Novel synthesis of bio-derived aromatic acid anhydride and synthesis of wholly aromatic bio-based polyimide

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1. Introduction

Currently, raw materials for synthetic polymers most depend on fossil resources. However, the deposition of fossil resources is much slower than photosynthesis. Ideal resource recycling is difficult in the form of current resource management. In order to solve this, biomass is used for polymer synthesis instead of fossil resources. Bio-based plastics have been put to practical use in part. If biomass is used as a raw material, it is possible to secure synthetic raw materials for plastic stably over the future. Bio-based plastics can contribute to reducing environmental burden by the concept of carbon neutral and carbon stock. Polylactic acid is a representative example of bio-based plastics that have come into practical use now. It is a biodegradable plastic and it helps to reduce plastic waste. But, since polylactic acid has low heat resistance, its application is limited. (Fig. 1.) In this research, in order to expand the possibility of bio-based plastics, we aimed to synthesize aromatic polyimide which is a representative super engineering plastic on a bio-based basis.

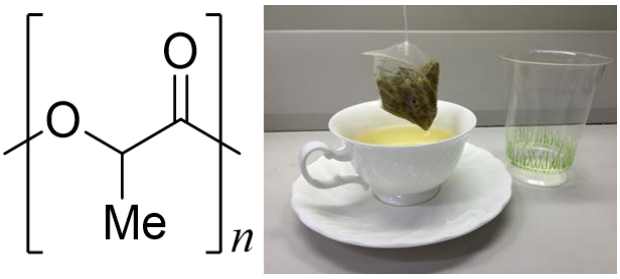
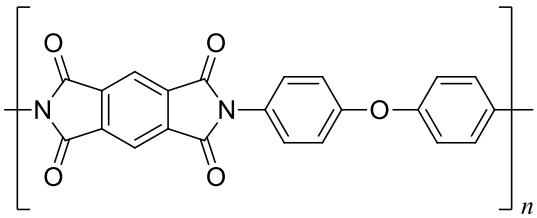


Fig. 1. Chemical structure of polylactic acid and polylactic acid cup and tea bag.

Aromatic polyimide has excellent mechanical properties and heat resistance, especially high dielectric breakdown and chemical resistance are located in the highest class among all polymers. Therefore, it has been found to be used in a very wide field from insulation materials for electronic devices to high purity graphene raw materials.

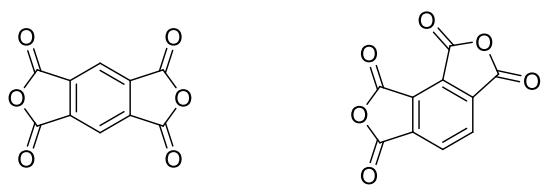
A representative aromatic polyimide is "Kapton" manufactured by Du Pont-Toray Co., Ltd. (Scheme 1). Kapton is commercially available as a brown film, but many aromatic polyimides also have the property of coloring brown in this manner. Processing of aromatic polyimide is difficult. It is insoluble in solvents and does not melt.



Scheme 1. Kapton ® is the most famous aromatic polyimide.

However, we have not established any syntheses routes of fully bio-based aromatic polyimides from natural products.

Actually we have already reported how to synthesize aromatic diamine from microorganismal compound, but we still have not synthesized fully aromatic bio-based tetracarboxylic acid. Then the previsouly-reported biopolyimides were derived from cyclobutanetetracarboxylic anhydride which reduce the thermal stability.In this research, we synthesize bio-based aromatic dianhydride, mellophanic dianhydride from 2,5-dimethylfuran and maleic acid anhydride, which both should be derived from biomass.



PMDA MLPDA

Scheme 2. Chemical structure of Pyromellitic dianhydride (PMDA) and mellophanic dianhydride(MLPDA)

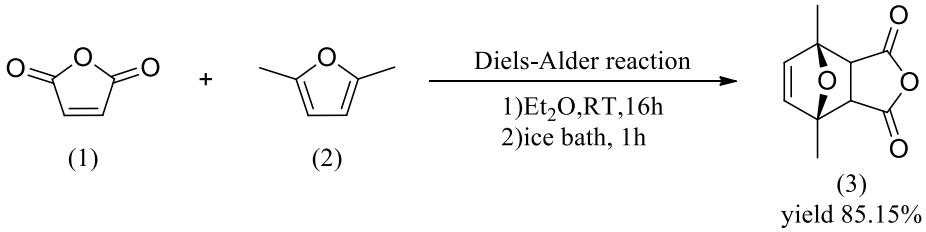
Meroophanic acid dianhydride is a structural isomer of pyromellitic dianhydride.(Scheme 2)

2. Experimental

2.1 Synthesis of Diels-Alder adduct

22.55 g (0.23 mol) of maleic anhydride (1) was taken in a 100 ml two-neck eggplant flask, and the atmosphere in the reactor was purged with nitrogen. Twenty milliliters of diethyl ether was added by a syringe and stirred, subsequently 25.00 ml (0.23 mol) of 2,5-dimethylfuran (2) was added by a syringe and stirring was continued. Maleic anhydride was insoluble in diethyl ether, but as soon as 2,5-dimethylfuran was mixed, it became a homogeneous solution and turned light yellow. After 3 hours of stirring at room temperature, precipitation of crystals was confirmed, and stirring was stopped 16 hours after the start of the reaction. The reactor was allowed to stand in an ice bath for 1 hour to sufficiently grow the crystals and then collected by suction filtration and vacuum dried.

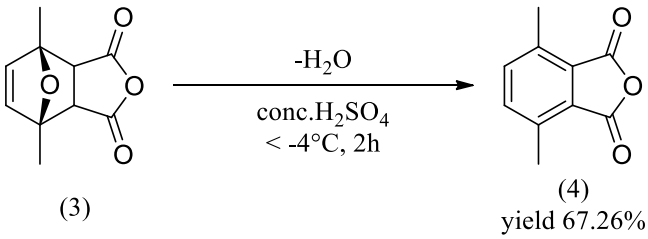
38.03 g (0.20 mol) of milky white crystals was obtained in a yield of 85.15%. 1 NMR spectrum of the recovered crystals was measured to confirm formation of Diels-Alder adduct (3). (Scheme 3)



Scheme 3. Synthesis of Diels-Alder adduct

2.2 Synthesis of 3,6-dimethylphthalic anhydride

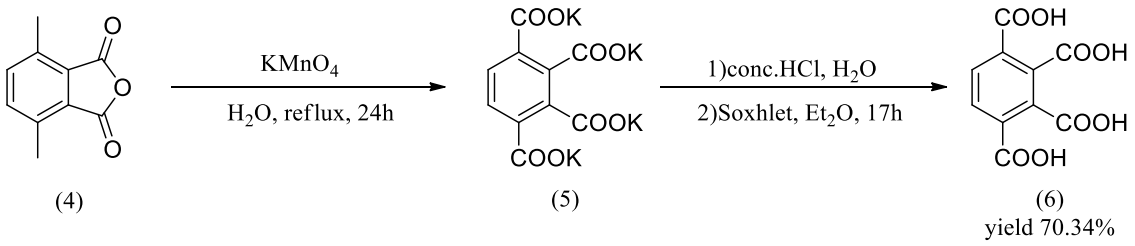
Weigh 120 ml of concentrated sulfuric acid into a 500 ml beaker and stir in an ice bath (+ salt, T: -4 ° C.) until the temperature of concentrated sulfuric acid drops sufficiently. 14.20 g (73.12 mmol) of Diels-Alder adduct (3) was poured little by little, and after adding the whole amount, it was vigorously stirred for 2 hours. The brown reaction solution was added dropwise into a ice bath with a Pasteur pipette to give a white precipitate. The white precipitate was collected by suction filtration and dried under vacuum.8.65 g (49.10 mmol) of milky white powder was obtained in a yield of 67.26%. 1 NMR spectrum of the recovered powder was measured and the product was identified as 3,6-dimethyl phthalic anhydride (4).



Scheme 4. Synthesis of 3,6-dimethylphthalic anhydride

2.3 Synthesis of Meroophanic Acid

Weigh 2.61 g (0.015 mol) of 3,6-dimethylphthalic anhydride (4) and 11.68 g (0.075 mol) of potassium permanganate in a 200 ml recovery flask, add 100 ml of pure water and heat reflux for 24 hours did. Methanol was added to quench after completion of reflux until the pink color of potassium permanganate disappeared, and manganese dioxide was removed by suction filtration. The filtrate was concentrated on a rotary evaporator and dried to dryness by vacuum drying. A small amount of pure water was added to the dried sample, and then the liquid property was adjusted from pH 12 to pH 1 with concentrated sulfuric acid to neutralize the potassium salt. The filtrate was again concentrated on a rotary evaporator and dried to dryness by vacuum drying. The crude product was packed in a cylindrical filter paper and purified by Soxhlet extraction with diethyl ether to obtain 2.68 g of a white powder in a yield of 70.34%. Formation of melophanic acid was confirmed by 1 H NMR and 13 C NMR spectrum measurement.

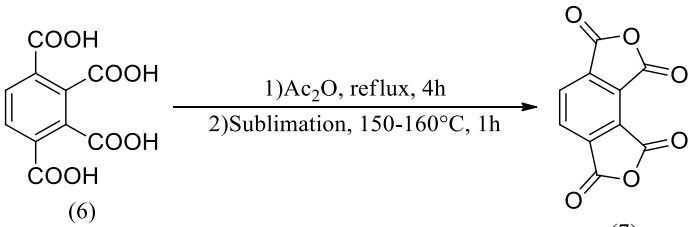


(4) (5) (6) yield 70.34%

Scheme 4. Synthesis of Meroophanic Acid

2.4 Synthesis of Melophanic Dianhydride (MLPDA)

2 g (7.9 mmol) of melophanic acid (6) was weighed into a 100 ml recovery flask, acetic anhydride 85 ml (7.9 mmol) was added and the mixture was heated under reflux for 4 hours. Acetic anhydride was distilled off from the reaction solution with a rotary evaporator and vacuum dried to recover a black powder as a crude product. The crude product was purified by sublimation at 150 to 160 ° C. for 1 hour to obtain 0.99 g of a white solid (7) in a yield of 58%. The product (7) was identified as MLPDA by 1 NMR, 13 NMR, APCI-FT-ICR Mass spectrum measurement.

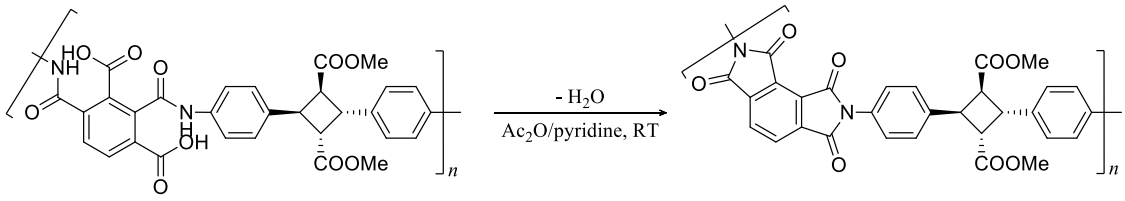


(6) (7) yield 58%

Scheme 5. Synthesis of Melophanic Dianhydride (MLPDA)

2.5 Synthesis of bio-based PI

812 mg (2.29 mmol) of 4,4'-diamino-α-truxillic acid dimethyl was taken in a 5 ml reactor, Under nitrogen atmosphere, 2 ml of dehydrated NMP was added and dissolved. 500 mg (2.29 mmol) of MLPDA was added to the diamine solution and stirred for 48 hours while heating to 50 ° C. to prepare a polyamic acid varnish. A chemical imidizing agent (acetic anhydride / pyridine, 2 ml / 0.86 ml) was added to the polyamic acid varnish,And the mixture was stirred at room temperature for 12 hours. When the reaction solution was reprecipitated with methanol, 0.78 g of milky white powderIt was obtained in a yield of 63.41%. The chemical imidizing agent was added at a ratio of Ac_2O / (COOH) PAA = 5 (Ac_2O / pyridine, v / v = 7/3).



PAA PI

Scheme 6. Synthesis of bio-based PI

3. Results and Discussion

Synthesized PAA should have two structures. If the reaction in the pattern of one of a pair is in progress, the imidization reaction is not complete. We need to control this reaction selectivity.

Synthesized PI showed lower heat resistance than previously-synthesized PI with pyromellitic dianhydride,which as due to the bent molecular chains structure of derived from mellophanic dianhydride.

Results were obtained that $T_{d\ 10}$ of PAA was 331 ° C. and that of PI was 389 ° C.

4. Conclusions

The mellophanic dianhydride is a structural isomer of pyromellitic dianhydride, I tried to newly synthesized from natural products.From the measurement results of NMR and MS, The final product was identified to be mellophanic dianhydride. Comparing the thermal properties of this synthesized fully bio-based aromatic polyimides and its analogs structure of the molecular chain bending showed the effect of thermal properties.