

Chemical Synthesis of Fully Biomass-Based Poly(butylene succinate) from Inedible-Biomass-Based Furfural and Evaluation of Its Biomass Carbon Ratio

Yuya Tachibana, Takashi Masuda, Masahiro Funabashi, and Masao Kunioka*

National Institute of Advanced Industrial Science and Technology (AIST),
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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We have produced fully biomass-based poly(butylene succinate) (PBS) from furfural produced from inedible agricultural cellulosic waste. Furfural was oxidized to give fumaric acid. Fumaric acid was hydrogenated under high pressure with a palladium–rhenium/carbon catalyst to give 1,4-butanediol, and with a palladium/carbon catalyst to give succinic acid. Dimethyl succinate was synthesized from fumaric acid by esterification and hydrogenation under normal pressure. Fully biomass-based PBS was obtained by polycondensation of biomass-based 1,4-butanediol and biomass-based succinic acid or dimethyl succinate. The biomass carbon ratio calculated from ^{14}C concentrations measured by accelerator mass spectroscopy (AMS) verified that the PBS obtained in this study contained only biomass carbon. The polycondensation of biomass-based 1,4-butanediol and petroleum-based terephthalic acid or dimethyl terephthalate gave partially biomass-based poly(butylene terephthalate), which is an engineering plastic.

Introduction

The use of petroleum for plastics production contributes to problems such as global warming. Depletion of petroleum supplies is also a problem. To reduce the amount of petroleum used for plastics production, plastics-producing companies and research organization have been developing various biomass-based plastics, and some, such as poly(lactic acid) (PLA),¹ poly(hydroxyl alkanooate),² nylon-11,³ and polyurethane⁴ have been used in manufacturing.

Much attention has been given to PLA produced from corn as a new biomass-based material because of its large-scale production^{1a} and environmentally friendly properties.^{1b} The properties of PLA are, however, different from those of commodity plastics and its physical properties and moldability are inferior to those of commodity plastics. Production companies and researchers have put a great deal of effort into the development of PLA modification technology.⁵ A further problem is that PLA is produced from edible biomass. For biomass-based plastics to become widely used, their properties need to be equivalent to those of the commodity plastics currently in use. The best solution would be to produce the commodity plastics currently in use from biomass feedstock. One such solution, the large-scale production of polyethylene from a bioethanol, has been proposed.⁶

We have focused on another environmental problem caused by plastics, that is, plastics waste.⁷ To solve the environmental problems caused by plastics waste, new biorecycling waste treatment systems such as composting or methane fermentation, and some biodegradable materials such as poly(butylene succinate) (PBS),⁸ PLA,⁹ poly(hydroxyl alkanooate),² and polycaprolactone¹⁰ have been developed. PBS is a commercially available biodegradable plastic and had already been used for several purposes when it was being produced from petroleum chemicals. Recently, many researchers have reported that the

PBS monomers, that is, 1,4-butanediol (BD) and succinic acid (SA), could be produced from biomass feedstock.¹¹ SA is found in some animals and plants, for example, shellfish. SA is produced by a chemical procedure from benzene via maleic anhydride.¹² We have confirmed that the commercially available SA as a food additive for seasoning was derived from petroleum-based materials.¹³ SA can be produced by a fermentation process¹⁴ and can be converted to BD by hydrogenation.¹⁵ Some companies have announced that in future SA would be produced from biomass feedstock by a fermentation process to produce biomass-based PBS.¹⁶ However, no one has yet reported the actual synthesis.

We have also focused on furan derivatives as the starting material for monomer synthesis. Furfural and furfuryl alcohol are used industrially as an organic solvent or resin and are valuable biomass compounds as they can be produced from inedible biomass like cellulose.¹⁷ Furfural has five carbon atoms and consists of an aromatic furan moiety and an aldehyde group. Around 100 years ago,^{18a} the chemistry of furfural was studied for its potential as an energy or materials resource, and some chemical reforming methods such as oxidation and reduction were developed to produce chemicals that are more useful than furfural.¹⁸

Several nations currently provide tax and purchase incentives to encourage the use of biomass-based products. When biomass-based PBS is synthesized, a method of verifying that the plastic has been produced from biomass feedstock will be necessary to distinguish it from petroleum-based plastics. Determining the biomass carbon ratio is the most practical and effective method of verifying that a plastic is biomass based. Recently, accelerator mass spectroscopy (AMS) methods for determining the biomass carbon ratio based on the American Society for Testing and Materials (ASTM) D6866 method, *Standard test methods for determining the biobased content of solid, liquid, and gaseous samples using radiocarbon analysis*, have become important

* To whom correspondence should be addressed. Tel.: +81-29-861-4584. Fax: +81-29-861-4589. E-mail: m.kunioka@aist.go.jp.

in the field of biomass.¹⁹ We have investigated the suitability of this method for evaluating the biomass carbon ratio of plastics.²⁰

In this paper, we report the first practical synthesis of fully biomass-based PBS from inedible biomass-based furfural. BD and SA were obtained from furfural by chemical reactions, and polymerized to PBS. The biomass carbon ratios of the synthesized materials were measured by the AMS method. To confirm the validity of the AMS method for the evaluation of biomass-based plastics, PBSs with various ratios of biomass-based monomer and petroleum-based monomer were polymerized and measured by the AMS method; the repeatability was also evaluated. Partially biomass-based poly(butylene terephthalate) (PBT), which is an engineering plastic, was synthesized from the biomass-based BD synthesized in this study and petroleum-based terephthalic acid.

Experimental Section

Materials and Methods. The furfural was purchased from Wako Pure Chemical Industries (Osaka, Japan) and used after distillation under reduced pressure. Other chemicals were reagent grade and used without further purification. A palladium–rhenium/carbon catalyst was prepared by a previously reported method.²¹ ¹H NMR spectra were recorded on a 400 MHz NMR spectrometer (JEOL, Tokyo, Japan, JNM-ECX400) using tetramethylsilane as an internal standard. The molecular weight of PBS was determined by gel permeation chromatography (GPC) with a refractive index detector and a combination of two columns (Tosoh Co., Tokyo, Japan, TSK GMHXL). The columns were eluted with chloroform (flow rate of 0.5 mL/min at 40 °C) and the molecular weights were calibrated with polystyrene standards. The molecular weight of PBT was determined by gel permeation chromatography (GPC) with a refractive index detector and a column (Showa Denko K.K., Tokyo, Japan, LF-404). The columns were eluted with hexafluoroisopropanol with 5 mM sodium trifluoroacetate (flow rate of 0.14 mL/min at 40 °C), and the molecular weights were calibrated with poly(methyl methacrylate) standards. The melting temperature was determined by a differential scanning calorimetry system (Seiko Instruments Inc., Chiba, Japan; SSC/5520) at a rate of 10 °C/min to 150 °C.

Sample Preparation for Measurement of Biomass Carbon Ratio. Pretreatment of the samples for AMS and measurements were performed at the Institute of Accelerator Analysis, Ltd. (IAA; Fukushima, Japan). All carbon atoms in the samples were transformed into graphite carbons by serial oxidation and reduction reactions using a quartz glass tube and a vacuum manifold system. The sample (6.5 mg) was mixed with CuO (1 g) and transferred to a quartz glass tube. The tube was closed after storage under a vacuum for 10 h. The sample in the tube was oxidized to CO₂ at 500 °C for 30 min and at 850 °C for 2 h. Subsequently, CO₂, CO, and H₂O were cold-trapped in another tube using dry ice/ethanol (−76 °C) connected to a closed vacuum line system. The cold-trap step was repeated twice. Pure CO₂ was cold-trapped in a quartz glass tube with pure ferrous powder in liquid N₂ (−196 °C); the other reactants, such as CO₂, CO, and H₂O, were cold-trapped in another tube under dry ice/ethanol. The CO₂ with ferrous powder was reduced to graphite at 650 °C for 10 h. After these processes, the pure graphite and oxidized iron (1 mg) were transferred to a sample holder (small rod shape; 1 mm hole).

Measurement of Biomass Carbon Ratio. The measurement of the ratios of the three carbon isotopes (¹⁴C, ¹³C, and ¹²C) using AMS was performed at the IAA (see Supporting Information for details). Our measurements were obtained using the 3 MV tandem accelerator system at the IAA. The carbon in graphite from the sample was ionized using a cesium cation beam. The reduced carbon atoms were accelerated using a 3 MV tandem accelerator (National Electrostatics Co., Middleton, WI, Pelletron 9SDH-2). The amounts of ¹²C and ¹³C were detected as a current using multi-Faraday cups. The ¹⁴C atoms were detected using

a Δ*E* – *E* detector. The percentage of modern carbon (pMC) was calculated from the ¹⁴C/¹²C concentration ratios for the sample. The biomass carbon ratio was determined from the ¹⁴C concentration measured using AMS based on the ASTM D6866 standard method. Reference materials were measured for the obtained graphite using AMS. The biomass carbon ratios were calculated as follows:

$$^{14}\text{As} = ^{14}\text{C}/^{12}\text{C} \text{ in sample} \quad (1)$$

$$^{14}\text{Ar} = ^{14}\text{C}/^{12}\text{C} \text{ in reference material (NIST SRM 4990c)} \quad (2)$$

$$\Delta^{14}\text{C} = [(^{14}\text{As} - ^{14}\text{Ar})/^{14}\text{Ar}] \times 1000(\%) \quad (3)$$

$$\text{pMC} = \Delta^{14}\text{C}/10 + 100(\%) \quad (4)$$

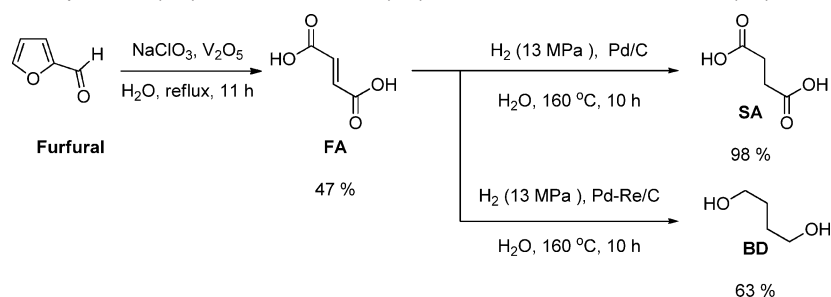
$$\text{biomass carbon ratio} = 0.93 \times \text{pMC}(\%) \quad (5)$$

Δ¹⁴C is the isotope differential ratio of ¹⁴C between the sample and reference material, and pMC is the percentage of modern carbon. Modern-carbon-based oxalic acid radiocarbon [standard reference material (SRM) 4990c, National Institute of Standards, U.S.A.] was used as the reference material. The pMC for a petroleum-based carbon is 0%. The pMC for biomass produced by fixation of CO₂ in the atmosphere by photosynthesis was 108–110% in 2002. The pMC can be slightly higher than 100% because of the continuing, but diminishing, effects of the 1950s nuclear-testing programs in the atmosphere. During this period, large amounts of ¹⁴C were emitted into the atmosphere. Because the ¹⁴C in all the samples is referenced to a “prebomb” standard, all pMC values must be multiplied by 0.93 to correct for the bomb carbon and to obtain the true biomass carbon ratio of the sample, as indicated in eq 5, based on ASTM D6866.

Oxidation of Furfural to Fumaric Acid (FA).^{18a} Furfural (40.0 g, 416 mmol) was added dropwise to a solution of sodium chlorate (90.0 g, 850 mmol) and vanadium pentoxide (400 mg, 2.20 mmol) in water (200 mL) at 85 °C for 2 h, and the mixture was stirred at 95 °C for 17 h. The mixture was cooled at 4 °C for 12 h and a white precipitate was obtained. The precipitate was filtered and recrystallized from 1 M HCl to give 22.6 g (47%) of FA as white crystals: mp 201.3 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 6.60 (s, 2H, –CH=) ppm. IR (diamond-ATR) 3083, 1654, 1421, 1319, 1270, 1227, 1211, 1002, 893, 781, 721 cm^{−1}.

Hydrogenation of FA to BD.²¹ FA (30.0 g, 258 mmol), 5% palladium–rhenium/carbon (8.0 g), and distilled water (70 mL) were added to a titanium autoclave (1.0 L). After purging the autoclave with 13 MPa of hydrogen at room temperature, the temperature was raised to 160 °C. The autoclave was kept at 160 °C for 10 h, and the pressure was gradually decreased to 9 MPa. After cooling, the resulting mixture was filtered with a glass filter, and the solution was distilled under a vacuum to give 14.9 g (64%) of BD as a colorless oil: bp 104 °C (6 kPa). ¹H NMR (400 MHz, DMSO-*d*₆) δ 4.12 (s, 2H, –OH), 3.45–3.42 (m, 4H, HO–CH₂–CH₂–), 1.50–1.43 (m, 4H, HO–CH₂–CH₂–) ppm. IR (diamond-ATR) 3290, 2936, 2868, 1435, 1376, 1174, 1049, 1007, 944 cm^{−1}.

Hydrogenation of FA to SA.²² FA (30.0 g, 258 mmol), 5% palladium/carbon (8.0 g), and distilled water (70 mL) were added to a titanium autoclave (1.0 L). After purging the autoclave with 13 MPa of hydrogen at room temperature, the temperature was raised to 160 °C. The autoclave was kept at 160 °C for 9.5 h, and the pressure was gradually decreased to 10 MPa. After cooling, the resulting mixture was filtered with a glass filter, and the solution was distilled under a vacuum to give 30.0 g (98%) of SA as a colorless solid: mp 185.4 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.95 (s, 2H, –COOH), 2.23 (s, 4H, –CH₂–) ppm. IR (diamond-ATR) 2930, 2625, 2532, 1677, 1409, 1304, 1195, 1175, 892, 801 cm^{−1}.

Scheme 1. Synthesis of 1,4-Propanediol (BD) and Succinic Acid (SA) from Furfural via Fumaric Acid (FA)

Esterification of FA to Dimethyl Fumarate (DF). Concentrated sulfuric acid (3.0 mmol) was added to a solution of FA (10.0 g, 86.2 mmol) in methanol (60 mL) at room temperature, and the mixture was heated under reflux for 8 h. The mixture was cooled and a white precipitate was obtained. The precipitate was filtered and sublimed under a vacuum to give 12.4 g (99%) of DF as white crystals: mp 101.9 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.86 (s, 2H, $-\text{CH}=\text{}$), 3.81 (s, 6H, $-\text{CH}_3$) ppm. IR (diamond-ATR) 3077, 3018, 2964, 1713, 1438, 1305, 1199, 1157, 1007, 989, 882, 773, 671 cm^{-1} .

Hydrogenation of DF to Dimethyl Succinate (DS). DF (11.0 g, 76 mmol) and 5% palladium/carbon (3.0 g) were added to methanol (500 mL). Hydrogen gas flowed through the reaction mixture at a rate of 50 mL/min at room temperature for 3 h. The resulting mixture was filtered with a glass filter, and the solution was distilled under reduced pressure to give 9.78 g (88%) of DS as a colorless oil: bp 100 °C (0.8 kPa). $^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ 3.50 (s, 4H, $-\text{CH}_2-$), 2.46 (s, 6H, $-\text{CH}_3$) ppm. IR (diamond-ATR) 2956, 1731, 1437, 1361, 1323, 1201, 1156, 1028, 845 cm^{-1} .

Direct Polycondensation of BD and SA to PBS.²³ A 10 mL flask was charged with SA (3.54 g, 30 mmol), BD (2.97 g, 33 mmol), and titanium tetraisopropoxide (4.2 mg, 14 μmol). The flask was provided with a gas inlet and outlet and heated at 243 °C for 1 h under a dry N_2 flow to remove the water produced by the esterification reaction. Subsequently, polycondensation was carried out under 10 Pa at 243 °C for 2 h. The resulting solid was dissolved in chloroform (20 mL) and the solution was poured into methanol (100 mL). The precipitate was filtered and dried under a vacuum at 80 °C to give 5.01 g (97%) of PBS as a white solid. The number average molecular weight was determined by GPC ($M_n = 85000$, $M_w/M_n = 2.6$).

Transesterification Polycondensation of BD and DS to PBS.²⁴ A 10 mL flask was charged with DS (292 mg, 2.00 mmol), BD (187 mg, 2.08 mmol), and titanium tetraisopropoxide (0.3 mg, 1.0 μmol). The flask was provided with a gas inlet and outlet and heated at 215 °C for 1 h under a dry N_2 flow to remove the methanol produced as a byproduct of the esterification. Subsequently, polycondensation was carried out under 10 Pa at 215 °C for 4 h. The resulting solid was dissolved in chloroform (2.0 mL) and the solution was poured into methanol (100 mL). The precipitate was filtered and dried under a vacuum at 80 °C to give PBS as a white solid. The number average molecular weight and melting temperature were shown in Supporting Information.

Typical PBS Data. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.14–4.10 (m, 4H, $-\text{O}-\text{CH}_2-$), 2.62 (s, 4H, $-(\text{C}=\text{O})-\text{CH}_2-$), 1.72–1.61 (m, 4H, $-\text{O}-\text{CH}_2-\text{CH}_2-$) ppm. IR (diamond-ATR) 2946, 1712, 1473, 1447, 1425, 1388, 1330, 1312, 1207, 1153, 1046, 955, 919, 806 cm^{-1} . Anal. Calcd for $\text{C}_8\text{H}_{12}\text{O}_4$: C, 55.81; H, 7.02. Found: C, 55.88; H, 7.03.

Direct Polycondensation of BD and Terephthalic Acid to PBT.²⁵ A 10 mL flask was charged with petroleum-based terephthalic acid (227 mg, 1.37 mmol) and biomass-based BD (209 mg, 2.32 mmol). Butylhydroxy tin oxide (0.9 mg, 4.3 μmol) and titanium tetrabutoxide (0.3 mg, 3.0 μmol) were added as a catalyst. The flask was provided with a gas inlet and outlet and heated at 220 °C for 1 h under a dry N_2 flow to remove the methanol produced as a byproduct of the esterification reaction. Subsequently, polycondensation was carried out under 10 Pa at 250 °C for 3 h. The resulting solid was dissolved in

hexafluoroisopropanol (3.0 mL) and the solution was poured into methanol (100 mL). The precipitate was filtered and dried under a vacuum at 80 °C to give 287 mg (95%) of PBT as a white solid. The number average molecular weight was determined by GPC ($M_n = 7400$, $M_w/M_n = 2.6$).

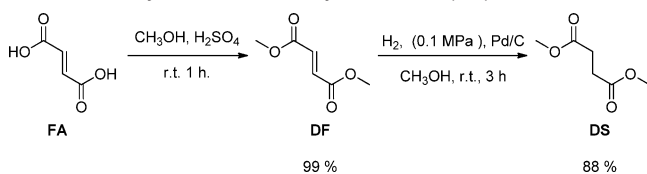
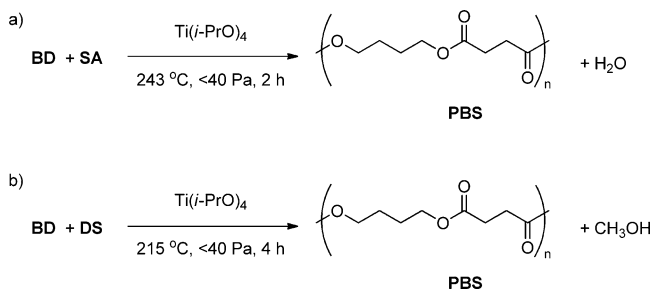
Transesterification Polycondensation of BD and Dimethyl Terephthalate.²⁶ A 10 mL flask was charged with petroleum-based dimethyl terephthalate (266 mg, 1.37 mmol), biomass-based BD (222 mg, 2.46 mmol), and titanium tetraisopropoxide (0.2 mg, 0.7 μmol). The flask was provided with a gas inlet and outlet, and heated at 220 °C for 1 h under a dry N_2 flow to remove the methanol produced as a byproduct of the esterification reaction. Subsequently, polycondensation was carried out under 10 Pa at 250 °C for 3 h. The resulting solid was dissolved in hexafluoroisopropanol (3.0 mL) and the solution was poured into methanol (100 mL). The precipitate was filtered and dried under a vacuum at 80 °C to give 280 mg (93%) of PBT as a white solid. The number average molecular weight was determined by GPC ($M_n = 9800$, $M_w/M_n = 2.4$).

Typical PBT Data. $^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3/\text{CF}_3\text{COOH}$) δ 8.16 (s, 4H, $-\text{phenyl-H}$), 4.55 (s, 4H, $-\text{O}-\text{CH}_2-$), 2.07 (s, 4H, $-\text{O}-\text{CH}_2-\text{CH}_2-$) ppm. IR (diamond-ATR) 1960, 1711, 1504, 1457, 1408, 1264, 1116, 1100, 1017, 936, 873, 725 cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_4$: C, 65.45; H, 5.49. Found: C, 65.11; H, 5.44.

Results and Discussion

Conversion of Furfural to Biomass-Based Monomer. The furfural used in this study was a commercially available chemical produced from biomass feedstock such as corn cobs, which is a cellulosic agricultural waste. The AMS method was used to verify that the furfural was biomass based. Furfural is an aromatic aldehyde and is therefore easily oxidized in air to a pale yellow and then red solution.²⁷ When an oxidative reagent and a catalyst are added to furfural, it can be further oxidized to give four-carbon compounds: maleic acid, fumaric acid, furan, and furan derivatives. In the case of addition of sodium chlorate and vanadium pentoxide catalyst, furfural was converted to a mixture of maleic acid and fumaric acid, which are *cis-trans* geometrical isomers (Scheme 1). The mixture was purified by recrystallization from 1 M aqueous hydrochloric acid to give fumaric acid as white crystals in 47% yield.

Fumaric acid can be catalytically hydrogenated to BD and SA, which are the monomers of PBS. In general, the hydrogenation of the double bonds in carboxylic acids under mild conditions is difficult. The hydrogenation is therefore carried out under high pressure and high temperature with a heterogeneous catalyst.²⁸ The alkene double bond of fumaric acid was hydrogenated with 5% palladium/carbon catalyst under high pressure hydrogen (13 MPa) at high temperature (160 °C) for 10 h to give SA as white crystals in 98% yield. The hydrogenation of the double bond of a carboxylic acid to an alcohol is more difficult with commercially available catalysts such as palladium/carbon. The hydrogenation of fumaric acid to BD

Scheme 2. Synthesis of Dimethyl Succinate (DS)**Scheme 3.** Polycondensation of PBS: (a) Direct Polycondensation; (b) Transesterification Polycondensation

has been reported by Pedersen et al.²¹ Fumaric acid was hydrogenated with 5% palladium–rhenium/carbon catalyst under 13 MPa hydrogen at 160 °C for 10 h to give BD selectively in 63% yield.

Hydrogenation of carboxylic compounds hardly occurs under normal pressure, even if the hydrogenation of fumaric acid is limited to the alkene double bond.

In contrast, the alkene double bond of an alkyl ester can be easily hydrogenated to give an aliphatic ester under normal pressure at room temperature. Because the condensation of a diol and a diester can easily give the corresponding polyester, the synthesis of diester succinate, a monomer of PBS, is useful in establishing the various synthetic routes to biomass-based PBS; the monomer synthesis uses little energy because the reaction takes place at normal pressure. Dimethyl succinate (DS) was synthesized from fumaric acid by esterification with concentrated sulfuric acid in a methanol solution to give dimethyl fumarate in 98% yield after purification by recrystallization from methanol (Scheme 2). Dimethyl fumarate was hydrogenated under normal pressure and room temperature for 1 h to give DS in 88% yield after distillation.

Biomass Carbon Ratios of Monomers. To verify that the PBS monomers we synthesized were obtained from biomass-based furfural rather than being petroleum-based, the biomass carbon ratios were measured by the AMS method. The biomass carbon ratios of furfural, FA, BD, and SA were 100.8, 100.4, 99.4, and 99.0%, respectively, showing that the chemicals had only biomass carbon. In the case of DS, there were four biomass carbon atoms, from the biomass-based SA unit, and two petroleum-based carbon atoms, from the petroleum-based methanol. The biomass carbon ratio of DS was 66.6%, verifying that the DS had 4/6 biomass carbons.

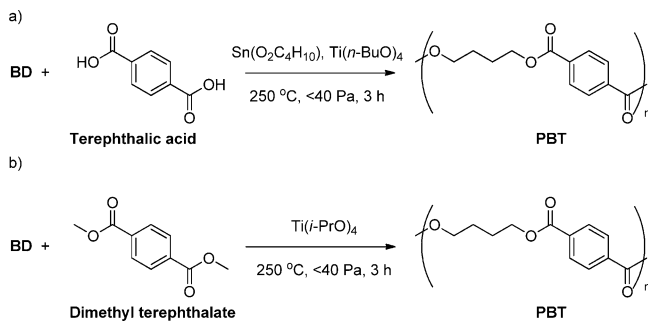
Fully Biomass-Based PBS by Polycondensation of BD and SA. Production of PBS by polycondensation is already used in industrial manufacturing worldwide. We demonstrated the polycondensation of biomass-based PBS by direct polycondensation of a diol and a dicarboxylic acid. The transesterification polycondensation of a diol and a diester was also carried out (Scheme 3). The direct polycondensation of BD and SA, with removal of water, was carried out using a titanium tetraisopropoxide catalyst at 243 °C under 1 mmHg for 2 h. The transesterification polycondensation of BD and DS, with removal of methanol, was carried out using a titanium tetraisopropoxide catalyst at 215 °C under 10 Pa for 4 h to give high molecular

weight PBSs in yields of over 90%. The properties of the biomass-based monomers should be the same as those of the petroleum-based monomers, and the properties of the PBS should be the same as those of petroleum-based PBS, except for the biomass carbon ratio.

Biomass Carbon Ratios of Fully and Partially Biomass-Based PBS. To confirm that the resulting PBSs had biomass carbon, the biomass carbon ratio of the PBSs were measured by the AMS method. The biomass carbon ratio of the PBS polymerized from all-biomass BD and SA was 100%. This was therefore the first synthesis of fully biomass-based PBS and it was verified that all the carbon atoms were derived from biomass feedstock. The biomass carbon ratio of the PBS from all-biomass BD and DS was also 100%. Although the DS included petroleum-based methanol, the resulting PBS was fully biomass-based because the methanol was eliminated in the transesterification polycondensation. To confirm that the biomass carbon ratio depended on the mixture ratio of the biomass-based and petroleum-based monomers, partially biomass-based PBSs with a mixture of biomass-based and petroleum-based monomers in various ratios were prepared under the same reaction conditions. PBSs produced from all-biomass-based BD and all-petroleum-based DS, from all-petroleum-based BD and all-biomass-based DS, and from 50% biomass-based BD and 50% biomass-based DS had 50% biomass carbons. The actual biomass carbon ratios were 49.11, 49.99, and 49.21, respectively. PBSs, including 10% biomass-based BD or DS, had 5% biomass carbons. The biomass carbon ratios were 5.08 and 4.88, respectively. The biomass carbon ratios of biomass-based PBSs agreed with the theoretical values of the mixture ratios of biomass-based and petroleum-based monomers, showing that number of biomass carbons in the PBS corresponded to the ratio of the biomass-based monomer in the mixture. We have already reported that the repeatability of the biomass carbon ratio of a partially biomass-based sample, a blend of biomass-based poly(lactic acid) and petroleum-based PBS, was slightly inferior to that of bioethanol, which has only biomass carbons.^{20b} It is possible that because the amount of sample used in the AMS method was very small (ca. 10 mg), the heterogeneity of the biomass-based sample and the petroleum-based sample affected the biomass carbon ratio of each measured sample. To evaluate the repeatability of the biomass carbon ratio of the polymer with biomass carbon and petroleum carbon, the biomass carbon ratio of a partially biomass-based PBS, which was a mixture of petroleum-based BD and petroleum-based biomass-based DS was measured six times by the AMS method. The average value of the biomass carbon ratio was 49.79%. The standard deviation ($1\sigma = 0.25$) of the repeated measurement for the biomass carbon ratio was smaller than the value ($\sigma = 0.84$) for the partially biomass-based sample which was a blend of biomass-based poly(lactic acid) and petroleum-based PBS.^{20d} Therefore, a mixture of biomass-based and petroleum-based monomer could provide a PBS that had a homogeneous distribution of biomass carbons. These biomass carbon ratio measurements indicated that the AMS method was suitable for the exact evaluation of material produced from biomass feedstock, even if part of the monomer was petroleum based.

Polycondensation of Partially Biomass-Based PBT from BD and Terephthalic Acid. PBT is useful as an engineering plastic because of its high heat resistance, chemical resistance, electrical properties, and good moldability. PBT is mainly used in parts of automobiles and in electrical products. The PBT monomer units are BD and terephthalate. Although terephthalic acid has not yet been produced from biomass feedstock, the

Scheme 4. Polycondensation of partially biomass-based poly(butylene terephthalate) (PBT) with BD synthesized from furfural and petroleum-based terephthalic acid



PBT polymerized from biomass-based BD with four carbons and petroleum-based terephthalic acid with eight carbons is a partially biomass-based plastic with 12 carbons in the polymer unit, and the biomass carbon ratio reaches 33.3% ($4/(4 + 8)$). Partially biomass-based engineering plastics are important in decreasing carbon dioxide emissions and in conserving petroleum resources, even if the biomass carbon ratio is 33%. We succeeded in synthesizing partially biomass-based PBT from biomass-based BD and petroleum-based terephthalic acid or dimethyl terephthalate (Scheme 4). The ^1H NMR spectrum, molecular weight, and melting point showed that the resulting material was the same as fully petroleum-based PBT. Both biomass carbon ratios of the partially biomass-based PBTs measured by the AMS method were 33.7%, which agreed with the theoretical value (Scheme 4). It was confirmed that the resulting PBTs were partially biomass-based PBT.

Conclusions

The effective use of biomass feedstock is a pressing problem. Biomass-based materials are needed for sustainable development as they can help to decrease carbon dioxide emissions and help to conserve petroleum resources. Biomass-based PBS is one solution. Furfural has long been known as a biomass chemical, but furfural is only used as a solvent and in special materials. We synthesized biomass-based PBS monomers BD, SA, and DS from furfural in polymer grade purity and polymerized these monomers to PBS with arbitrary biomass carbon ratios. We also succeeded in polymerizing the monomers to PBS with arbitrary biomass carbon ratios. This PBS was the first fully biomass-based material; this was verified by the AMS method. A verification method for the biomass carbon ratio of plastics which have both biomass-based monomers and petroleum-based monomers had not been previously reported. Measurements on PBS with a low biomass carbon ratio showed that the AMS method could be useful in verifying the biomass carbon ratio from high ratios (100%) to low ratios (5%); its repeatability was stable. Furthermore, partially biomass-based PBT, which is an important engineering material for automobiles and electrical applications, was synthesized from biomass-based BD and petroleum-based terephthalic acid and identified as a 33.3% (four carbons from biomass-based BD/12 carbons) biomass-based material.

When materials are supplied from biomass feedstocks in the future, this verification method will be indispensable and widely used. We demonstrated the first chemical synthesis of fully biomass-based PBS and evaluated the AMS method as a verification method. This fully inedible-biomass-based PBS will join the biomass plastics family, which includes PLA and PHB.

The use of the AMS method as the standard verification method for biomass-based plastics could promote the change from petroleum-based plastics to biomass-based plastics. These fully and partially biomass-based PBSs can be used as standard materials for the measurement of biomass carbon ratios using the AMS method because the PBSs have arbitrary biomass carbon ratios and homogeneous biomass carbon compositions.

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Supporting Information Available. Details of AMS method. The law data of biomass carbon ratio, the melting temperature, the number average molecular weight, and yield of each polymer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

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