

**Plastics to Fertilizer: Guiding Principles for Functionable and Fertilizable Fully Bio-based Polycarbonates**

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## ARTICLE

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## Plastics to Fertilizer: Guiding Principles for Functionable and Fertilizable Fully Bio-based Polycarbonates

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Nowadays, commodity polymers are required to be environmentally friendly due to resource depletion and the still low recycling rates associated with plastics, which has promoted the development of circular materials systems. Poly(isosorbide carbonates) (PICs), i.e., bio-based polycarbonates synthesized from non-toxic and biodegradable isosorbide (ISB), which is derived from glucose, have attracted substantial interest as an alternative to conventional petroleum-based polymers on account of their superior thermal stability and transparency. Recently, we have established a novel concept in which PICs are used as a source of fertilizer after treatment with ammonia. PICs can be degraded by ammonolysis to give a mixture of isosorbide and urea, which can be directly used as a fertilizer, i.e., PICs are used not only as a promising engineering plastic, but also as a fertilizer source, leading to innovative chemical recycling systems that provide solutions to the global food-production problem on account of the ever-increasing human population. In this study, a modification method that endows PICs with further functions and/or tunable properties is introduced in order to establish a guiding principle for the design of materials based on PICs. Namely, we focused on 1,3:4,6-di-*O*-benzylidene-*D*-mannitol (**DBM**), which contains two hydroxy groups and two acetal structures, and is synthesized from *D*-mannitol. **DBM** was successfully copolymerized with ISB to afford fully bio-based polycarbonates with a thermal stability that is comparable to that of conventional petroleum-based polycarbonates. The characteristics of the resulting polymers were easily modified by deprotection of the acetal group on the DBM units and subsequent post-modification with boronic acid to form boronate esters. Finally, the bio-based polycarbonates were successfully converted to fertilizer via ammonolysis, demonstrating a guiding principle for the design of materials based on a novel concept in which what has historically been considered waste plastic is used as a source of fertilizer.

### Introduction

Recently, great efforts have been made to develop a sustainable society due to the growing interest in perilous environmental problems. In particular, the design of polymeric materials using biomass has attracted great interest in the context of solving the resource-depletion problems associated with commodity polymers.<sup>1–7</sup> To date, numerous bio-based polymers have been developed, e.g., poly(trimethylene terephthalate) (PTT), polyhydroxylalkanoates (PHAs), poly(ethylene furanoate) (PEF), poly(butylene succinate) (PBS), poly(limonene carbonate) (PLimC), poly(lactic acid) (PLA), bio-based poly(ethylene terephthalate) (bioPET), and bio-based polyethylene (bioPE).<sup>8</sup> Among the bio-based polymeric materials, PLA, bioPET, and bioPE are the main ones currently used in consumer products; however, other bio-based polymeric materials are not widely used due to their high cost or inferior properties compared to conventional petroleum-based

polymeric materials.<sup>9</sup> Therefore, the production of bio-based polymeric materials represented only 1% of the total polymer production as of 2018, with the remaining 99% being petroleum-based polymers.<sup>10</sup>

The production ratio of bio-based polymeric materials is expected to increase during the changeover from petroleum- to bio-based polymeric materials on account of the increasing environmental concerns and the realization that global petroleum resources are finite. However, it has been speculated that the types of bio-based polymer materials will be limited to starch plastics, PE, polyesters, and epoxy resins.<sup>9</sup> To promote further extension to other types of polymeric materials, the development of new bio-based polymeric materials with outstanding properties or functions comparable to those of conventional petroleum-based polymeric materials is required.

Polycarbonates (PCs) represent a class of engineering plastics with high thermal stability and high transparency.<sup>11–13</sup> Furthermore, the materials cycle of PCs renders them attractive materials in terms of sustainability. Specifically, PCs can be synthesized via ring-opening polymerization or melt-polycondensation using monomers derived from carbon dioxide or directly synthesized from carbon dioxide via a catalytic pathway,<sup>14–23</sup> which reduces the emission of carbon dioxide and thus contributes significantly to carbon-neutrality. Moreover, in the end-of-life stage, chemical recycling of PCs via treatment with alcohols or amines affords not only their diol

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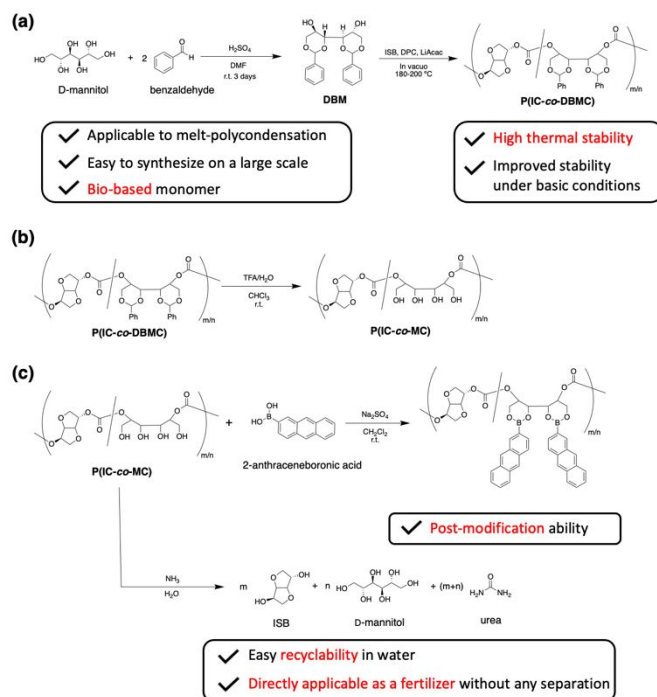
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monomers, but also small carbonyl compounds that can be used as functional molecules.<sup>24–28</sup> Thus, the chemical recycling of PCs is quite efficient compared to the chemical recycling of polyesters or olefin-based polymers, pushing PC-based materials to the forefront of advanced environmentally friendly materials. However, most PCs are currently synthesized using the petroleum-derived diol monomer bisphenol A, which causes endocrine-disruption problems in humans.<sup>29–34</sup> This fact has encouraged us to develop non-toxic bio-based PCs to overcome the toxicity and resource-depletion issues. Among bio-based PCs, poly(isosorbide carbonates) (PICs), which are synthesized from sugar-based isosorbide (ISB), have attracted interest as an alternative to conventional PCs, as PICs also exhibit high thermal stability and high transparency.<sup>35–44</sup> Recently, we have established a novel concept in which PICs are used as a source of fertilizer via treatment with ammonia. PICs can undergo degradation by ammonia (ammonolysis) to give a mixture of isosorbide and urea, which can be used directly as fertilizer. In other words, PICs represent not only a promising class of engineering plastics, but also a fertilizer source, leading to innovative chemical recycling systems that provide solutions to the food-production problem associated with the ever-increasing global population. To establish a guiding principle for the design of materials based on PICs, modification methods that endow PICs with further functions and/or tunable properties are needed, because PICs themselves do not exhibit good mechanical properties and special functions that would surpass those of conventional petroleum-based PCs.

In this study, we have focused on 1,3:4,6-di-*O*-benzylidene-*D*-mannitol (**DBM**) as a comonomer to modify the properties of PICs. **DBM** is a diol monomer with an acetal structure that is easily synthesized from *D*-mannitol and benzaldehyde, which can be derived from sugar and bitter almond oil, respectively.<sup>45</sup> As **DBM** has a rigid structure, ISB-based PCs copolymerized with **DBM** are expected to exhibit high thermal stability (**Scheme 1a**). The acetal structure of the **DBM** units in the copolymers can be deprotected to introduce hydroxy groups into PICs (**Scheme 1b**); these groups can be expected to not only improve the hydrophilicity of PICs, but also to act as a scaffold for further chemical modifications. Improvement of the hydrophilicity of PICs is critical to control the ammonolysis reaction rate in aqueous media. The most important aim of our developing a novel concept in which waste plastic is used as a source of fertilizer is that all decomposition products after ammonolysis of the copolymer are directly applicable as fertilizers, as both *D*-mannitol and ISB are bio-based compounds (**Scheme 1c**). Further modifications based on the hydroxy groups introduced in the PCs would be an ideal tool to functionalize such PICs (**Scheme 1c**). Thus, copolymers of PIC and **DBM** are expected to be fully bio-based PCs with high thermal stability whose characteristics can be tuned via post-modifications, i.e., deprotection and further chemical transformation of the generated hydroxy groups. Furthermore, such copolymers can be expected to be converted to fertilizer upon treatment with ammonia after use (**Scheme 1c**).



**Scheme 1.** (a) Synthesis of **DBM** and **P(IC-co-DBMC)**, (b) synthesis of **P(IC-co-MC)**, and (c) post-modification and ammonolysis of **P(IC-co-MC)**.

## Experimental

### Materials

All reagents and solvents were purchased from Tokyo Chemical Industry (Tokyo, Japan), Kanto Chemical (Tokyo, Japan), FUJIFILM Wako Pure Chemical Corporation (Tokyo, Japan), or Sigma-Aldrich (MO, USA). Prior to using isosorbide (ISB) and diphenyl carbonate (DPC), these were recrystallized from ethyl acetate/hexane and ethanol, respectively. All other reagents were used as received.

### Measurements

$^1\text{H}$  NMR spectra were recorded on a Bruker AVANCE III HD500 spectrometer in dimethyl sulfoxide- $d_6$  ( $\text{DMSO}-d_6$ ) or chloroform- $d$  ( $\text{CDCl}_3$ ) at 25 °C. For the diffusion-ordered NMR spectroscopy (DOSY), the LED method was used (pulse program: ledbpgp2s; diffusion time: 40 ms; diffusion gradient length: 2000  $\mu\text{s}$ ; maximum gradient strength: 51 G/cm in  $\text{DMSO}-d_6$  at 25 °C).<sup>46</sup> Gel-permeation chromatography (GPC) was performed at 40 °C on a JASCO HSS-1500 system with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000, and 2500), and a refractive-index (RI) detector. *N,N*-Dimethylformamide (DMF) with lithium bromide (5 mM) was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene standards (number-average molecular weight ( $M_n$ ) = 4430–3242000  $\text{g mol}^{-1}$ ; polydispersity index (PDI) = 1.03–1.08) were used to calibrate the GPC system. The glass-transition-temperature ( $T_g$ ) values of the synthesized polymers were estimated using differential-scanning-calorimetry (DSC) measurements carried out on a SHIMADZU DSC-60A Plus with a heating rate of 10 °C/min under a flow of  $\text{N}_2$ . The thermal-decomposition-temperature ( $T_d$ ) values of the synthesized polymers were estimated using

thermogravimetric-analysis (TGA) measurements on a SHIMADU DTG-60, and all samples were heated to 600 °C at a rate of 10 °C/min. Solid-state fluorescence spectra were recorded on a JASCO FP-8550 spectrometer under excitation by UV light ( $\lambda_{\text{ex}} = 365$  nm). Fast-atom-bombardment-mass-spectrometry (FAB-MS) measurements were carried out on a JEOL JMS-700 spectrometer.

### Synthesis of poly(isosorbide carbonate-co-DBM carbonate) (P(IC-co-DBMC))

**DBM** was synthesized according to a published procedure, except for the purification.<sup>47</sup> D-Mannitol (75.0 g, 0.412 mol), benzaldehyde (90.0 mL, 0.891 mol), and *N,N*-dimethylformamide (225 mL) were added to a round-bottom flask (500 mL). Then, concentrated sulfuric acid (15.0 mL) was slowly added to the mixture, which was stirred for 3 days under ambient conditions. After the reaction was finished, the reaction mixture was poured into water (2250 mL) containing hexane (375 mL) and potassium carbonate (40.5 g, 0.293 mol) to afford a white solid. The solid was filtered off and washed with an excess of water and chloroform. The residue was recrystallized from ethanol, and **DBM** was obtained as a white solid (yield: 33.4 g, 22.6%).

**P(IC-co-DBMC)** was synthesized via a one-pot polycondensation method, in which the transesterification and polycondensation reactions were conducted in the same reactor consecutively. ISB (2.50 g, 17.1 mmol, 0.95 eq), **DBM** (323 mg, 0.900 mmol, 0.05 eq), DPC (3.86 g, 18.0 mmol, 1 eq), and LiAcac (1.00 mg, 9.42  $\mu\text{mol}$ ) were placed in a two-neck round-bottom flask (100 mL) equipped with a mechanical stirrer. During the transesterification stage, the reactants were heated to 180 °C under a nitrogen atmosphere and stirred for 2 h. The temperature was then gradually increased to 200 °C and maintained for 30 min. During the polycondensation stage, the reaction system was continuously stirred under vacuum (10–20 mmHg) at 200 °C for 30 min and then under high vacuum (<1 mmHg) at 220 °C for 1 h to remove phenol. After the reaction was finished, the reaction system was cooled to room temperature under a  $\text{N}_2$  atmosphere. The product was then dissolved in chloroform, followed by precipitation from methanol. After drying under vacuum, **P(IC-co-DBMC)** was obtained as a white solid (yield: 3.20 g, 97.1%).

### Deprotection of P(IC-co-DBMC)

**P(IC-co-DBMC)** (1.50 g) dissolved in 15 mL of chloroform was placed in a round-bottom flask (150 mL). Then, a solution of  $\text{CF}_3\text{COOH}/\text{H}_2\text{O} = 9/1$  (v/v) (8 mL) was added slowly at room temperature while stirring, and the resulting mixture was further stirred for 30 min at room temperature. The product was then precipitated from methanol and the obtained solid was filtered off. After drying under vacuum, **P(IC-co-MC)** was obtained as a white solid (yield: 1.41 g, 96.5%).

### Ammonolysis of ISB-based PCs

The ISB-based PC (250 mg) was placed in a round-bottom flask (30 mL), before water and 20 equivalents of aqueous ammonia (14.8 mol/L) were added. Then, the flask was sealed, and the reaction mixture was stirred vigorously at 30 °C. After 1, 3, 6, (9), 12, and 24 h, an aliquot (1 mL) of the reaction mixture was collected and freeze-

dried to remove ammonia and water. The dried degradation products were used for characterization.

### Modification of P(IC-co-MC)

**P(IC-co-MC)** (100 mg), 2-anthracene boronic acid (63.7 mg, 287  $\mu\text{mol}$ ), and  $\text{Na}_2\text{SO}_4$  (201 mg, 1.42 mmol) were placed in a round-bottom flask (20 mL), before dichloromethane (3 mL) was added under a  $\text{N}_2$  atmosphere. The reaction mixture was stirred for 3 days at room temperature, followed by filtration with a filter agent to remove  $\text{Na}_2\text{SO}_4$ . Then, the filtrate was poured into methanol and the obtained solid was removed and dried under reduced pressure (yield: 74.2 mg, 66.8%).

### Measurement of the weight of the remaining degradation products during/after ammonolysis

PIC (25.0 mg), water (1.00 mL), and aqueous ammonia (14.8 M, 200  $\mu\text{L}$ ) were added to four sample tubes (2 mL). In each tube, the reaction mixture was stirred vigorously at 30 °C. After 3, 6, 12, or 24 h, the mixture was filtered, and the residue was washed with water and methanol, respectively. The obtained solid was dried under reduced pressure and weighed. For each reaction time, the weight of the residual degradation products was measured three times and the average was calculated.

**P(IC-co-MC)** (25.0 mg), water (989  $\mu\text{L}$ ), and aqueous ammonia (14.8 M, 198  $\mu\text{L}$ ) were added to a sample tube (2 mL) and the procedure was carried out in the same manner as described above.

### Plant-growth test

Seeds of *Arabidopsis thaliana* ecotype Col-0 were surface-sterilized with bleach and sown onto a medium (**Table S1**) solidified with 1% gellan gum supplemented with 1% sucrose. The concentrations of all nutrients, except the nitrogen source, were based on literature values.<sup>43</sup> After incubation for two days at 4 °C, the plates were placed vertically and grown at 22 °C for two weeks under 16 h light/8 h dark conditions.

## Results and discussion

### Synthesis of P(IC-co-DBMC) and P(IC-co-MC)

To introduce hydroxy groups into ISB-based PCs (PICs), copolymerization between ISB and a diol monomer with an acetal structure, which acts as a typical protecting group toward hydroxy groups, is the easiest method. In order to retain the excellent features of native PICs, such as their bio-based origin, excellent thermal stability, and high transparency, the selection of an appropriate comonomer is of paramount importance. In addition, diol monomers are desirable because PICs are generally synthesized in an environmentally friendly melt-polycondensation system involving condensations between diol monomers and reactive carbonate compounds, such as diphenyl carbonate, which act as a source of carbonyl groups.<sup>15,16</sup> However, melt-polycondensations require relatively harsh reaction conditions (>200 °C), and thus, the reactants must be able to withstand the high temperatures. To design fully bio-based PCs with excellent properties and

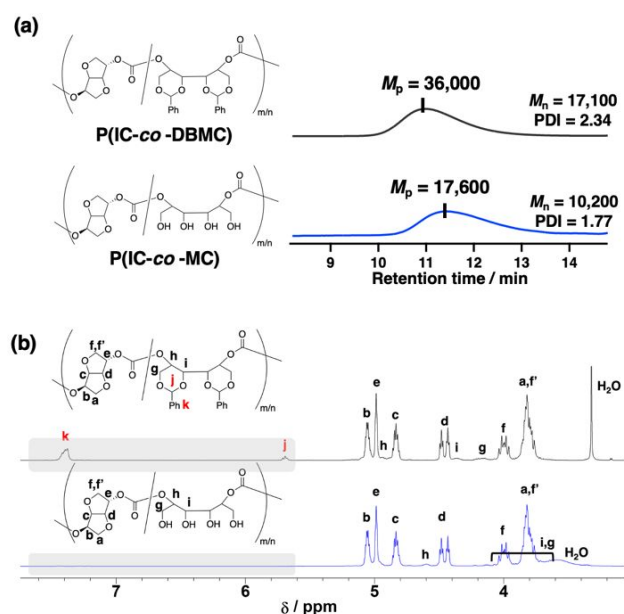
functionalities that can be synthesized via an environmentally friendly melt-polycondensation process, **DBM**<sup>47</sup> was chosen as an ideal partner for the PIC.

**DBM** is easily synthesized from D-mannitol and benzaldehyde, which can be produced from sugar and bitter almond oil, respectively.<sup>45</sup> In this synthetic procedure,<sup>47</sup> chromatographic purification is not required, which significantly reduces the amount of organic solvent consumed. This aspect is very important for an environmentally friendly synthesis in accordance with the principles of green chemistry.<sup>48</sup> Furthermore, this procedure can be up-scaled, which is a practical advantage for e.g., commercial or industrial applications. It should be stressed here that **DBM** is a fully bio-based diol monomer and an easily accessible compound.

We synthesized and purified **DBM** according to published procedure<sup>47</sup>, which was confirmed by <sup>1</sup>H NMR analysis (Figure S1). We then carried out the copolymerization of **DBM** with ISB. Generally, the reaction temperature in the melt-polycondensation of ISB-based PCs is gradually increased from 100–180 °C to 240–280 °C.<sup>35–42</sup> However, the thermal stability of the acetal skeleton is relatively low.<sup>49</sup> Prior to the polycondensation of ISB and **DBM**, the thermal stability of **DBM** was examined via TGA measurements to determine the maximum possible reaction temperature during the melt-polycondensation. The TGA trace revealed that **DBM** decomposes above 200 °C (Figure S2), and accordingly, we employed 200 °C as the maximum reaction temperature during the transesterification stage.

A 9.5:0.5 ratio of ISB and **DBM** was combined with diphenyl carbonate (DPC) as a carbonyl source and lithium acetyl acetonate (LiAcac) as a catalyst. The copolymerization was carried out as a one-pot melt-polycondensation process in which the transesterification and polycondensation reactions were conducted consecutively in the same reactor. During the transesterification stage, the reaction temperature was kept at 180–200 °C, as **DBM** might decompose at higher temperatures (*vide supra*). Subsequently, during the polycondensation stage, the reaction temperature was increased to 220 °C, since we anticipated that the oligomerized **DBM** with ISB would exhibit an improved thermal stability. Poly(isosorbide carbonate-co-DBM carbonate) (**P(IC-co-DBMC)**) was obtained in 97.1% yield as a white solid with a number-average molecular weight ( $M_n$ ) of 17100 and a polydispersity index (PDI) of 2.34 (Figure 1a, black). A <sup>1</sup>H NMR analysis was carried out in order to characterize the polymeric product. The signals in the NMR spectrum were in good agreement with those expected for the protons in the **P(IC-co-DBMC)** molecular chain (Figure 1b, black). The copolymerization ratio of **DBM** units in **P(IC-co-DBMC)** was 4.4%, which was calculated based on the integration ratios of the signals corresponding to **DBM** and those of ISB-derived signals in the <sup>1</sup>H NMR spectrum. The copolymerization ratio was consistent with the feed ratio of the diol monomer. A thin film of **P(IC-co-DBMC)** cast from a chloroform solution exhibited significantly higher transparency comparable to a thin film of the corresponding PIC (Figure S3). We also carried out the copolymerization at ISB/**DBM** in ratios of 9:1 and 8.5:1.5 (mol/mol). While 10% **DBM** could be successfully introduced into **P(IC-co-DBMC)** ( $M_n = 15800$ , PDI = 2.06; Figure S5 and S6), 15% **DBM** could not be introduced due to the low reactivity of **DBM** compared to that of ISB.

Subsequently, we carried out the deprotection of the hydroxy groups in **P(IC-co-DBMC)**. For that purpose, **P(IC-co-DBMC)** was treated with trifluoroacetic acid in chloroform to deprotect the acetal structure. This reaction proceeded heterogeneously, given that trifluoroacetic acid is a poor solvent for **P(IC-co-DBMC)**. After the reaction, the signals corresponding to the protected group disappeared from the <sup>1</sup>H NMR spectrum (Figure 1b, blue). The monophasic peak observed in the GPC profile was shifted to longer retention time, which was attributed to changes in the polarity and the hydrodynamic radius (Figure 1a). Furthermore, the OH stretch in FT-IR spectra (around 3500 cm<sup>-1</sup>) appeared after deprotection reaction (Figure S4). To demonstrate the stability of the polymer main chain under these acidic conditions, we investigated the dependence of the deprotection reaction on the reaction time. Reaction times from 10 min to 1 h afforded fully deprotected **P(IC-co-MC)** without any change in the molecular weight (Figure S7 and S8). These results indicate that the main chain of **P(IC-co-DBMC)** is stable under the conditions applied in this deprotection reaction; in other words, the acetal structures were deprotected selectively without any degradation of the polymer main chain. We also tested acetic acid instead of trifluoroacetic acid for the deprotection reaction. No changes were observed in either the <sup>1</sup>H NMR spectrum or the GPC profile (Figures S9 and S10), albeit that the reaction mixture was homogeneous, unlike in the case of trifluoroacetic acid. These results revealed that the acetal structure of **P(IC-co-DBMC)** cannot be deprotected by the relatively weak acetic acid. Conversely, **P(IC-co-DBMC)** was stable under weakly acidic conditions to which polymeric materials used in daily life are often exposed. This result demonstrates the practical utility of **P(IC-co-DBMC)**.

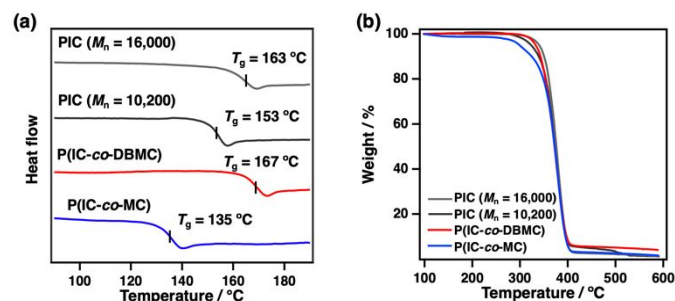


**Figure 1.** (a) GPC profiles of **P(IC-co-DBMC)** (black) and **P(IC-co-MC)** (blue) (eluent: DMF; detector: RI; calibration: PS standards). (b) <sup>1</sup>H NMR spectra of **P(IC-co-DBMC)** (black) and **P(IC-co-MC)** (blue) (500 MHz, 25 °C, DMSO-*d*<sub>6</sub>).



### Thermal stability of ISB-based PCs

The thermal properties of the synthesized co-polycarbonates were investigated using DSC and TGA measurements (Figure 2, Table 1). The results were compared with those for the homopolycarbonate (PIC) with a similar molecular weight, which was synthesized according to a previous report using zinc acetate or sodium hydrogen carbonate as a catalyst.<sup>28</sup> The glass-transition temperature of **P(IC-co-DBMC)** (copolymerization ratio: 5%;  $T_g = 167^\circ\text{C}$ ) is comparable to that of the corresponding PIC with a similar molecular weight ( $M_n = 16000$ ,  $T_g = 163^\circ\text{C}$ ). The 5%-weight-loss temperature ( $T_{d-5\%} = 333^\circ\text{C}$ ) is also comparable to that of the corresponding PIC ( $T_{d-5\%} = 340^\circ\text{C}$ ). Furthermore, thermal properties of **P(IC-co-DBMC)** (copolymerization ratio: 10%,  $M_n = 15800$ ) was  $T_g = 169^\circ\text{C}$  and  $T_{d-5\%} = 308^\circ\text{C}$  (Figure S11, Table S2). Although slight decrease in the  $T_{d-5\%}$  value was observed, the value was still high ( $>300^\circ\text{C}$ ), and  $T_g$  value was increased as introducing DBM units. Thus, the DBM units can be introduced into ISB-based PCs without significant loss of their outstanding thermal properties.



**Figure 2.** (a) DSC traces and (b) TGA traces of PIC, **P(IC-co-DBMC)**, and **P(IC-co-MC)**.

**Table 1.** Glass-transition temperature ( $T_g$ ) and 5%-weight-loss temperature ( $T_{d-5\%}$ ) of PIC, **P(IC-co-DBMC)**, and **P(IC-co-MC)**

Sample	$M_n$ (PDI) <sup>a</sup>	$T_g / ^\circ\text{C}$ <sup>b</sup>	$T_{d-5\%} / ^\circ\text{C}$ <sup>c</sup>
PIC	16000 (1.79)	163	340
PIC	10200 (1.69)	153	323
<b>P(IC-co-DBMC)</b>	17100 (2.34)	167	333
<b>P(IC-co-MC)</b>	10200 (1.77)	135	299

a) Determined by GPC (eluent: DMF; detector: RI; calibration: PS standards). b) Determined by DSC; the DSC data given refer to the second heating at a heating rate of  $10^\circ\text{C}/\text{min}$ . c) Determined by TGA; heating rate:  $10^\circ\text{C}/\text{min}$ .

Furthermore, the  $T_g$  and  $T_{d-5\%}$  values of **P(IC-co-MC)** ( $T_g = 135^\circ\text{C}$ ,  $T_{d-5\%} = 299^\circ\text{C}$ ) are lower than those of **P(IC-co-DBMC)** ( $T_g = 167^\circ\text{C}$ ,  $T_{d-5\%} = 304^\circ\text{C}$ ) and of PICs with  $M_n = 16000$  ( $T_g = 163^\circ\text{C}$ ,  $T_{d-5\%} = 340^\circ\text{C}$ ) and  $M_n = 10200$  ( $T_g = 153^\circ\text{C}$ ,  $T_{d-5\%} = 323^\circ\text{C}$ ). This was attributed to the increased flexibility of the polymer chain due to the introduction of hydroxy groups, which replace the rigid cyclic acetal structures in the polymer main chain. In other words, the rigid acetal structure contributes to the high thermal stability of **P(IC-co-DBMC)**. Although the  $T_g$  of **P(IC-co-MC)** was lower than that of **P(IC-co-DBMC)**, it was higher than that of commodity plastics such as polystyrene (*ca.*  $100^\circ\text{C}$ )<sup>50</sup> and poly(ethylene terephthalate) (*ca.*  $67\text{--}81^\circ\text{C}$ ).<sup>51</sup> This result suggests that even at a ratio of less than 5%, the DBM units in PIC allow controlling the thermal properties, especially the  $T_g$ , which is

one of the most critical parameters to consider when choosing a material for a polymer application.

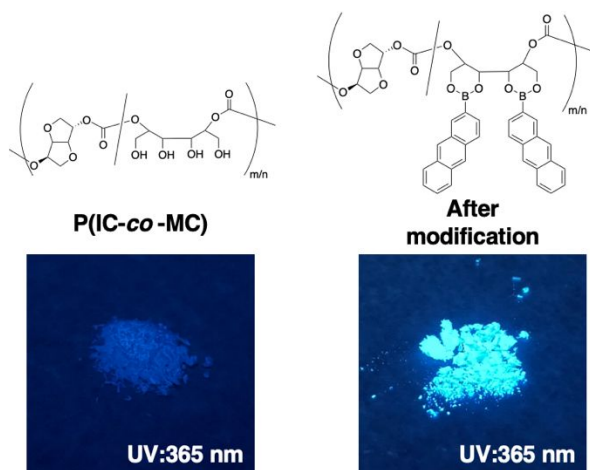
### Modification of P(IC-co-MC)

To increase the utility of **P(IC-co-MC)**, we modified **P(IC-co-MC)** by using the hydroxy groups in the polymer main chain as reactive sites. Such hydroxy groups in the polymer main chain can be modified using various reagents, e.g., carboxylic anhydrides and isocyanates. In particular, the hydroxy groups in **P(IC-co-MC)** are adjacent to one another, and thus can react with boronic acid to form a boronate-ester structure.<sup>52,53</sup>

We used 2-anthraceneboronic acid, which is fluorescent, to monitor the modification of **P(IC-co-MC)**. The modification reaction was performed in the presence of sodium sulfate as a dehydrating agent. The modified **P(IC-co-MC)** was first characterized using GPC. The peak of the modified **P(IC-co-MC)** appeared at an earlier retention time in the GPC profile, which was attributed to the change in polarity as a result of the formation of the boronate ester and removal of the hydroxy groups, in addition to the increase in molecular weight (Figure S12). The modified **P(IC-co-MC)** was also characterized using  $^1\text{H}$  DOSY measurements. In the  $^1\text{H}$  DOSY spectrum, the signals corresponding to the **P(IC-co-MC)** main chain and anthracene were confirmed to have the same diffusion coefficient (Figure S13), which suggests that the anthracene moieties are covalently bound to the polymer main chain. The success of the modification reaction was also supported by the observation of fluorescence from the polymer samples. The samples after the modification reaction showed fluorescence under irradiation with UV light ( $\lambda_{\text{ex}} = 365\text{ nm}$ ; Figure 3). Solid-state fluorescence spectra also revealed anthracene-derived fluorescence from the modified **P(IC-co-MC)** (Figure S14). The thermal stability of the **P(IC-co-MC)** modified with 2-anthraceneboronic acid was investigated using DSC and TGA (Figure S16, Table S3). The  $T_g$  of the modified **P(IC-co-MC)** increased from  $135^\circ\text{C}$  to  $150^\circ\text{C}$  due to the generation of rigid 6-membered cyclic boronate esters in the main chain. Furthermore, the  $T_{d-5\%}$  also increased. These results indicate that the modification of **P(IC-co-MC)** with boronic acid not only endow the polymer with functionality, but also tune its thermal stability. Moreover, a thin film cast from a solution of the modified **P(IC-co-MC)** showed fluorescence and comparable transparency to PIC without losing its film-forming properties (Figure S17).

Two types of boronate ester could conceivably result from the modification of **P(IC-co-MC)** with boronic acid, i.e., the formation of two boronate esters from four hydroxy groups and two boronic-acid moieties (Mode I), or the formation of one boronate ester from two hydroxy groups and two boronic-acid moieties, with two hydroxy groups remaining (Mode II) (Figure S18). We thus synthesized a model compound, i.e., a D-mannitol derivative in which two hydroxy groups are protected by benzyl groups (Scheme S3). This model compound was treated with two boronic-acid reagents, namely, 4-methylphenylboronic acid and 2-anthraceneboronic acid (Scheme S4 and S5). The main signals in the  $^1\text{H}$  NMR spectra of the resulting products corresponded only to Mode I products (Figures S19 and S21). We confirmed that these products had the corresponding molecular weights using FAB-MS (Figures S20 and S22). All results

suggest that four hydroxy groups in the **P(IC-co-MC)** main chain form two boronate esters. The modification ratio of **P(IC-co-MC)** calculated based on the  $^1\text{H}$  NMR spectrum (Figure S23) was 34.8%. Although the steric hindrance of the initially introduced anthracene moieties and/or the polymer main chain might prevent a quantitative modification, the modification reaction of **P(IC-co-MC)** with boronic acid was successfully achieved by simply mixing **P(IC-co-MC)** and the boronic-acid reagent at room temperature. It is thus feasible to expect that various types of functional groups can be introduced onto **P(IC-co-MC)** to change its original properties using boronic acids, given that the choice of boronic acid reagents is virtually infinite.<sup>54–56</sup>

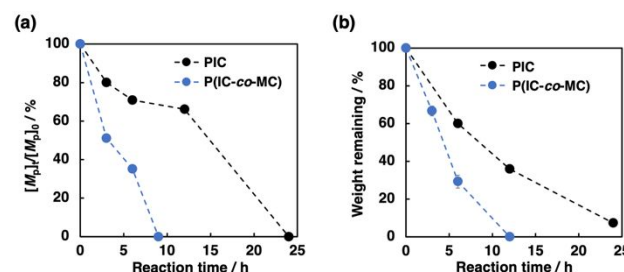


**Figure 3.** Photographs of **P(IC-co-MC)** before and after modification with 2-anthraceneboronic acid.

### Ammonolysis of ISB-based PCs

Unlike the PIC homopolymer, **P(IC-co-MC)** contains hydrophilic hydroxy groups in the polymer main chain. Therefore, we speculated that **P(IC-co-MC)** would exhibit increased hydrophilicity, which can be expected to promote main-chain scission via enhancement of the ammonolysis reaction rate in water. To compare the ammonolysis behavior of PIC and **P(IC-co-MC)**, we used a PIC with a molecular weight similar to that of **P(IC-co-DBMC)** ( $M_n = 16000$ ,  $\text{PDI} = 1.79$ ), considering that **P(IC-co-MC)** has same chain length with its precursor **P(IC-co-DBMC)**. The ammonolysis reaction was performed in the same manner for both samples, i.e., at  $30\text{ }^\circ\text{C}$  with 20 equivalents of ammonia relative to the carbonate-bond content. The ammonolysis behavior was characterized using the residual polymer ratio ( $[M_p]_t/[M_p]_0$ ), i.e., the ratio of the peak-top molecular weight at a given reaction time ( $[M_p]_t$ ) relative to the initial value ( $[M_p]_0$ ), where  $[M_p]_t/[M_p]_0 = 0$  would indicate the complete absence of polymer in the degradation products; the  $[M_p]$  values were estimated based on the GPC profiles during the reaction (Figure S24a and S24c). The thus obtained results demonstrated that **P(IC-co-MC)** was completely degraded within 9 h, while complete degradation of the PIC required 24 h (Figure 4a). The ammonolysis behavior was also characterized using the weight of the insoluble residual parts, as shown in Figure 4b. These results also show a significant difference between PIC and **P(IC-co-MC)**, i.e., they clearly indicate that the degradation reaction in aqueous ammonia is enhanced by the

introduction of hydrophilic hydroxy groups in the PIC main chain. These results were also observed in comparison with a PIC with a similar  $M_n$  value calculated from GPC ( $M_n = 10200$ ,  $\text{PDI} = 1.69$ ) (Figure S24b and S25). They also demonstrate that **P(IC-co-MC)** can be degraded into small molecules at lower energy than PIC, which is an excellent feature of this polymeric material in terms of sustainability.

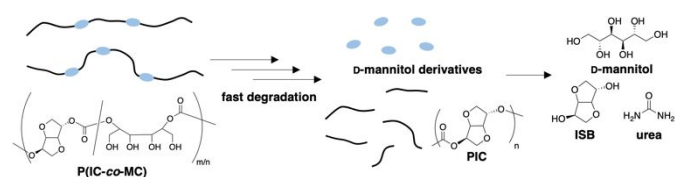


**Figure 4.** (a)  $[M_p]_t/[M_p]_0$  (residual polymer ratio) and (b) weight of the remaining degradation products of PIC (black) and **P(IC-co-MC)** (blue) during ammonolysis.

To investigate the degradation mechanism of the ammonolysis reaction of **P(IC-co-MC)**, we then quantitatively analyzed the degradation products using  $^1\text{H}$  NMR spectroscopy with the addition of an internal standard and calculated the yield of the degradation products during ammonolysis before complete degradation. The signal corresponding to the D-mannitol units in **P(IC-co-MC)** completely disappeared after 1 h (peak h in Figure S26), and the yield of D-mannitol was 71.4% despite the low yield of ISB (only 6.15%) (Figure S27). This result suggests that the D-mannitol units in the **P(IC-co-MC)** main chain are more easily degraded than the ISB units, suggesting that the scission of the **P(IC-co-MC)** main chain preferentially occurs at the D-mannitol units to give PICs with a smaller molecular weight (Figure 5), which provides a kind of booster effect to the ammonolysis reaction. This suggestion is also supported by the result of residual polymer ratio (Figure 4a), i.e., the molecular weight of **P(IC-co-MC)** decreased rapidly in 3 h on account of its main chain scission. Here, D-mannitol units must be randomly incorporated into their main chain, not block-like, for such significant decrease in molecular weight at an early stage. In other words, the randomness of D-mannitol incorporation is also important factor for booster effect.

Finally, we applied the optimized reaction conditions for PIC<sup>28</sup> to the degradation reaction of **P(IC-co-MC)**, i.e., 30 eq. of ammonia relative to the carbonate-bond content at  $90\text{ }^\circ\text{C}$ , and calculated the yield of the degradation products after complete degradation based on the  $^1\text{H}$  NMR spectrum with an internal standard (Figure S28). ISB, D-mannitol, and urea were obtained in >99%, >99%, and 71.4% yield, respectively, and the molar ratio calculated from their integration ratios was 95:4.9:69.1, which is in good agreement with the copolymerization ratio. It should be noted here that the decarboxylation reaction occurs during the ammonolysis reaction of PIC, leading to a decrease in the yield of urea.<sup>28</sup> The degree of the decrease was almost identical to that in the ammonolysis reaction of PIC, in which urea was obtained in 69.4% yield. Therefore, it was clear that, as in the case of PIC, the ammonolysis reaction of **P(IC-co-MC)** produced the monomer and urea in a ratio of 10:7.

We also investigated the ammonolysis behavior of **P(IC-co-DBMC)**, which is the precursor of hydroxy-group-containing **P(IC-co-MC)**. The degradation behavior of **P(IC-co-DBMC)** ( $M_n = 17100$ ) was compared to that of PIC with a similar molecular weight ( $M_n = 16000$ ). **P(IC-co-DBMC)** was not completely degraded, with some polymer components remaining after 24 h, although PIC was completely degraded into small molecules (**Figure S29**), suggesting that the increased hydrophobicity due to the introduction of the **DBM** units affected the degradation behavior. Specifically, the stability of **P(IC-co-DBMC)** under these weakly basic conditions was improved by introducing **DBM** units into the ISB-based polycarbonates. This notable feature of **DBM** indicates the feasibility of the use of **P(IC-co-DBMC)** as a polymeric material.



**Figure 5.** Schematic illustration of the degradation mechanism of **P(IC-co-MC)** in aqueous ammonia.

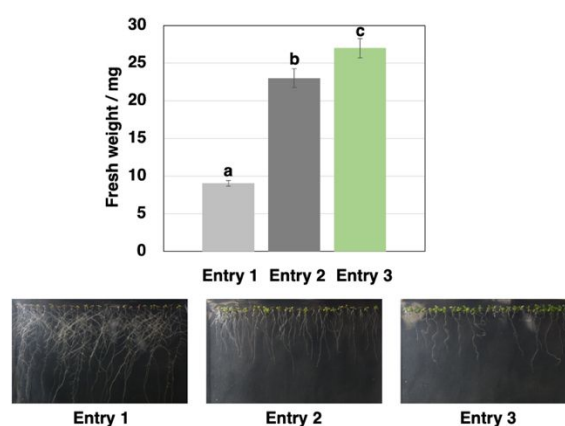
#### Utilization of the degradation products as fertilizer

As the products of the degradation of PIC by ammonolysis, i.e., ISB and urea, were directly used as fertilizer in our previous report,<sup>28</sup> we expected that the degradation products of **P(IC-co-MC)**, which contain D-mannitol in addition to ISB and urea, could also be used as fertilizer. D-Mannitol was expected to exhibit no negative impact on plant growth because D-mannitol represents a minor component of the degradation products and is a non-toxic sugar-based compound similar to ISB. We used the degradation products as fertilizer and compared their effect on plant growth with that of urea alone and the plant growth in the absence of fertilizer (**Table 2**). We grew *Arabidopsis thaliana* as a model plant and measured the fresh weight of the grown plant after 2 weeks using the same procedure as in the previous report. The plants in the degradation-product group grew well without any problems (**Figure 6**). Furthermore, the fresh weight of these plants was higher than that of the plants to which only urea was administered as a fertilizer. This result suggests that D-mannitol has no negative impact on the plant-growth experiment. Therefore, we found that **P(IC-co-MC)** and its precursor **P(IC-co-DBMC)** are excellent materials, showing not only function but also sustainability derived from the **DBM** units, as the products of their degradation via ammonolysis can be used as fertilizer.

**Table 2.** Fertilizers used in the plant-growth experiment (for details, see: **Table S1**)

Entry	Urea (210 mM)	Degradation Products (300 mM)*	Water with other minerals	Total Volume
1	0 mL	0 mL	250 mL	250 mL
2	2.5 mL	0 mL	247.5 mL	250 mL
3	0 mL	2.5 mL	247.5 mL	250 mL

\* The concentration was adjusted based on the total amount of monomer; 300 mM of degradation products contains ~210 mM of urea.



**Figure 6.** Fresh weight (10 plants) of *Arabidopsis thaliana* and photographs of *Arabidopsis thaliana* under three different conditions. Data represent mean values  $\pm$  standard deviation ( $n=5$ ). Different characters indicate statistical differences ( $p < 0.05$ , Tukey HSD test).

#### Conclusions

To establish a guiding principle for the design of materials based on isosorbide-based polycarbonate (PIC) that can be used as plant fertilizer after treatment with ammonia, a modification method by which the PIC can be endowed with further functions and/or tunable properties, was developed in this study. We focused on 1,3:4,6-di-*O*-benzylidene-D-mannitol (**DBM**) as the key comonomer to modify the properties of the PIC. Fully bio-based PCs with an acetal structure (**P(IC-co-DBMC)**) and hydroxy groups (**P(IC-co-MC)**) were successfully synthesized via the copolymerization of ISB with **DBM**, which was easily synthesized on a large scale from the biomass D-mannitol. The characteristics of the resulting polymers were easily tuned by deprotection and subsequent post-modification with boronic acid, in which the generated hydroxy groups were used as a scaffold to form boronate esters. Finally, **P(IC-co-MC)** was more rapidly decomposed in aqueous ammonia than PIC to afford ISB, D-mannitol, and urea. The obtained decomposition products were directly used as fertilizer, demonstrating a guiding principle for materials design based on a novel concept in which something that has hitherto been considered waste plastic is used as a source of fertilizer. We believe that the present study represents a milestone toward the new era of polymeric materials based on innovative recycling models "bread from plastics".

#### Conflicts of interest

There are no conflicts to declare.



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