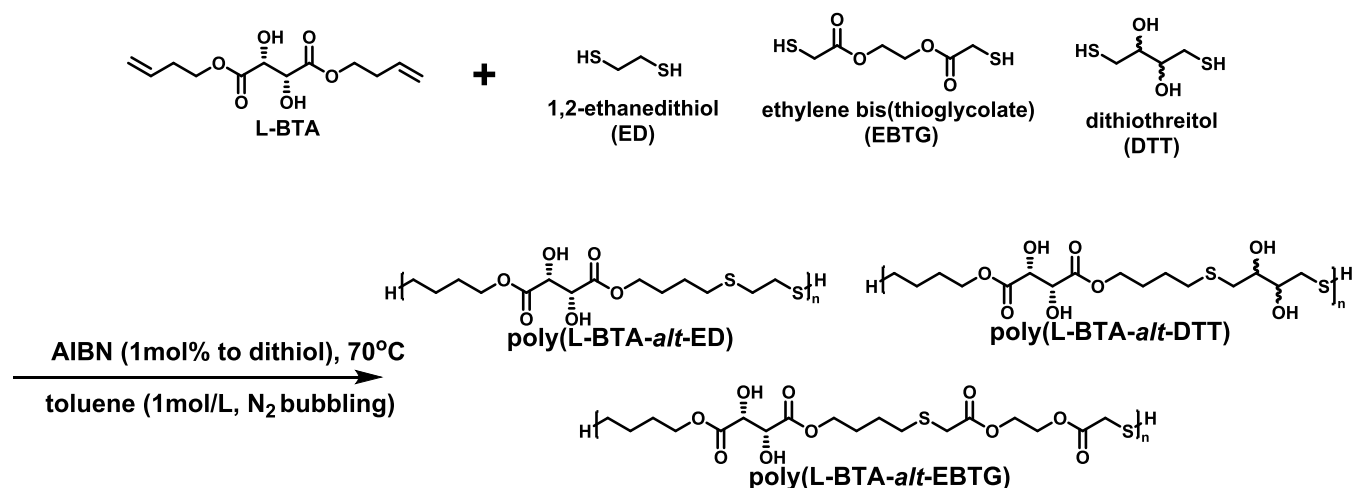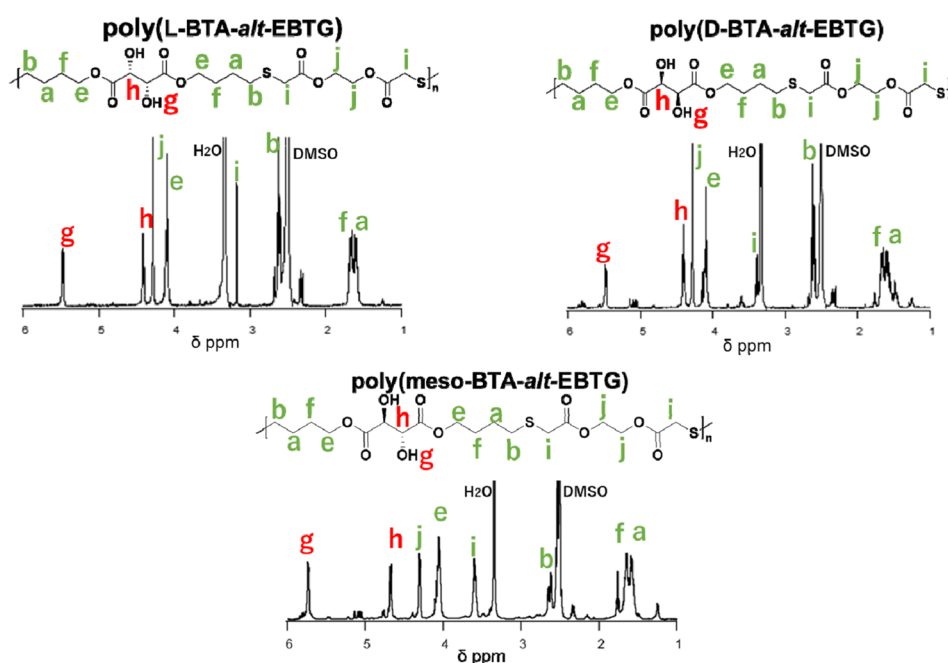




**Figure 1.** $^1$H NMR spectra of poly(BTA-*alt*-EBTG)s (in DMSO-$d_6$, 400 MHz, TMS).

malic acid-based poly (ester-thioether)s,[34] in which the tartaric acid-based dialkenes were similarly derived from chemoselective esterification of L-, D-, and *meso*-tartaric acids by 3-butene-1-ol, and we evaluated their biodegradability by biochemical oxygen demand (BOD).

## EXPERIMENTAL SECTION

**Materials.** L-Tartaric, D-tartaric, and *meso*-tartaric acids were purchased from Nacalai Tesque. 3-Buten-1-ol, Sc(OTf)$_3$, ethylene bis(thioglycolate) (EBTG), 1,2-ethanedithiol (ED), D,L-dithiothreitol (DTT), 1,4-butanedithiol (BD), and 2,2′-azobis(isobutyronitrile) (AIBN) were obtained from Wako Pure Chemical Industries.

**Measurement.** $^1$H NMR (400 MHz) measurements were acquired at 27 °C on a Bruker Analytik DPX400 spectrometer with tetramethylsilane (TMS) as an internal standard (0 ppm). The number-average molecular weight ($M_n$) and molecular

weight distribution ($M_w/M_n$) of the polymers were measured by using a size exclusion chromatography (SEC) system consisting of a JASCO PU-4185 pump system, a JASCO RI-4035 differential refractometer, a TSK-gel supermultipore-M column, and a JASCO co-2065 plus intelligent column oven (eluent, tetrahydrofuran; flow rate, 0.35 mL min$^{-1}$; temperature, 40 °C; Tosoh Corp.), calibrated by a poly(styrene) standard. Differential scanning calorimetry (DSC) measurements were performed with a DSC7020 instrument (HITACHI). The heating was conducted from 30 to 80 °C; the temperature was then cooled to −100 °C. The second scan was conducted from −90 to 80 °C. The rate of temperature change was 10 °C min$^{-1}$, and all measurements were performed under N$_2$ gas flow. The specific rotation ($[\alpha]_D^{25}$) was measured in a THF solution (0.01 g mL$^{-1}$) at 25 °C using a JASCO P-1000 digital polarimeter.

**Scheme 2. Preparation of Di(3-butenyl) Tartrates via Chemoselective Esterification of L-, D-, and *meso*-Tartaric Acids by 3-Butene-1-ol (2 equiv to −COOH)**
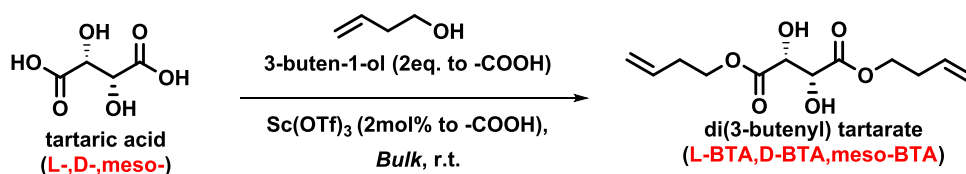


*Synthesis of Poly(ester-thioether)s via Thiol−Ene Polymerization.* BTA and an equimolar amount of each dithiol were mixed with an azo-type initiator (2,2′-azobis-(isobutyronitrile); 1 mol % to BTA) and toluene in an eggplant flask. After the mixture was stirred at 70 °C under a N$_2$ atmosphere for the indicated times, reprecipitation using chloroform and *n*-hexane as a good and a poor solvent, respectively, was carried out, and the precipitate was isolated by vacuum filtration and drying under reduced pressure. The characterization of the poly(ester-thioether)s was carried out using NMR, SEC, and DSC.

*Poly(L-BTA-alt-EBTG), 85% Yield.* $^1$H NMR (400 MHz, DMSO-$d_6$, δ, ppm): 1.60 [dt, 4H, −CH$_2$CH$_2$CH$_2$OC(=O)−, 7.4 Hz], 1.66 [dt, 4H, −CH$_2$CH$_2$OC(=O)−, 6.5 Hz], 2.60−2.66 [br, 4H, −CH$_2$CH$_2$CH$_2$CH$_2$OC(=O)−], 3.17 [d, 4H, −OC(=O)CH$_2$S−, 5.0 Hz], 4.09 [t, 4H, −CH$_2$OC(=O)CH(−OH)−, 7.5 Hz], 4.28 [t, 4H, −C(=O)-OCH$_2$CH$_2$OC(=O)−, 5.7 Hz], 4.41 [d, 2H OC(=O)-CH(−OH)CH(−OH)−,7.9 Hz], 5.47 [d, 2H −CH(−OH)−, 7.8 Hz] (Figure 1).

*Poly(D-BTA-alt-EBTG), 77% Yield.* $^1$H NMR (400 MHz, DMSO-$d_6$, δ, ppm): 1.57 [dt, 4H, −CH$_2$CH$_2$CH$_2$OC(=O), 16.0 Hz], 1.67 [dt, 4H, −CH$_2$CH$_2$OC(=O)−, 13.0 Hz], 2.55−2.66 [brm, 4H, −CH$_2$CH$_2$CH$_2$CH$_2$OC(=O)−], 3.39 [d, 4H, −OC(=O)CH$_2$S−, 12.8 Hz], 4.10 [t, 4H, −CH$_2$OC-(=O)CH(−OH)−, 6.1 Hz], 4.44 [t, 4H, −C(=O)-OCH$_2$CH$_2$OC(=O)−, 7.2 Hz], 4.42 [d, 2H OC(=O)-CH(−OH)CH(−OH)−, 7.8 Hz], 5.47 [d, 2H −CH(−OH)−, 7.8 Hz] (Figure 1).

*Poly(meso-BTA-alt-EBTG), 72% Yield.* $^1$H NMR (400 MHz, DMSO-$d_6$, δ, ppm): 1.59 [dt, 4H, −CH$_2$CH$_2$CH$_2$OC(=O)−, 11.6 Hz], 1.65 [dt, 4H, −CH$_2$CH$_2$OC(=O)−, 13.5 Hz], 2.60−2.66 [br, 4H, −SCH$_2$−], 3.59 [d, 4H, −OC(=O)CH$_2$S−, 6.6 Hz], 4.05 [t, 4H, −CH$_2$OC(=O)CH-(−OH)−, 6.2 Hz], 4.30 [t, 4H, −C(=O)OCH$_2$CH$_2$OC(=O)−, 5.4 Hz], 4.67 [d, 2H OC(=O)CH(−OH)CH(−OH)−, 6.2 Hz], 5.73 [d, 2H −CH(−OH)−, 4.8 Hz] (Figure 1).

*Poly(L-BTA-alt-DTT), 73% Yield.* $^1$H NMR (400 MHz, DMSO-$d_6$, δ, ppm): 1.55 [t, 4H, −CH$_2$CH$_2$CH$_2$OC(=O)−, 14.2 Hz], 1.67 [t, 4H, −CH$_2$CH$_2$OC(=O)−, 13.5 Hz], 2.34 [d, 4H, −SCH$_2$C(−OH)−, 1.9 Hz], 2.65−2.70 [brm, 4H, −SCH$_2$CH$_2$−], 3.59 [d, 2H, −SCH$_2$CH(−OH), 6.2 Hz], 4.10 [t, 4H, −CH$_2$OC(=O)CH(−OH)−, 6.4 Hz], 4.40 [d, 2H, −SCH$_2$C(−OH)−, 5.36Hz], 4.69 [d, 2H, OC(=O)-CH(−OH)CH(−OH)−, 5.4 Hz], 5.48 [d, 2H −OC(=O)CH(−OH)−, 5.8 Hz] (Figure S8).

*Poly(D-BTA-alt-DTT), 83% Yield.* $^1$H NMR (400 MHz, DMSO-$d_6$, δ, ppm): 1.59 [t, 4H, −CH$_2$CH$_2$CH$_2$OC(=O)−, 15.0 Hz], 1.67 [t, 4H, −CH$_2$CH$_2$OC(=O)−, 14.9 Hz], 2.33 [d, 4H, −SCH$_2$C(−OH)−, 1.82 Hz], 2.58−2.69 [brm, 4H, −SCH$_2$CH$_2$−], 3.59 [t, 2H, −SCH$_2$CH(−OH), 6.4 Hz], 4.10 [t, 4H, −CH$_2$OC(=O)CH(−OH)−, 6.4 Hz], 4.41 [d, 2H −SCH$_2$C(−OH)−, 7.1 Hz], 4.67 [d, 2H, OC(=O)-

CH(−OH)CH(−OH)−, 6.6 Hz], 5.47 [d, 2H −OC(=O)CH(−OH)−, 7.1 Hz] (Figure S9).

*Poly(meso-BTA-alt-DTT), 88% Yield.* $^1$H NMR (400 MHz, DMSO-$d_6$, δ, ppm): 1.52−1.64 [br, 4H, −CH$_2$CH$_2$CH$_2$OC-(=O)−], 1.64−1.73 [br, 4H, −CH$_2$CH$_2$OC(=O)−], 2.33 [d, 4H, −SCH$_2$C(−OH)−, 14.2 Hz], 2.58−2.66 [br, 4H, −SCH$_2$CH$_2$−], 3.61 [t, 2H, −SCH$_2$CH(−OH), 6.7 Hz], 4.05 [t, 4H, −CH$_2$OC(=O)CH(−OH)−, 11.4 Hz], 4.23 [s, 2H OC(=O)CH(−OH)CH(−OH)−], 4.31 [d, 2H, −SCH$_2$C-(−OH)−, 5.0 Hz], 5.72 [d, 2H −OC(=O)CH(−OH)−, 4.6 Hz] (Figure S10).

*Examination of Biodegradation of Poly(ester-thioether) by BOD Testing.* About 10 mg of each poly(ester-thioether)-casted film was dissolved into 10 mL of tetrahydrofuran and placed in a bottle (*n* = 2 per polymer). Activated sludge (2.65 mg mL$^{-1}$), obtained from the Nagoya City Waterworks and Sewerage Bureau, was added to the incubation medium (11.46 mL) comprising in mg L$^{-1}$: K$_2$HPO$_4$, 218; KH$_2$PO$_4$, 85; Na$_2$HPO$_4$, 334; NH$_4$Cl, 5; CaCl$_2$, 28; MgSO$_4$·7H$_2$O, 23; and FeCl$_3$·6H$_2$O, 0.25. The prepared incubation medium (pH 7.2−7.6) containing activated sludge was then added to each sample bottle to give a fixed polymer concentration (100 mg L$^{-1}$). Aniline was also examined as a reference compound. Bottles were incubated in a water bath at 25 °C for 28 days, and changes in the bottle atmosphere were recorded. BOD at 25 °C was determined by oxygen consumption using a BOD tester (model 200F, TAITEC Co., Koshigaya-shi, Japan), essentially according to ISO standard guidelines (ISO 14851). Values are presented as a ratio of theoretical oxygen demand (TOD; i.e., BOD/TOD, %) with experimental errors of ±5%.

*Hydrolysis Test of Poly(BTA-alt-DTT)s.* We conducted a weekly hydrolysis test of 10 mg of each sample using the basic culture medium that was also used for the BOD test at 25 °C for 7 days. After the test, the water was removed, the weight of each sample was measured, and the molecular weight and molecular weight distribution were determined by SEC calibrated based on linear PSt standards in THF (Table S1).

## ■ RESULTS AND DISCUSSION

First, we carried out monomer synthesis by chemoselective esterification of L-, D-, and *meso*-tartaric acids using an excess amount of 3-butene-1-ol (2 equiv), which proceeded in a bulk condition using 1 mol % of Sc(OTf)$_3$ as a catalyst (Scheme 2 and for the experimental procedure, please see Supporting Information). On stirring at room temperature for 24 h, the expected L- (Figure S1), D- (Figure S2), and *meso*-di(3-butenyl) tartrates (Figure S3) (L-, D-, and *meso*-BTAs) were prepared in 33, 32, and 37% yields, respectively (see also Figures S4-S6).

Next, we demonstrated the polyaddition of the BTAs with three kinds of alkanedithiol, namely, ED (Figure S7), EBTG (Figure 1), and DTT (Figures S8-10) according to Scheme 1, in which the reaction mixture was stirred in toluene at 70 °C

## Table 1. Thiol−Ene Polymerization of BTA with Dithiols[a]

| run | dialkene monomer | dithiol | yield[b] (%) | $M_n^c$ (kDa) | $M_w/M_n^c$ | $X_n^c$ | $T_g^d$ (°C) | BOD[e] (%) | $[\alpha]_D^{25h}$ (degree) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | L-BTA | ED | 82 | 9.0 | 2.5 | 50 | −12 | 8 | +11.2 |
| 2 | L-BTA | EBTG | 85 | 7.4 | 1.7 | 32 | −20 | 32 | +7.4 |
| 3 | D-BTA | EBTG | 77 | 4.2 | 1.8 | 18 | −22 | 70 | −8.5 |
| 4 | meso-BTA | EBTG | 72 | 3.3 | 1.6 | 14 | −25 | 43 | −0.6 |
| 5 | L-BTA | DTT | 73 | 1.0 | 2.1 | 4.8 | −11 | 10 | +10.7 |
| 6 | D-BTA | DTT | 83 | 1.1 | 1.3 | 5.2 | −13 | 2 | −10.5 |
| 7 | meso-BTA | DTT | 88 | 0.9 | 1.4 | 4.4 | −8 | 2 | −0.1 |
| 8[f] | L-BMA | ED | 42 | 5.3 | 1.6 | 24 | −47 | 13 | |
| 9[f] | L-BMA | EBTG | 58 | 4.4 | 1.7 | 20 | −41 | 23 | |
| 10[g] | L-BTA | DTT | 96 | 3.3 | 1.9 | 16 | −9 | 21 | +10.7 |
| 11[g] | D-BTA | DTT | 84 | 3.2 | 2.0 | 16 | −8 | 23 | −10.5 |
| 12[g] | meso-BTA | DTT | 64 | 1.9 | 1.4 | 9.0 | −8 | 21 | −0.1 |

[a]Conditions: in toluene ($[M]_0 = 1.0$) at 70 °C for 24 h using AIBN (1 mol % to dithiol). [b]After reprecipitation using chloroform and n-hexane as a good and a poor solvent, respectively. [c]Determined by SEC calibrated based on linear PSt standards in THF. [d]Determined by DSC measurements (heating rate: 10 °C min$^{-1}$). [e]BOD/TOD after 28 days. [f]Runs 8 and 9 were data from ref 34. [g]Conditions: higher total monomer concentration $[M]_0$ of 15.0 M. [h]Specific rotation measured by a polarimeter in THF (0.01 g mL$^{-1}$).
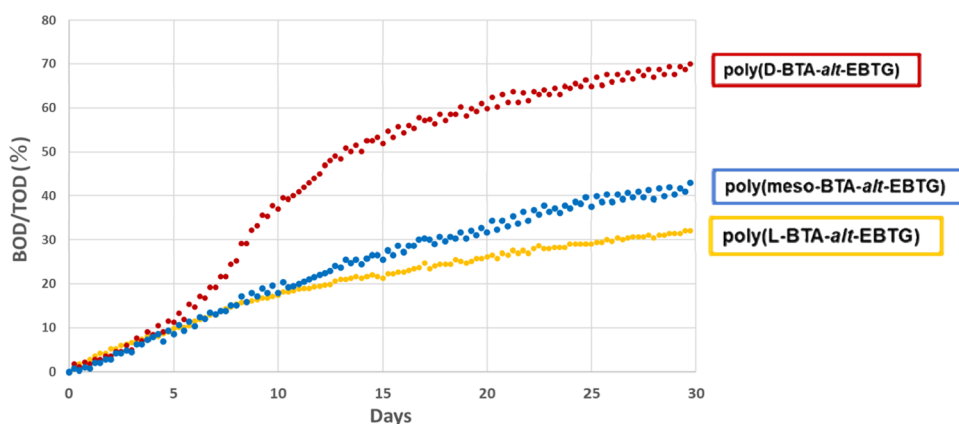


**Figure 2.** Changes of BOD/TOD values in the biodegradation of poly(L-BTA-*alt*-EBTG) ($M_n = 7.4 \times 10^3$), poly(D-BTA-*alt*-EGTG) ($M_n = 4.2 \times 10^3$), and poly(*meso*-BTA-*alt*-EBTG) ($M_n = 3.3 \times 10^3$) in activated sludge (25 °C).

for 24 h using AIBN (1 mol % to dithiol) as a radical trigger (Table 1). After the reaction, the reaction mixture was added to an excess methanol solvent to precipitate a polymeric material. $^1$H NMR indicated the corresponding poly(BTA-*alt*-EBTG)s (Figure 1) and poly(BTA-*alt*-ED)s (run 1 in Table 1 and Figure S7), which confirmed that the polyaddition proceeded via thiol−ene click polymerization (total monomer initial concentration $[M]_0 = 1.0$ M).

Using the SEC measurements, $M_n$s of the poly(BTA-*alt*-EBTG)s ranged from $3.3 \times 10^3$ to $7.4 \times 10^3$ with a molecular weight distribution ($M_w/M_n$) of 1.6−1.8 (runs 2−4 in Table 1). Polyaddition of BTAs with DTT also occurred to afford poly(L-BTA-*alt*-DTT) (run 5 in Table 1: $M_n = 1.0 \times 10^3$, $M_w/M_n = 2.1$, Figure S8), poly(D-BTA-*alt*-DTT) (run 6 in Table 1: $M_n = 1.1 \times 10^3$, $M_w/M_n = 1.3$, Figure S9), and poly(run 7 in Table 1: *meso*-BTA-*alt*-DTT) ($M_n = 0.9 \times 10^3$, $M_w/M_n = 1.4$, Figure S10), respectively. Because the molecular mass did not increase, the same operation was performed using a higher total monomer concentration ($[M]_0 = 15$ M) close to the bulk condition. As a result, $M_n$s of the poly(L-BTA-*alt*-DTT)s ranged from $1.9 \times 10^3$ to $3.3 \times 10^3$ with a molecular weight distribution ($M_w/M_n$) of 1.4−2.0 (runs 10−11 in Table 1). The yields were also satisfactory at 64−96%. DSC of all of the poly(ester-thioethers)s gave single glass transition ($T_g$) in each run and did not show endothermic peaks, indicating the absence of crystalline domains that melt under the examined

conditions. The $T_g$ of poly(L-BTA-*alt*-DTT)s (−13 to −8 °C) tended to be higher than that of poly(L-BTA-*alt*-EBTG)s (−25 to −20 °C). The higher $T_g$ values indicated more restricted molecular motion of poly(L-BTA-*alt*-DTT)s as compared with poly(L-BTA-*alt*-EBTG)s, which might be the reason for the lower $M_n$ values. The specific rotation ($[\alpha]_D^{25}$) of the poly(ester-thioether)s consisting of tartaric acids was also measured in THF using a polarimeter (Table 1). The poly(ester-thioether)s containing L-BTA (runs 2, 5, 8) and D-BTA (runs 3, 6, 11) showed positive and negative signs, respectively, with the same absolute values, indicating that no racemization occurred during the step polymerization. As a negative control, the poly(ester-thoether)s containing *meso*-BTA (runs 4, 7, 12) did not show optical activities.

In the biochemical oxygen demand (BOD) test using activated sludge, poly(L-BTA-*alt*-EBTG), poly(D-BTA-*alt*-EBTG), and poly(*meso*-BTA-*alt*-EBTG) all showed biodegradability, with 32, 70, and 43% biodegradation (as defined by BOD/TOD), respectively, after 28 days (Figure 2), in which time retardation of the degradation was not apparent. Interestingly, we observed both enantio and diastereo effects on biodegradation; in other words, the degradation of poly(D-BTA-*alt*-EBTG) (70%) was relatively higher than that of poly(L-BTA-*alt*-EBTG) (32%) or poly(*meso*-BTA-*alt*-EBTG) (43%). $T_g$s of poly(L-BTA-*alt*-EBTG) (−20 °C), poly(D-BTA-*alt*-EBTG) (−22 °C), and poly(*meso*-BTA-*alt*-EBTG) (−25
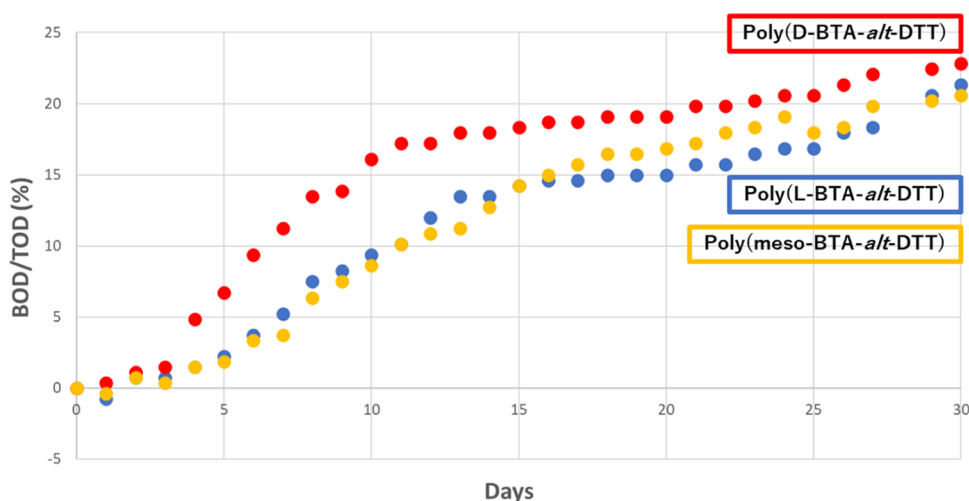
**Figure 3.** Changes of BOD/TOD values in the biodegradation of poly(L-BTA-*alt*-DTT) ($M_n = 3.3 \times 10^3$, run 10), poly(D-BTA-*alt*-DTT) ($M_n = 3.2 \times 10^3$, run 11), and poly(*meso*-BTA-*alt*-DTT) ($M_n = 1.9 \times 10^3$, run 12), in activated sludge (25 °C).
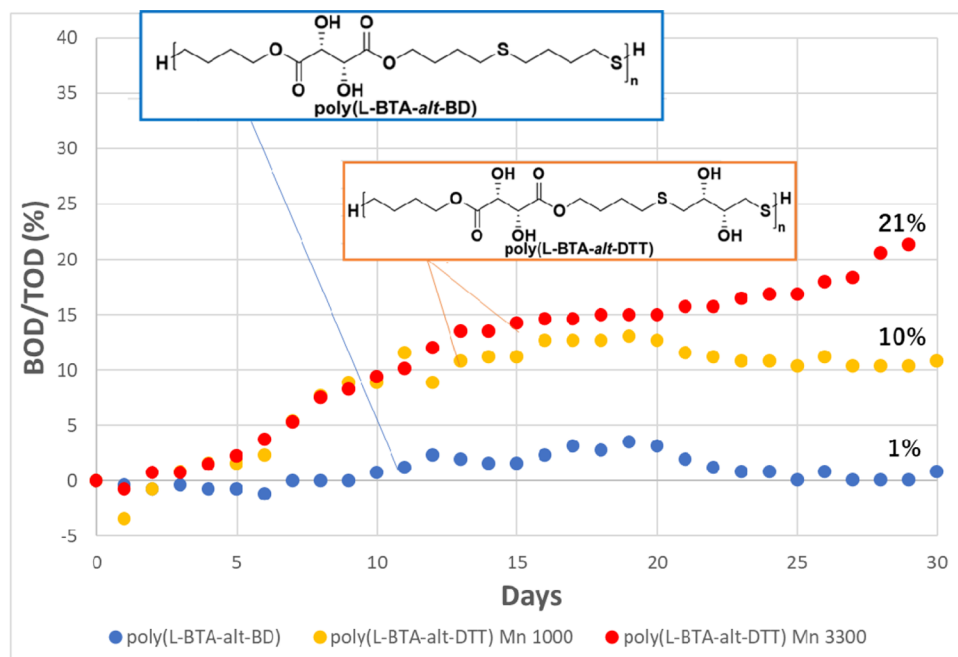


**Figure 4.** BOD/TOD curves of the biodegradation of poly(L-BTA-*alt*-DTT) ($M_n = 3.3 \times 10^3$, run 10 in Table 1), poly(L-BTA-*alt*-DTT) ($M_n = 1.0 \times 10^3$, run 5 in Table 1), and poly(L-BTA-*alt*-BD) ($M_n = 14.0 \times 10^3$) in activated sludge (25 °C).

°C) were almost the same (see Table 1). Therefore, we expected that the fast degradation of poly(D-BTA-*alt*-EBTG) is ascribed to substrate specificity. Compared with polyester prepared by polycondensation of tartaric acid and 1,5-pentanediol,[36] the biodegradation of poly(ester-thioether)s is slow because of the low molar ratio of the ester linkage in the polymer chain.

On the other hand, we observed slow biodegradation of poly(BTA-*alt*-DTT)s, whereby poly(L-BTA-*alt*-DTT), poly(D-BTA-*alt*-DTT), and poly(*meso*-BTA-*alt*-DTT) showed 21−23% biodegradation and poly(D -BTA-*alt*-DTT) indicated the fastest biodegradation (Figure 3), even though their $M_n$ values were lower ($M_n = (1.9−3.3) \times 10^3$). The tendency was similar to that of poly(BTA-*alt*-EBTG)s. We suspect that their higher $T_g$ values (see above) might result in their slower biodegradation.

In the BOD test of corresponding monomers, L-BTA, D-BTA, and *meso*-BTA, as shown in Figure S11, remarkable diastereoselectivity as well as enantioselectivity was not confirmed, which indicated that the polymeric effect in the poly(ester-thioether)s influenced the biodegradability.

Next, we compared the biodegradation of these poly(ester-thioether)s with that of our previously reported malic acid-based poly(ester-thioether)s: poly(L-BMA-*alt*-ED) (run 8 in Table 1) and poly(L-BMA-*alt*-EBTG) (run 9 in Table 1). They showed BOD/TOD values of 13 and 23%, respectively,[34] which were comparable to the corresponding BOD/TOD values of poly(L-BTA-*alt*-ED) (8%) and poly(L-BTA-*alt*-EBTG) (32%), respectively. As we previously reported,[34] poly(L-BMA-*alt*-EBTG) and poly(L-BMA-*alt*-ED) showed lower $T_g$ values (−41 and −47 °C, respectively); thus, the asymmetric structure of the malate units and hydroxyl groups

in the tartrate unit via hydrogen bonding are reflected in only $T_g$s, but a remarkable difference in their biodegradation in activated sludge was not observed in this experimental condition.

Lastly, in order to investigate the pendent hydroxyl groups on biodegradation, we compared the biodegradation of poly(L-BTA-*alt*-DTT) ($M_n = 1.0 \times 10^3$ from run 5 in Table 1) and poly(L-BTA-*alt*-DTT) ($M_n = 3.3 \times 10^3$ from run 10 in Table 1) with poly(L-BTA-*alt*-BD) ($M_n = 14.0 \times 10^3$) (Figure 4). After 28 days of biodegradation, BOD/TOD values of poly(L-BTA-*alt*-DTT)s (10 and 21%, respectively) were higher than that (1%) of poly(L-BTA-*alt*-BD), even though the former had a higher $T_g$ (−11 °C) than that the $T_g$ (−30 °C) of the latter, in which it seems that the difference of the $M_n$ did not influence the biodegradation of poly(L-BTA-*alt*-DTT)s. As a negative control, we demonstrated a hydrolysis test of poly(BTA-*alt*-DTT)s (see Table S1). As a result, all of the samples show a weight loss of 25−76% and decreases in molecular weights ($M_n$s), accompanied by a broadening of $M_w/M_n$. The result suggests that they are hydrolyzed in the absence of microorganisms, in which poly(*meso*-BTA-*alt*-DTT) indicated the highest accessibility toward hydrolysis and differed from the results of BOD measurements. Now we concluded, therefore, that the pendent hydroxyl groups in the poly(ester-thioether)s induced hydrogen bonding between polymer backbones, which reflected in the higher $T_g$, and increased hydrophilicity as well as substrate specificity (stereochemistry) for the degradation enzyme is the reason for the faster biodegradation.

## CONCLUSIONS

In this study, we synthesized tartaric acid-based poly(ester-thiether)s via thiol−ene click polymerization of dialkenes containing L-, D-, and *meso*-tartrate units with several dithiols. The polymerization proceeded via a step polymerization mechanism to give the expected poly(ester-thiether)s. The biodegradation of the synthesized poly(ester-thiether)s was evaluated by the BOD value, which indicated that poly(ester-thiether) containing D-BTA had the highest biodegradability during the 28 day test. Both enantio and diastereo effects on biodegradability were observed, providing insights into the design of new types of biomass-based biodegradable polymers containing chiral centers.

## ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c07627.

> Representative spectral and analytical data; $^1$H NMR spectrum of L-BTA; $^1$H NMR spectrum of *meso*-BTA; ESI-MS spectrum of L-BTA; ESI-MS spectrum of *meso*-BTA; $^1$H NMR spectrum of poly(L-BTA-*alt*-DTT); $^1$H NMR spectrum of poly(*meso*-BTA-*alt*-DTT); hydrolysis test of poly(BTA-*alt*-DTT)s (PDF)

## AUTHOR INFORMATION

### Corresponding Author

Akinori Takasu − *Department of Life Science and Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan;* ⓞ orcid.org/0000-0003-3059-4463; Email: takasu.akinori@nitech.ac.jp

### Authors

Ryota Imamura − *Department of Life Science and Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan*

Kota Oto − *Department of Life Science and Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan*

Kaho Kataoka − *Department of Life Science and Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c07627

### Notes

The authors declare no competing financial interest.

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