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Chemical modification of poly(isosorbide carbonate)-based copolymers with boronic acids and the ammonolysis of the modified copolymers

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Here, the functionalization of bio-based polycarbonates by post-polymerization modification with boronic acids was demonstrated as an effective method for tuning the thermal and physical properties of original polymers without losing their original nature, i.e., the degradability into monomers and urea by ammonolysis. Poly(isosorbide carbonate)-based copolymers with hydroxy groups in the polymer main chain were modified using low-molecular-weight boronic acids and polymers-containing boronic acids, respectively. The modifications significantly changed the glass transition temperature, solubility, and mechanical properties. In particular, the use of modifiers with two or more boronic acids noticeably varied the mobility of the polymer, resulting in cross-linked structures. All the modified polymers, including the cross-linked polymers, were successfully degraded to monomers and urea by aqueous ammonia treatment. Thus, this study provides a design guideline to control the physical properties of PIC copolymers by balancing their stability as a polymer material and their degradability after use.

Introduction

In recent years, significant efforts have been made to conserve petroleum resources for the construction of a sustainable society. Polymeric materials, which are essential in modern society, are conventionally synthesized from petroleum-derived compounds. To address the problem of the depletion of petroleum resources, the use of the polymeric materials synthesized from bio-based compounds to replace conventional polymeric materials has been attracting attention.[1-9] Some bio-based polymer materials, such as poly(lactic acid) (PLA)[10], bio-poly(ethylene terephthalate) (bioPET)[11], and bio-polyethylene (bioPE)[12] have been used industrially, and these bio-based polymers are used as consumer products. To reduce the environmental impact of these bio-based polymeric materials, recycling by various methods, *e.g.* thermal, mechanical, and chemical recycling, were required.[13-24] In particular, chemical recycling has been vigorously investigated because it can regenerate, and reuse wasted polymeric materials through the repolymerization of monomers obtained by depolymerization and decomposition.[25-27]

Polyisosorbide carbonate (**PIC**)[28-34] is a biobased polycarbonate synthesized from isosorbide (**ISB**)[35, 36], which is a glucose-derived monomer. Further, it has recently attracted significant attention as an alternative material to polycarbonates synthesized from conventional petroleum-derived monomers. This is because of its high transparency, thermal stability, and mechanical properties. To expand the range of applications as an alternative material, copolymerization has been conducted to control the properties, and some PIC copolymers are being used industrially.[37-46]

However, as isosorbide is a bio-based compound, the unit cost is high. Therefore, it would be very attractive if it could be reused through chemical recycling because of the excellent thermal and mechanical properties of **PIC**s. Recently, we have focused on the ammonolysis of carbonate bonds in **PIC**s and PIC copolymers, and we have demonstrated that this reaction yields a mixture of monomers and urea as the decomposition product. The decomposition products of a PIC homopolymer can be directly used as fertilizer. [47] Furthermore, the degradation rate of PIC copolymers in aqueous ammonia can be varied

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depending on the chemical structure of the introduced comonomer. Additionally, PIC copolymers with generic comonomers can be similarly degraded to **ISB**, urea, and comonomers by ammonolysis. These studies indicate that a new chemical recycling system can be constructed using the ammonolysis reaction of PIC copolymers with ammonia.

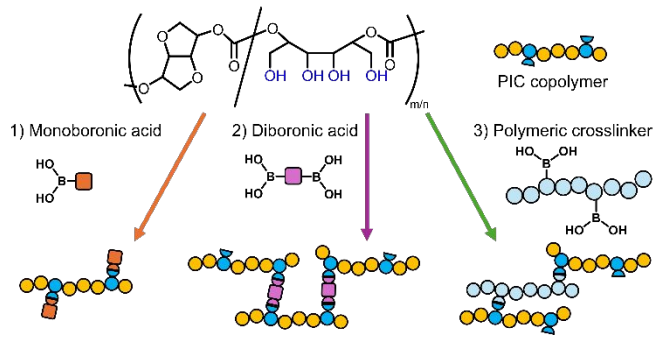


Figure 1. Post-modification of polyisosorbide carbonate (PIC)-based polymers using three types of boronic acids, 1) monoboronic acid, 2) diboronic acid, and 3) polymeric crosslinker with boronic acids in the side chain.

PIC copolymers with the required physical properties could be prepared by copolymerization with the proper kind and ratio of comonomer.[37, 41, 45] In our previous study, PIC copolymers were synthesized from **ISB** and mannitol derivatives. Further, they had hydroxy groups in the main chain, which could be reacted with anthraceneboronic acids to afford fluorescent properties via boronic ester formation between the hydroxy groups and boronic acids.[48] Post-modification by the formation of boronic acid ester structures is also used in the condensation of polyol with boronic acid polymers based on polycarbonate and polyester scaffolds. [49, 50]

In this study, we focus on a post-polymerization modification reaction using the hydroxy groups in the PIC-based copolymers as the reaction point. Further, we investigate the influence of the modification reaction on the physical properties and the ammonolysis behavior of the resulting polymers. It is expected that the post-polymerization modification with boronic acids can be achieved using not only low-molecular-weight boronic acids but also polymers containing boronic acids. [51-55] If this can be achieved, various functions and properties can be tuned from a single PIC copolymer depending on the modification agents, boronic acids to be introduced. The PIC copolymers used in this study have mannitol-derived comonomers. Therefore, it is a completely bio-based polycarbonate, which can be degraded by ammonia, and the boronic acid compounds used for modification can be easily separated.

The PIC copolymer used in this study is a completely biobased polycarbonate including mannitol-derived comonomers, and if its properties can be controlled by modification, it is expected to expand the range of applications as a polymer material and make a significant contribution to replacing petroleum-derived polycarbonates. If it becomes clear that not only low-molecular-weight compounds but also high-molecular-weight compounds can be selected as modifying molecules, it is expected that the tuning of the material properties will be significantly broadened. We believe that clarifying ammonolysis behavior is very important to understand the recycling properties of chemically modified PIC copolymers and that it will be possible to incorporate monomers and urea into the recycling system described above simply by isolating the modifying molecules from the degradation products. Modification with polymers having boronic acid is expected to facilitate the separation of the boronic acid polymer from the monomer or urea derived from the PIC copolymer after ammonia degradation.

As modification agents, three boronic acids were studied and categorized according to their molecular weights (Fig. 1). As the low-molecular-weight types, 1) monoboronic acid and 2) diboronic acid were applied. As the high-molecular-weight type, 3) polymeric crosslinkers with boronic acids in the side chains were applied. The effect of the modification with boronic acids on the thermal properties of the PIC-based polymers was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). For the mechanical properties of modified polymers, viscoelastic measurement was applied. Finally, their ammonolysis behavior was investigated by using nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC).

Experimentals

Materials

All reagents and solvents were purchased from Tokyo Chemical Industry (Tokyo, Japan), Kanto Chemical (Tokyo, Japan), FUJIFILM Wako Pure Chemical Corporation (Tokyo, Japan), and Sigma-Aldrich (MO, USA) and used as received.

Measurement

^{1}H NMR magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III HD 400M and AVANCE NEO 500 spectrometer, in dimethyl sulfoxide-d_6 (DMSO-d_6) or chloroform-d ($CDCl_3$) at 25 °C. For the diffusion-ordered NMR spectroscopy (DOSY), the LED method was used (pulse program: ledbpgp2s; diffusion time: 100 ms; diffusion gradient length: 2000 µs; maximum gradient strength: 51 G/cm in DMSO-d_6 at 25 °C).[56]

Gel permeation chromatography (GPC) was performed at 40 °C on a JASCO HSS-1500 system with a guard column (TOSOH TSKgel® guardcolumn SuperH-L), three columns (TOSOH TSKgel® 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 for GPC at a flow rate of 0.6 ml min^{-1}.

Polystyrene standards (number average molecular weight (M_n) 1,920−2,630,000 g mol^{-1}; polydispersity index (PDI) = 1.03−1.08) were used to calibrate the GPC system. Thermal decomposition temperature ($T_{d\text{-}5\%}$) of synthesized polymers were estimated by thermogravimetric analysis (TGA) measurements carried out on SHIMADZU DTG-60A, and all samples were heated to 550 °C at a rate of 10 °C min^{-1} under ambient atmosphere. The glass transition temperature (T_g) values of the synthesized PIC copolymers were estimated using differential scanning calorimetry (DSC) measurements carried out on a SHIMADZU DSC-60A Plus with a heating rate of 10 °C min^{-1} under a flow of N_2. The T_g values were determined from DSC data refer to second heating. The viscoelastic measurement was operated on an Anton-Paar MCR 302e.

Synthesis of P(IC-*co*-DBMC)

P(IC-*co*-DBMC) (**ISB** : **comonomer** = 9 : 1) was synthesized by a one-pot polycondensation method. **ISB** (39.46 g, 270 mmol, 0.9 eq), 1,3:4,6-di-O-benzylidene-D-mannitol (**DBM)** [57] (10.75 g, 30 mmol, 0.1 eq), diphenyl carbonate (**DPC**) (64.26 g, 300 mmol, 1 eq) and lithium acetylacetonate (LiAcac, 15.9 mg, 150 μmol, 0.05 mol%) were charged into a 200 mL two-necked round-bottomed flask equipped with a mechanical stirrer. In the transesterification stage, the reactants were heated to 180 °C under nitrogen atmosphere and stirred for 2 h. The temperature was then gradually increased to 200 °C and maintained for 30 min. In the polycondensation stage, the reaction system was continuously stirred under vacuum (about 10 mmHg) at 200 °C for 30 min and then under high vacuum (less than 0.2 mmHg) at 200 °C for 1.5 h to remove phenol. After the reaction was finished, the reaction system was cooled to room temperature under nitrogen atmosphere. Then, the product was dissolved in chloroform, followed by precipitation from methanol. After drying under vacuum, **P(IC-*co*-DBMC)** was obtained as a white solid (Yield: 47.42 g, 81.9%).

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

P(IC-*co*-DBMC) (30.0 g, 155 mmol) and 300 mL of chloroform were charged into a 500 mL round bottomed flask. While stirring slowly, trifluoroacetic acid/H_2O = 9/1 (v/v) solution (30 mL) was added to the solution slowly, followed by being stirred for 30 min at room temperature. Then, product was precipitated from methanol and obtained solid was filtered off. After drying under vacuum, **P(IC-*co*-MC)** was obtained as a white solid (Yield: 24.3 g, 89.1%).

Synthesis of the polymeric crosslinker with boronic acid pinacol ester

P(nBA-*co*-PBPE) was synthesized by free radical copolymerization (Scheme 2). *n*-Butyl acrylate (2.31 g, 18 mmol), 4-vinylphenylboronic acid (0.208 g, 2 mmol), 2,2'-azobis(isobutyronitrile) (65.7 mg, 0.4 mmol) and 20 mL of toluene was charged into 50 mL eggplant flask. The solution was bubbled by N_2, followed by heating the system at 70 °C and stirring for 16 h in the oil bath. The product was precipitated from methanol and decanted to remove the solvent, followed by drying under vacuum. **P(nBA-*co*-PBPE)** was obtained as a viscous liquid (Yield: 2.07 g, 82.3 %).

Deprotection of the polymeric crosslinkers

P(nBA-*co*-PBPE) (2.0 g) and 20 mL chloroform were charged into a 50 mL eggplant flask. 1.65 mL of trifluoroacetic acid (TFA) and phenylboronic acid (1.77 g, 14.5 mmol, 10 eq.) were added dropwise to the solution. The solution was stirred vigorously at room temperature, followed by the precipitation from the cold methanol to remove the excess of phenylboronic acid. The solution was decanted, and the obtained viscous liquid was dried under vacuum overnight (Yield: 1.43 g, 75.8 %).

Modification of P(IC-*co*-MC) with mono boronic acid

P(IC-*co*-MC) (1.76 g), phenylboronic acid (1.22 g, 10 mmol), sodium sulfate (7.10 g, 50 mmol) and 50 mL of DMF were charged into a 100 mL round bottomed flask. The solution was stirred at 60 °C for 16 hours, followed by the filtration to remove sodium sulfate. Then, the product was precipitated from methanol and obtained solid was filtered off. After drying under vacuum, **P(IC-*co*-MC)PB** was obtained as a white solid (Yield: 1.61 g, 88.1 %).

Modification of P(IC-*co*-MC) with diboronic acid

P(IC-*co*-MC) (1.76 g), phenylenediboronic acid (1.65 g, 10 mmol), sodium sulfate (7.10 g, 50 mmol) and 50 mL of DMF were charged into a 100 mL round bottomed flask. The solution was stirred at 60 °C for 16 hours, followed by the filtration to remove sodium sulfate. Then, product was precipitated from methanol and obtained solid was filtered off. After drying under vacuum, **P(IC-*co*-MC)PDB** was obtained as a white solid (Yield: 1.75 g).

Modification of P(IC-*co*-MC) with polymeric crosslinker

P(IC-*co*-MC), **P(nBA-*co*-PB)**, and 10 mL of DMF were charged into a 50 mL eggplant flask, in which the ratio of the mannitol units (4 OH) of **P(IC-*co*-MC)** and the boronic acid units ($B(OH)_2$) of **P(nBA-*co*-PB)** was set to 1:0.5 and 1:1. The system was heated toward 100 °C to dissolve the polymer, as followed by stirring overnight. The solution was cooled down and evaporated to remove DMF. Obtained solid was processed by the hot-press method by MeltPrep VCM at 80 °C for 15 minutes, followed by cooling at room temperature. The processed polymer was used for DSC measurement and viscoelastic measurement.

Ammonolysis of PIC copolymers

PIC copolymers were placed into a 50 mL reactor. The ammonia solution was added to the reactor to be 20 times to the carbonate linkage in polymer in the case of **P(IC-*co*-MC)** and **P(IC-*co*-MC)PB**. The reaction mixture was

heated and stirred in the oil bath. The reaction mixture was taken to vial, followed by freeze-drying to remove the ammonia and water.

P(IC-*co*-MC)PDB was decomposed in harsh condition, *i.e.*, at 90 °C in 14.8 mol/L of ammonia solution. The polymer sample (100 mg) and 15 mL of aqueous ammonia were charged into a 50 mL reactor. The solution was heated and stirred in the oil bath. The reaction mixture was evaporated to remove the ammonia and water, followed by vacuum drying. Their products were dissolved into DMF and/or DMSO-d_6 to use for GPC measurement and ^{1}H NMR spectroscopy for the evaluation of the ammonolysis behavior of PIC copolymers.

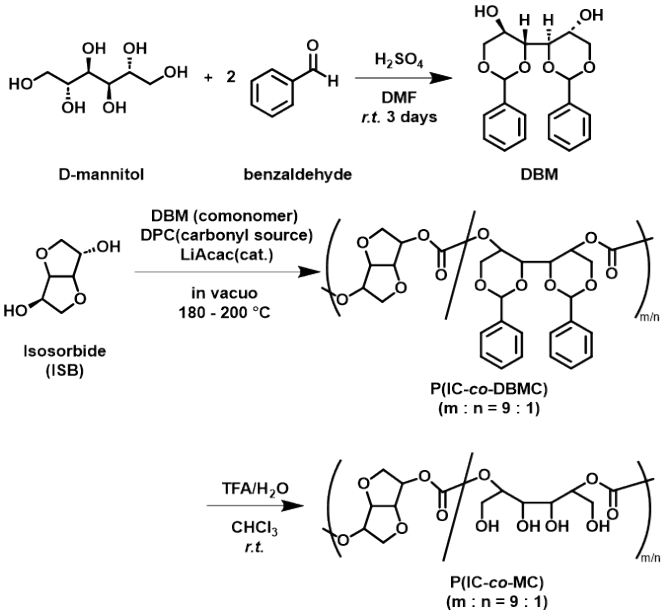
The mixture of **P(IC-*co*-MC)** and **P(nBA-*co*-PB)**, in which the ratio of the mannitol units of **P(IC-*co*-MC)** and the boronic acid units of **P(nBA-*co*-PB)** was 1:1, was also decomposed in harsh condition, *i.e.*, at 90 °C in 14.8 mol/L of ammonia solution. The sample (152 mg) and 15 mL of aqueous ammonia were charged into a 50 mL reactor. The solution was heated and stirred in the oil bath for 24 hours. The reaction mixture was filtrated, and the aqueous phase was evaporated to remove ammonia and water. Obtained solids were dried under vacuum. Their products were dissolved into DMF and/or DMSO-d_6 to use for GPC measurement and ^{1}H NMR spectroscopy for the evaluation of the ammonolysis behavior of PIC copolymers.

Results and discussion

Synthesis of poly(isosorbide carbonate) copolymers

P(IC-*co*-DBMC), the copolymer synthesized from isosorbide and 1,3:4,6-di-O-benzylidene-D-mannitol **(DBM)** with a specific feeding ratio (9 : 1), and **P(IC-*co*-MC)**, the copolymer synthesized from the deprotection of the acetal groups in **P(IC-*co*-DBMC)**, were prepared by a previously reported procedure (Scheme 1).

Scheme 1. Synthesis and deprotection of **P(IC-*co*-DBMC)**.



P(IC-*co*-DBMC) was treated with trifluoroacetic acid in chloroform for the deprotection of the hydroxy groups in the polymer chain. This reaction proceeded heterogeneously, given that the trifluoroacetic acid is a poor solvent for **P(IC-*co*-DBMC)**. After the reaction, the signals corresponding to the phenyl group disappeared from the ^{1}H NMR spectrum (Fig. 2 and Fig. S1), indicating that **P(IC-*co*-MC)** was successfully synthesized.

Modification of P(IC-co-MC)

In previous studies, the hydroxy group of the mannitol-derived comonomer in the **P(IC-*co*-MC)** main chain has been shown to be available as a reaction point. The chemical post-modification can be achieved by condensation of two adjacent hydroxyl groups and the boronic acid to form a boronate ester structure. Although post-modification of PIC copolymers has previously been achieved only with monoboronic acid, in this study we have also demonstrated that modification with diboronic acid and multi boronic acid on polymer chain is also attempted.

For the modification with monoboronic acids, only linear polymers were obtained because of the direct addition of the boronic acid to the main chain (Fig. 1-1). However, for the modification with diboronic acids, cross-linked structures were produced (Fig. 1-2). To investigate the effect of the cross-linked structure, phenylboronic acid and phenylenediboronic acid were chosen as the monoboronic and diboronic acids, respectively. These boronic acids have similar structures, *i.e.*, they possess the phenyl group. The modification of **P(IC-*co*-MC)** using the boronic acids was performed with sodium sulfate as a dehydrating agent. **P(IC-*co*-MC)PB**, the copolymer modified with phenylboronic acids, was characterized by GPC measurement (Fig. 3). After the deprotection of **P(IC-*co*-DBMC)**, the peak in GPC was shifted to a relatively late elution time (**P(IC-*co*-MC)**), whereas the peak appeared at

an early elution time after modification with boronic acid (**P(IC-co-MC)PB**). This was a result of the change in the polarity of the polymer chain because of the introduction of a hydroxy group by deprotection and the formation of a boronate ester structure after treatment with monoboronic acids.

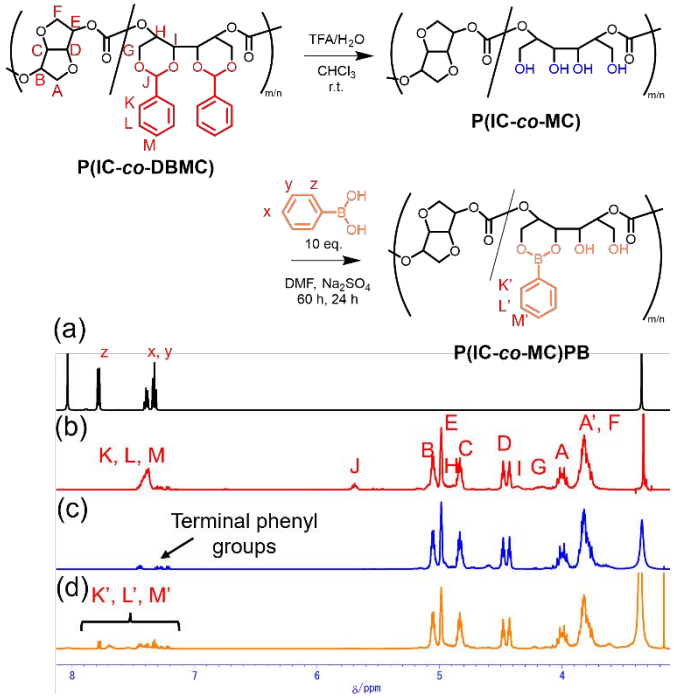


Figure 2. ^{1}H NMR spectra of (a) phenylboronic acid, (b) **P(IC-*co*-DBMC)**, (c) **P(IC-*co*-MC)**, and (d) **P(IC-co-MC)PB** (500 MHz, 25 °C, DMSO-d_6).

P(IC-*co*-MC)PB showed peaks derived from the phenyl groups of phenylboronic acid in the ^{1}H NMR spectrum (Fig. 2d). The modification degree was determined to be 52% based on the ratio of this signal relative to the signal of the proton combined with the polymer main chain. This incomplete modification degree, despite the reaction with excess amounts of boronic acids, was assumed to be the steric hindrance around the hydroxy groups. When a boronic acid is added to two adjacent hydroxy groups, it would be difficult for another boronic acid to be added because of the steric hindrance. Additionally, the modification by monoboronic acid was confirmed by diffusion-ordered spectroscopy (DOSY, Fig. S2). The signal from the phenyl groups of boronic acids indicated that the diffusion coefficient was comparable to that of the polymer main chain, which suggested that the modification proceeded successfully.

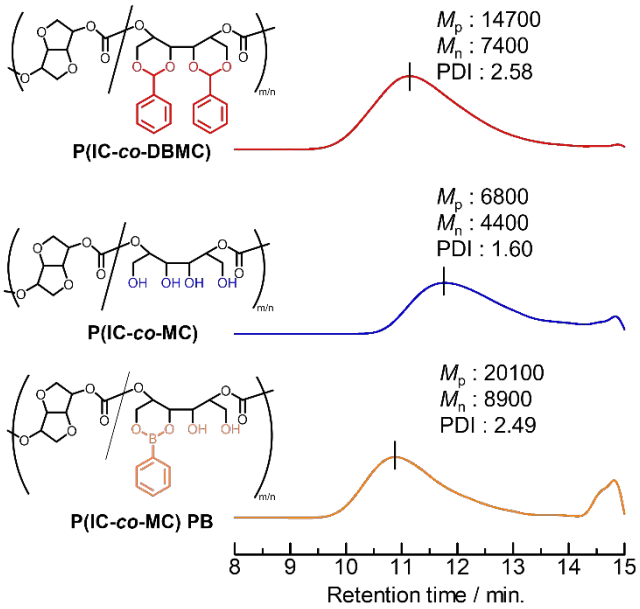


Figure 3. GPC profiles of **P(IC-*co*-DBMC)**, **P(IC-*co*-MC)**, and **P(IC-*co*-MC)PB**. (Detector: IR, Eluent: DMF, Standard: polystyrene)

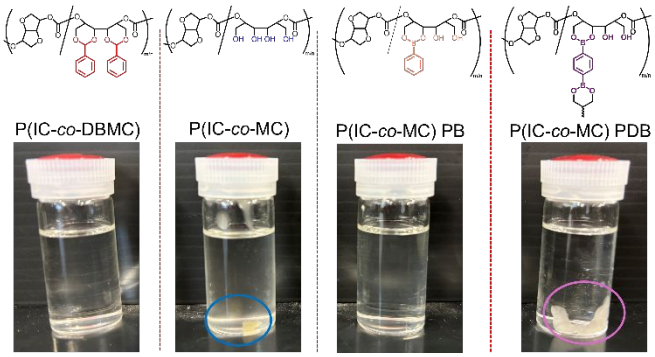


Figure 4. Solubility of the PIC copolymers in chloroform (10 mg/mL).

Table 1. Thermal properties of PIC copolymers

Sample ID	T_g[a] (°C)	$T_{d\text{-}5\%}$[b] (°C)
PIC	163	312
P(IC-*co*-DBMC)	153	314
P(IC-*co*-MC)	108	288
P(IC-*co*-MC)PB	115	308
P(IC-*co*-MC)PDB	144	318

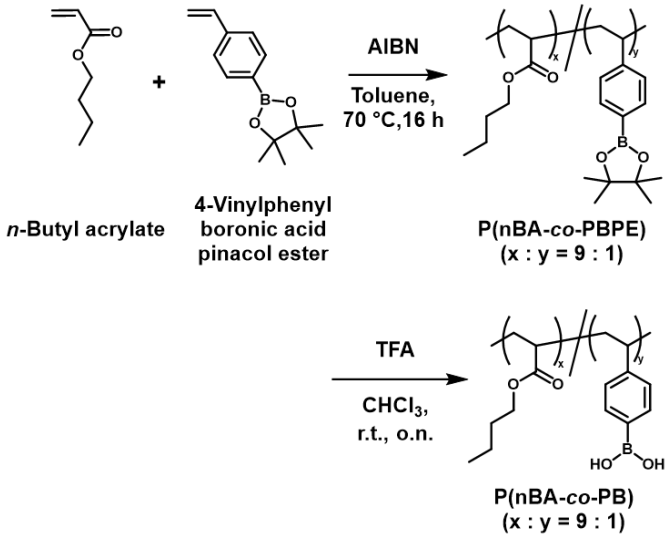
[a]Determined by DSC; DSC data refer to the second heating at a heating rate of 10 °C min^{-1}. [b]Determined by TGA (heating rate of 10 °C min^{-1}).

The modification of **P(IC-*co*-MC)** with diboronic acids was first visually confirmed by its solubility in the solvent (Fig. 4). **P(IC-*co*-MC)PDB** was hardly soluble in chloroform and remained as a solid. **P(IC-*co*-DBMC)** was easily soluble in chloroform, whereas **P(IC-*co*-MC)** was insoluble because of the change in the polarity of the main

chain caused by the introduction of the hydroxy group. Based on these results, the insolubility of **P(IC-*co*-MC)PDB** in chloroform suggested the formation of cross-linked structures by diboronic acid.

The modification with the polymeric crosslinker

Scheme 2. Synthesis and deprotection of **P(*n*BA-*co*-PBPE)**.



P(nBA-*co*-PBPE), a copolymer of *n*-butyl acrylate and 4-vinylphenylboronic acid pinacol ester was synthesized as a polymer-type modification agent that has boronic acids in the side chain, by free radical polymerization. The resulting polymer was characterized by NMR and GPC measurements. Composition of *n*-butyl acrylate and 4-vinylphenylboronic acid pinacol ester in polymer were 9:1 which is almost consisted with feed ratio of each monomer (9:1). The synthesized polymer contains a pinacol ester structure in the comonomer moieties, which was deprotected under acidic conditions with TFA to obtain the target polymer, **P(nBA-*co*-PB)** (Scheme 2 and Fig. S3-S5).

The condensation of the synthesized **P(nBA-*co*-PB)** with **P(IC-*co*-MC)** was demonstrated. The synthesized **P(nBA-*co*-PB)**, which was the sticky solid (T_g = –37 °C, Fig. S6), was mixed with **P(IC-*co*-MC)** in DMF and dried to obtain the modified **P(IC-*co*-MC)**. After removing DMF by evaporation and drying under a vacuum, the modified polymer afforded a yellow solid, which was processed by the hot-press method into a plate disk. The processed disks of **P(IC-*co*-MC)** with **P(nBA-*co*-PB)** were softer than that of the original **P(IC-*co*-MC)** (Fig. S6). In this system, it is not possible to remove the unreacted polymer, but we discuss the changes in physical properties including the unreacted polymers which contributes to the formation and exchange of dynamic covalent bonds.

Thermal properties

The thermal properties of the resulting polymers were investigated by TGA and DSC (Fig. 5 and Table 1). These results were compared with those of the PIC homopolymers with a similar molecular weight, which were synthesized with a previously reported procedure. As shown in Fig. 5a, the $T_{d\text{-}5\%}$ value of **P(IC-*co*-MC)** ($T_{d\text{-}5\%}$ = 288 °C) was lower than those of other polymers ($T_{d\text{-}5\%}$ = 308 °C ∼ 318 °C). This result might be caused by the existence of hydroxy groups in **P(IC-*co*-MC)**. The T_g value of **P(IC-*co*-DBMC)** (153 °C) was slightly lower than that of the PIC homopolymer (163 °C). T_g value of **P(IC-*co*-MC)** (T_g = 108 °C) was significantly lower than those of the PIC homopolymer (T_g = 163 °C). This was because the flexibility of the polymer main chain increased after the deprotection of the acetal structure. These results were consistent with our previous report. [48]

The T_g value of **P(IC-*co*-MC)PB** (T_g = 115 °C) was higher than those of **P(IC-*co*-MC)** (T_g = 108 °C). This indicated that the introduction of the boronate ester structure reduced the flexibility of the polymer main chain. The small increase in T_g (7 °C) might be attributed to the flexibility of the remaining unmodified comonomer moieties.

The T_g value of **P(IC-*co*-MC)PDB** (T_g = 144 °C) was significantly higher than those of **P(IC-*co*-MC)** (T_g = 108 °C). These results indicated that the reduced mobility of the entire polymer chain was caused by the formation of the cross-linked structures via the boronate ester structure.

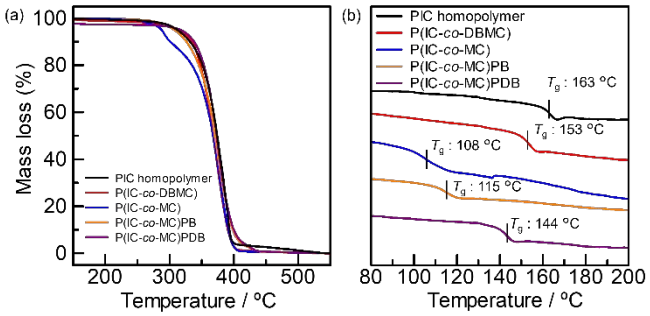


Figure 5. (a)TGA traces and (b)DSC curves of PIC copolymers.

Further, the thermal properties of the modified **P(IC-*co*-MC)**s with polymer-containing boronic acids were investigated by DSC (Fig. 6). Interestingly, the T_g value of **P(nBA-*co*-PB)**, polymer type modifier, was very low (–37 °C, Fig. S7), whereas the T_g value of the mixture of **P(IC-*co*-MC)** and **P(nBA-*co*-PB)** was dramatically increased as the amount of **P(nBA-*co*-PB)**. When the ratio of the mannitol part in **P(IC-*co*-MC)** to the boronic acid part in **P(nBA-*co*-PB)** (MC : PB ratio) increased, the T_g values became higher. These results indicated that the cross-linked structure between **P(IC-*co*-MC)** and **P(nBA-*co*-PB)** was successfully constructed.

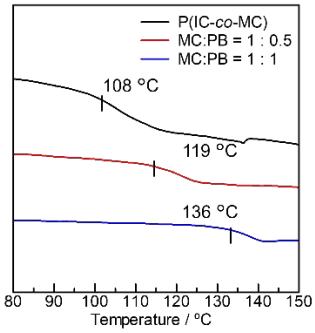


Figure 6. DSC curves of **P(IC-*co*-MC)** and cross-linked **P(IC-*co*-MC)**s.

Shear rheology properties

P(IC-*co*-MC) was molded into a transparent disk; however, it was brittle and easily cracked. When **P(nBA-*co*-PB)** was added, it became relatively soft as the mixing ratio increased. These samples were characterized using viscoelastic measurements.

The results of the viscoelastic measurements are shown in Fig. 7. As shown in Fig. 7a, a rapid decrease in G' is observed above 130 °C, which is roughly consistent with the T_g determined by DSC, indicating the glass transition of the polymer. At over 150 °C, the profiles could not be measured correctly because of the fluidity of **P(IC-*co*-MC)**. When **P(nBA-*co*-PB)** was added to **P(IC-*co*-MC)**, the viscoelastic behavior was significantly changed. As shown in Fig. 7b, when the MC : PB was 1:0.5, the fluidity of the polymer mixture was successfully measured at a relatively high temperature (ca. 170 °C). As shown in Fig. 7c, interestingly, when the MC:PB was 1:1, the sample did not exhibit fluidity and the profile showed the plateau region in the high-temperature range. In addition, frequency dependence of G' and G'' was measured at 140 °C, the temperature over T_g and less than one which showed fluidity (ca. 170 °C) (Fig. S8). As PB amount to MC increased, the fluidity of the sample decreased. These results supported that the crosslinking between **P(IC-*co*-MC)** and **P(nBA-*co*-PB)** was formed. We successfully changed the physical properties of bio-based polycarbonate by post-polymerization modification with polymer type modifier. As the options for the selection of the polymer composition which is used as polymer type modifier, is almost infinite, it should be possible to prepare materials with different physical properties by judiciously choosing appropriate polymer compositions.

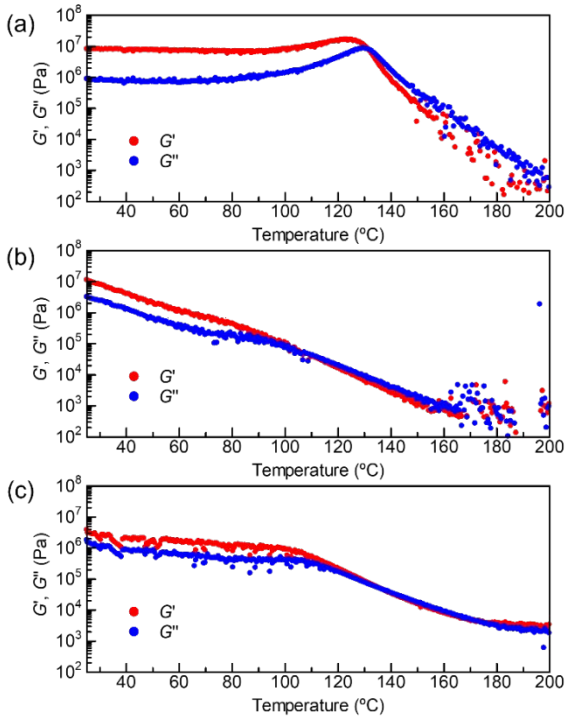


Figure 7. Temperature dependence of *G'* and *G''*. (a)**P(IC-*co*-MC)**, (b)MC:PB = 1:0.5, (c)MC:PB = 1:1.

Ammonolysis of modified P(IC-*co*-MC)

To investigate the effect of boronic acid modification on ammonia degradation behavior, **P(IC-*co*-MC)** and **P(IC-*co*-MC)PB** were treated in ammonia water. The hydrophilic ammonia degradation reactions of the hydroxy groups were performed in the same manner for both samples, *i.e.* with 20 equivalents of ammonia to the carbonate bond at 30 °C. The ammonia degradation behavior was analyzed using the value of the molecular weight (M_p) of the peak top in the GPC profiles before and after degradation. The molecular weight before the degradation reaction was set to $[M_p]_0$, the molecular weight at the degradation reaction time t was set to $[M_p]_t$, and the progress of degradation was evaluated by the ratio of these, $[M_p]_t/[M_p]_0$. Before the degradation, this ratio is 1, and this value decreases with the progress of degradation. When degradation is complete, $[M_p]_t/[M_p]_0 = 0$ (Fig. 8 and Fig. S9 and S10).

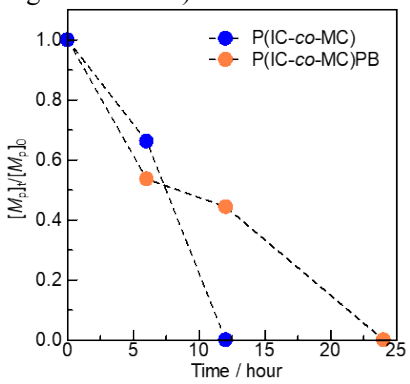


Figure 8. Ammonolysis of **P(IC-*co*-MC)** and **P(IC-*co*-MC)PB**

$[M_p]_t/[M_p]_0$ indicated that the ammonolysis of **P(IC-*co*-MC)** completed within 12 h, whereas the ammonolysis of **P(IC-*co*-MC)PB** required another 12 h for complete degradation. Further, the ^{1}H NMR spectra of the reaction mixtures showed the absence of the signal derived from the polymer, which the proton was combined with the carbon adjacent to the carbonate bond (Fig. S11 and S12). These results suggested that **P(IC-*co*-MC)** modified with boronic acid became more hydrophobic owing to the introduction of the boronic ester structure and the phenyl group. [58]Resultantly, the ammonia degradation reaction of **P(IC-*co*-MC)PB** in an aqueous solution was suppressed. Further, **P(IC-*co*-MC)** was suggested to degrade faster than the homopolymer not only because of the hydrophilicity of the hydroxy group, but also owing to the booster effect on ammonia degradation caused by the introduced D-mannitol structure. The formation of this boronate ester structure might inhibit this booster effect. [48]

Since the degradation of **P(IC-*co*-MC)PDB** was expected to be even slower than that of **P(IC-*co*-MC)PB** because of the formation of the cross-linked structures, the degradation reaction was performed under considerably harsh conditions, *i.e.*, 90 °C and excess ammonia relative to carbonate bonds. Since all PIC copolymers are insoluble in water, the degradation reaction in aqueous ammonia started from a heterogeneous solution. However, the reaction solution became homogeneous after 24 h (Fig. 9). The disappearance of the water-insoluble moieties derived from the high-molecular-weight compound indicated that it was converted into a low-molecular-weight compound by the ammonolysis. The ^{1}H NMR spectra of the decomposition reaction products showed that there were no peaks attributable to the presence of carbonate bonds. Further, the peaks attributed to isosorbide and urea were mainly confirmed, indicating that the decomposition was completed even though polymers were cross-linked (Fig. 9). Furthermore, no signals of the high-molecular-weight compound or oligomer were observed in the DOSY spectra of the decomposition products (Fig. S13). The decomposed comonomer and boronic acid were not clearly observed in ^{1}H NMR spectrum because these moieties were of low fraction ratio in the polymer, *i.e.* mannitol was 10% of the polymeric chain and the diboronic acid was less.

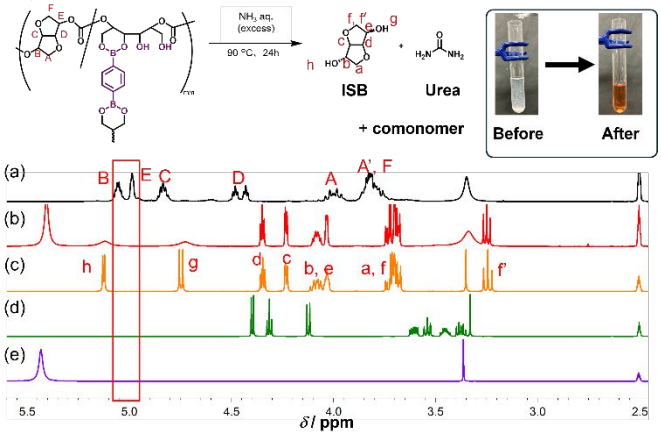


Figure 9. ^{1}H NMR spectra of (a)**P(IC-*co*-MC)**, (b) the decomposition product of the ammonolysis of **P(IC-*co*-MC)PDB**, (c) ISB, (d) D-mannitol, and (e) urea. (500 MHz, 25 °C, DMSO-d_6).

Ammonolysis behavior of the modified P(IC-*co*-MC) with the polymeric crosslinker

The ammonolysis behavior of modified **P(IC-*co*-MC)** with the polymeric crosslinker was also investigated. We used the polymer mixture prepared with 1 : 1 ratio of MC and PB units. The sample, which is roughly cross-linked as proven by DSC and shear rheology, was reacted in a harsh condition, *i.e.* with the treatment by excess ammonia at 90 °C. In the case of this sample, it was expected that only **P(IC-*co*-MC)** was selectively decomposed, which result in **P(nBA-*co*-PB)** remained as the solid after the reaction (Fig. 10). The reaction proceeded heterogeneously, the aqueous phase and solid were separated by the filtration after the 24 h of reaction. The aqueous phase was evaporated to remove ammonia and water, followed by vacuum drying. The solid in the reaction solution was dried under vacuum. These decomposition products were obtained with the high yield (> 90%) and characterized by ^{1}H NMR and GPC measurement. The ^{1}H NMR spectra of the aqueous phase of the decomposition product showed that there were no peaks indicating the presence of carbonate bonds, and the peaks assigned to isosorbide and urea were mainly observed (Fig. 11). No polymeric peaks were confirmed in the GPC profile, supporting that the ammonolysis of **P(IC-*co*-MC)** was completely achieved after the reaction (Fig. 12). The filtrated solid was also characterized by ^{1}H NMR (Fig. S14). The solid was mainly composed of **P(nBA-*co*-PB)**, indicating that the polymeric crosslinker was not decomposed during the reaction. These results showed that PIC copolymer was decomposed despite partially cross-linked by the modification with the polymeric modifier, and the filtrated polymeric modifier was easily separated and isolated.

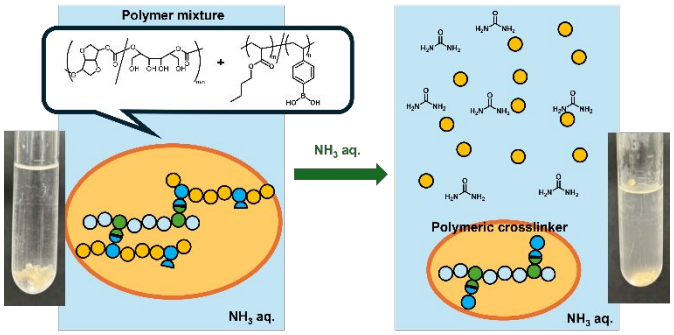


Figure 10. Schematic image of the ammonolysis of the polymer mixture which includes **P(IC-*co*-MC)** and **P(nBA-*co*-PB)**.

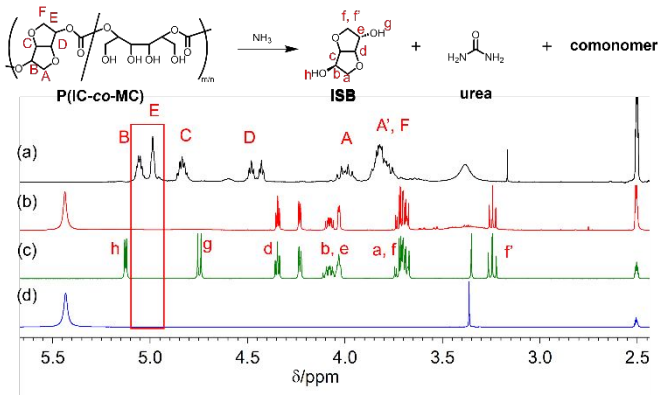


Figure 11. ^{1}H NMR spectra of (a)**P(IC-*co*-MC)**, (b) the aqueous phase of decomposition product, (c) ISB, and (d) urea. (500 MHz, 25 °C, DMSO-d_6).

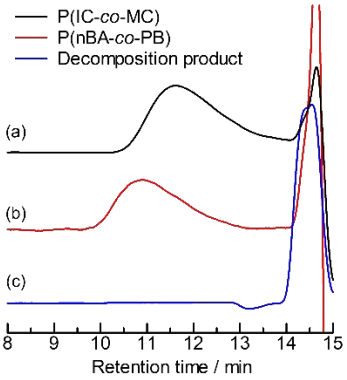


Figure 12. GPC profiles of a) **P(IC-*co*-MC)**, b) **P(nBA-*co*-PB)**, and c) the decomposition product in water soluble part after ammonolysis (eluent: DMF, detector: RI, standard: PS).

Conclusions

In this study, we focused on the post-polymerization modification reaction of PIC copolymers, which can be converted into monomers and urea by the treatment with ammonia, to investigate the influence of the modification reaction on the physical properties and the ammonolysis behavior of modified polymers. The modification that endowed PICs with further functions and/or tunable properties was achieved by the treatment with not only low-molecular-weight boronic acids but also the polymer with boronic acids, as the modifiers. These modifications were fully supported by an increase in T_g determined from DSC and a change in storage and loss modulus investigated by viscoelastic measurements. Finally, selective decomposition of PIC copolymer part in modified polymers was achieved by the ammonolysis even though modified polymers were partially crosslinked. As the options for the modifiers, especially polymer with boronic acids, are almost infinite, we believe that the present study showed a guideline for the post-polymerization modification for tuning the function and property of PIC copolymers without losing the degradability which is essence to achieve chemical recycling.

Author contributions

K. Rikiyama and D. Aoki conceived and designed the experiments. K. Rikiyama, A. Matsunami, and S. Fujimata performed the experiments. K. Rikiyama, T. Taniguchi, and D. Aoki analysed the data. K. Rikiyama and D. Aoki wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included in the main text and as part of the ESI.

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The data supporting this article have been included in the main text and as part of the ESI.