Electronic supplementary information

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

Takumi Abe,[a] Takehiro Kamiya,[b] Hideyuki Otsuka, *[a] and Daisuke Aoki*[c]

[a]*Department of Chemical Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan*

[b] *the Laboratory of Plant Nutrition and Fertilizers, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo, 113-8657, Japan.*

[c]*Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba-shi, Chiba 263-8522, Japan*

Corresponding Authors
* D. Aoki. E-mail: daoki@chiba-u.jp
* H. Otsuka. E-mail: otsuka@mac.titech.ac.jp

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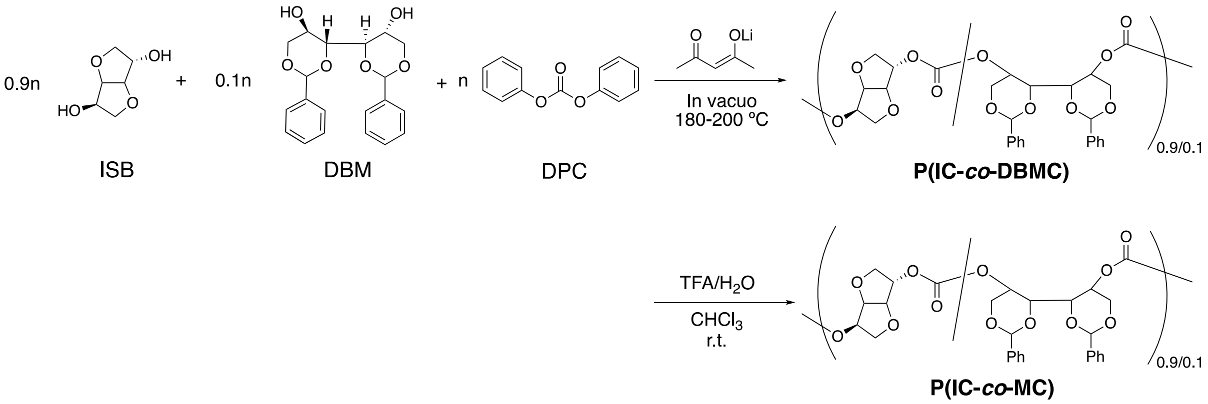
1. Experimental procedures

Synthesis of **P(IC-*co*-DBMC)** and **P(IC-*co*-MC)** (copolymerization ratio: 10%)



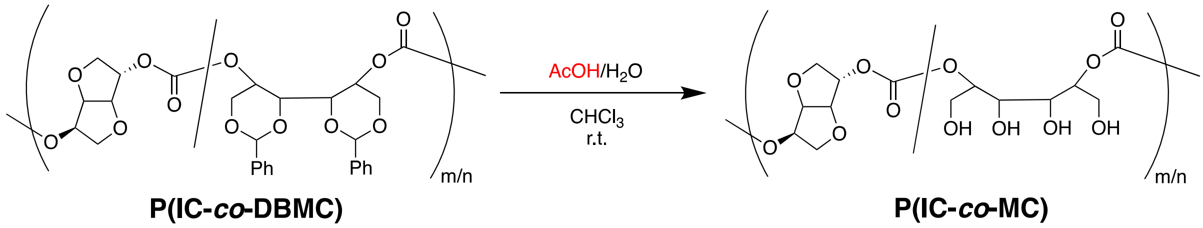
Scheme S1. Synthesis of **P(IC-*co*-DBMC)** and **P(IC-*co*-MC)** (copolymerization ratio: 10%).

P(IC-*co*-DBMC) was synthesized by a one-pot polycondensation method, in which the transesterification and polycondensation reactions were conducted in the same reactor continuously. ISB (2.50 g, 17.1 mmol, 0.9 eq), **DBM** (681 mg, 1.90 mmol, 0.1 eq), DPC (4.07 g, 19.0 mmol, 1 eq) and LiAcac (1 mg, 9.42 μmol) were placed in a two-necked round-bottomed flask (100 mL) equipped with a mechanical stirrer. During the transesterification stage, the reactants were heated to 180 °C under nitrogen atmosphere and stirred for 1.5 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 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: 3.58 g, 97.3%).

P(IC-*co*-DBMC) (1.50 g) dissolved in 15 mL of chloroform were placed in a round-bottomed flask (50 mL). While stirring at room temperature, CF_3COOH/H_2O = 9/1 (v/v) solution (8 mL) was added slowly, followed by being stirred for 30 min at room temperature. Then, the 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: 1.35 g, 97.5%).

Characterization data are in **Figure S5** and **S6.**

Deprotection reaction of **P(IC-*co*-DBMC)** with acetic acid

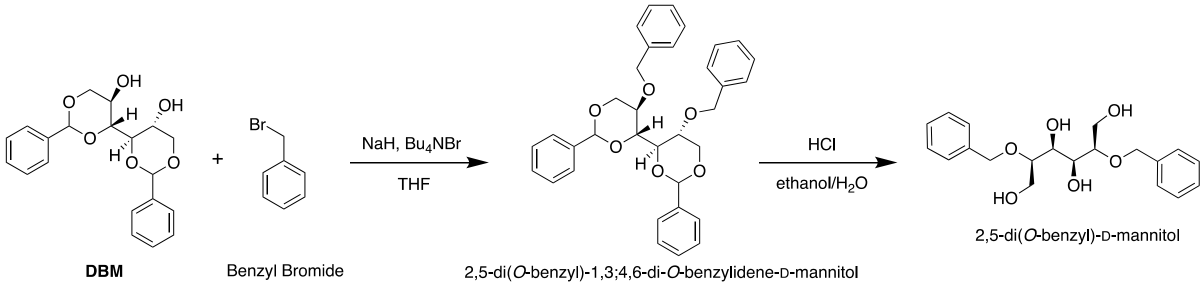


Scheme S2. Deprotection reaction of **P(IC-*co*-DBMC)** with acetic acid.

P(IC-*co*-DBMC) (30.1 mg) dissolved in 300 μL of chloroform were placed in a 10 mL sample tube. While stirring at room temperature, CH_3COOH/H_2O = 9/1 (v/v) solution (144 μL) was added slowly, followed by being stirred for 1 h at room temperature. Then, the product was precipitated from methanol, and obtained solid was filtered off and dried under vacuum. Characterization data are in **Figure S9** and **S10**.

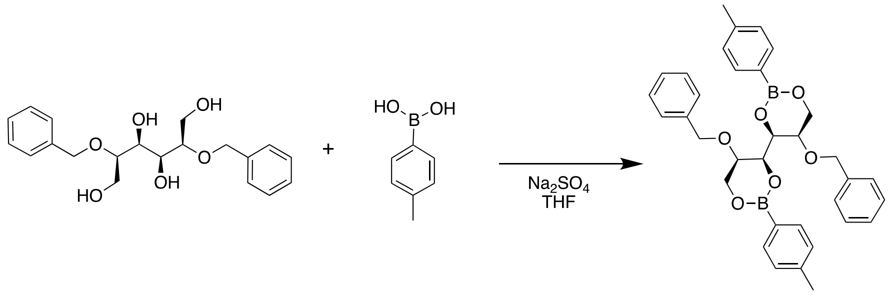
Synthesis of model compound (2,5-di(*O*-benzyl)-D-mannitol)

Model compound was synthesized following published procedure[1].

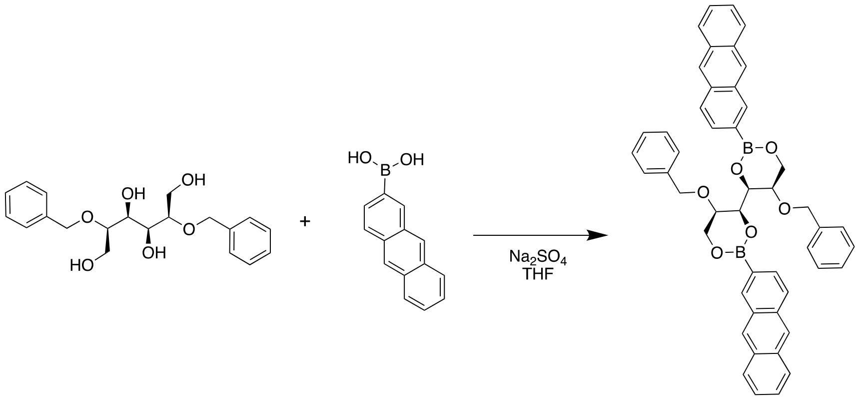


Scheme S3. Synthesis of the model compound (2,5-di(*O*-benzyl)-D-mannitol).

Model reaction for the modification reaction of **P(IC-*co*-MC)** with boronic acid



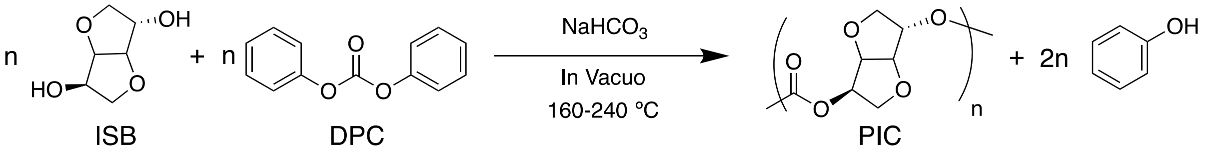
Scheme S4. Reaction between 2,5-di(*O*-benzyl)-D-mannitol and 4-methylphenylboronic acid.



Scheme S5. Reaction between 2,5-di(*O*-benzyl)-D-mannitol and 2-anthraceneboronic acid.

2,5-di(*O*-benzyl)-D-mannitol (25.0 mg, 69.0 μmol), 4-methylphenylboronic acid or 2-anthraceneboronic acid (2.1 eq.), and sodium sulfate (98.0 mg, 689 μmol) were placed into a 20 mL round-bottomed flask, before dried THF (5 mL) was added to the flask under nitrogen atmosphere. The reaction mixture was stirred for 24 h and filtered with filter agent to remove sodium sulfate. The organic solvent was evaporated and dried under vacuum.

Synthesis of PIC with molecular weight similar to **P(IC-*co*-MC)** (M_n = 10,200, PDI = 1.77, copolymerization ratio: 5%)



Scheme S6. Synthesis of PIC with molecular weight similar to **P(IC-*co*-MC)** (M_n = 10,200, PDI = 1.77, copolymerization ratio: 5%)

PIC with molecular weight similar to **P(IC-*co*-MC)** (M_n = 10,200, PDI = 1.77) was synthesized in similar manner. ISB (5.00 g, 34.2 mmol), DPC (7.33 g, 34.2 mmol) and sodium hydrogen carbonate (29.3 mg, 349 μmol) were placed in a two-necked round-bottomed flask (100 mL) equipped with a mechanical stirrer. During the transesterification stage, the reactants were heated to 160 °C under nitrogen atmosphere and stirred for 2.5 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 220 °C for 30 min and then under high vacuum (<1 mmHg) at 240 °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, PIC was obtained as a white solid (yield: 5.43g, 92.2%,

M_n = 10200, PDI = 1.69).
Characterization data are in **Figure S30** and **S31**

Synthesis of PIC with molecular weight similar to **P(IC-*co*-DBMC)** (M_n = 17,100, PDI = 2.34, copolymerization ratio: 5%)

PIC with molecular weight similar to **P(IC-*co*-DBMC)** (M_n = 17,100, PDI = 2.34) was synthesized in similar manner. ISB (10.0 g, 68.5 mmol), DPC (14.7 g, 68.5 mmol) and zinc acetate (62.0 mg, 341 μmol) were placed in a two-necked round-bottomed flask (100 mL) equipped with a mechanical stirrer. In the transesterification stage, the reactants were heated to 160 °C under nitrogen atmosphere and stirred for 3 h. The temperature was then gradually increased to 200 °C and maintained for 1 h. In the polycondensation stage, the reaction system was continuously stirred under vacuum (10-20 mmHg) at 240 °C for 1 h and then under high vacuum (<1 mmHg) at 260 °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, PIC was obtained as a white solid (yield: 11.1 g, 93.8%, M_n = 16000, PDI = 1.79).
Characterization data are in **Figure S32** and **S33**

Ammonolysis of **P(IC-*co*-MC)** at 90 °C (copolymerization ratio: 5%)

P(IC-*co*-MC) (M_n = 10,200, PDI = 1.77, 50.0 mg) was placed in round-bottomed flask (10 mL). Then, water (1.98 mL) and aqueous ammonia (14.8 M, 0.396 mL) was added to the flask. The reaction mixture was vigorously stirred at 90 °C for 9 h, and freeze-dried to remove water and ammonia. The obtained products were dissolved in DMSO-d_6 (2 mL) and toluene (50 μL, internal standard). 1mL of the solution was used for ^{1}H NMR analysis.
Characterization data are in **Figure 28**.

Plant growth experiment

The seeds of *Arabidopsis thaliana* ecotype Col-0 were surface-serialized with bleach and sown onto medium (**Table S1**) solidified with 1% Gellan Gum supplemented with 1% sucrose. The concentration of each nutrient, except for nitrogen source, was based on Fujiwara *et al.*[2] After incubation for two days at 4 °C, the plates were placed vertically and grown at 22 °C for two weeks under 16h light/8 h dark condition.

Table S1. Composition of growth medium

Entry	1	2	3
200 × Pi	1.25 mL	1.25 mL	1.25 mL
200 × Mg	1.25 mL	1.25 mL	1.25 mL
200 × micro	1.25 mL	1.25 mL	1.25 mL
1M $CaCl_2$	500 µL	500 µL	500 µL
200 × K_2SO_4 (300 mM)	1.25 mL	1.25 mL	1.25 mL
210 mM urea	0 mL	2.50 mL	0 mL
300 mM degradation products (ISB + D-mannitol = 300 mM, urea = 210 mM)	0 mL	0 mL	2.50 mL

200 x Pi: 350 mM NaH_2PO_4, 350 mM Na_2HPO_4

200 x Mg: 300 mM $MgSO_4$

200 x micro: 200 µM $CuSO_4$, 6 mM H_3BO_3, 34 µM $(NH_4)_6Mo_7O_{24}$, 26 µM $CoCl_2$, 13.4 mM Na_2-EDTA, 1.72 mM $FeSO_4$, 2.06 mM $MnSO_4$, 200 µM $ZnSO_4$

2. Supplemental figures

2.1. Preparation of **P(IC-*co*-MC)** and **P(IC-*co*-DBMC)**

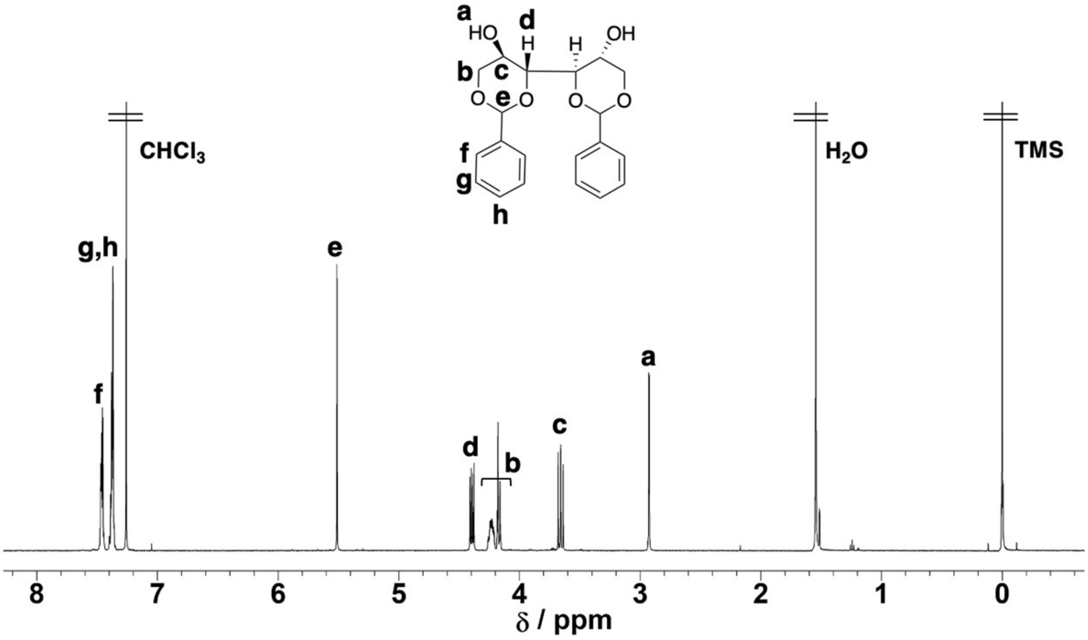


Figure S1. ^{1}H NMR spectrum of **DBM** (500 MHz, 25 °C, $CDCl_3$)

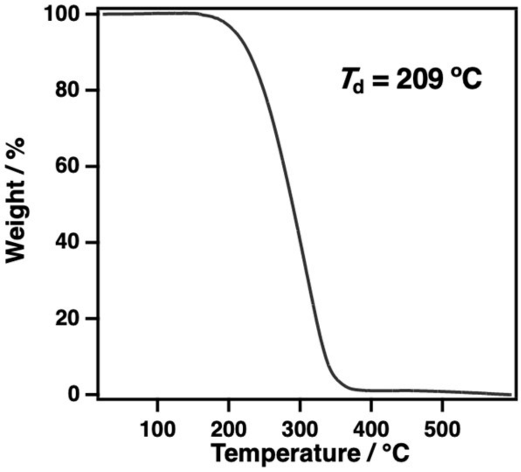


Figure S2. TGA trace of **DBM**.

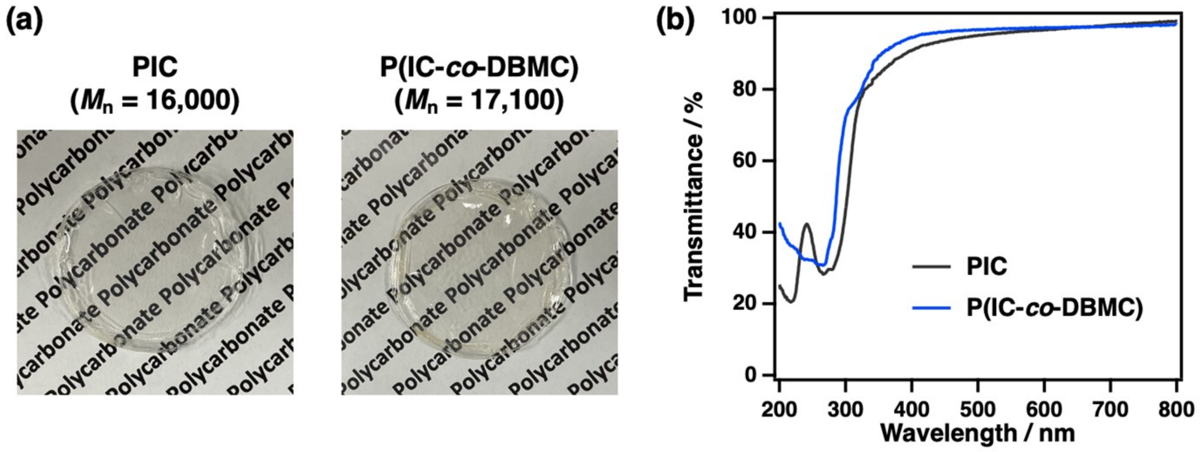


Figure S3. (a) Photographs of PIC and **P(IC-*co*-DBMC)** (copolymerization ratio: 5%) film prepared by solvent-cast method from chloroform solution. (b) UV-vis spectra of the films.

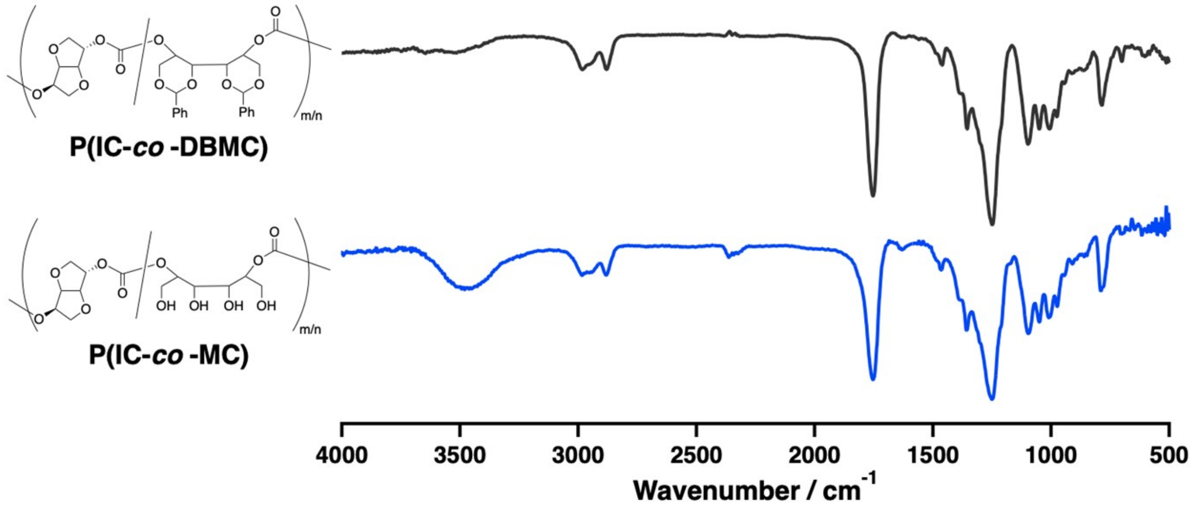


Figure S4. FT-IR spectra of **P(IC-*co*-DBMC)** (black) and **P(IC-*co*-MC)** (blue) (copolymerization ratio: 5%; KBr).

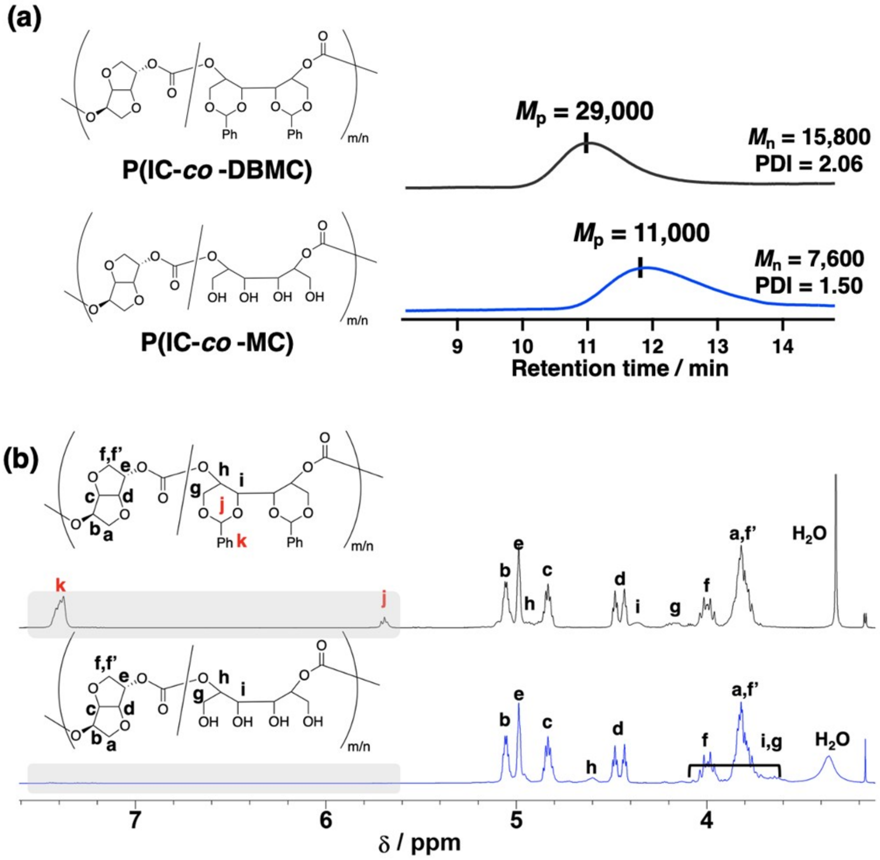


Figure S5. (a) GPC profiles of **P(IC-*co*-DBMC)** (black) and **P(IC-*co*-MC)** (blue) (copolymerization ratio: 10%; eluent: DMF; detector: RI; PS standard). (b) ^{1}H NMR spectra of **P(IC-*co*-DBMC)** (black) and **P(IC-*co*-MC)** (blue) (copolymerization ratio: 10%, 500 MHz, 25 °C, DMSO-d_6).

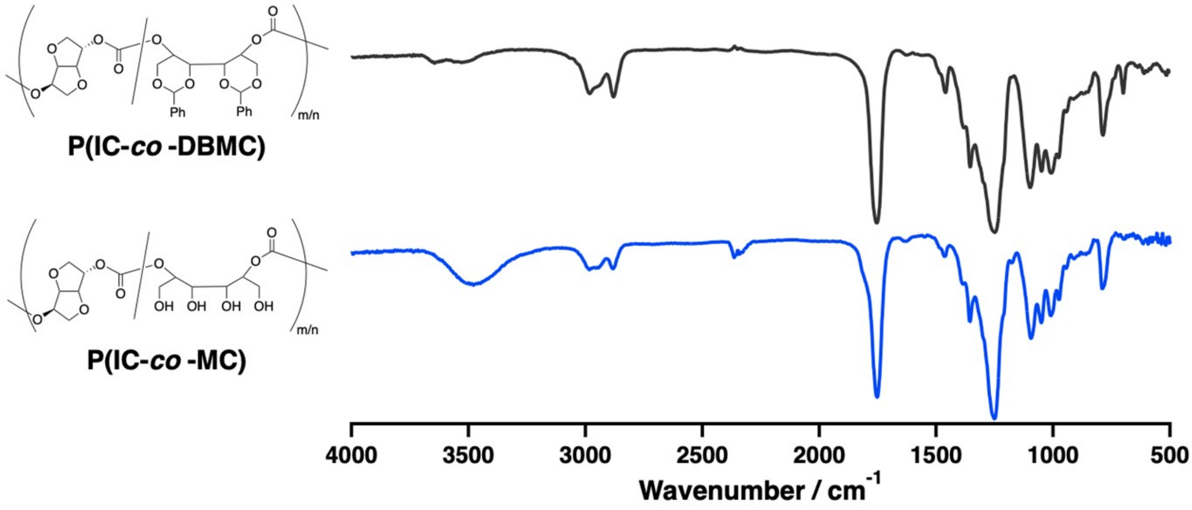


Figure S6. FT-IR spectra of **P(IC-*co*-DBMC)** (black) and **P(IC-*co*-MC)** (blue) (copolymerization ratio: 10%; KBr).

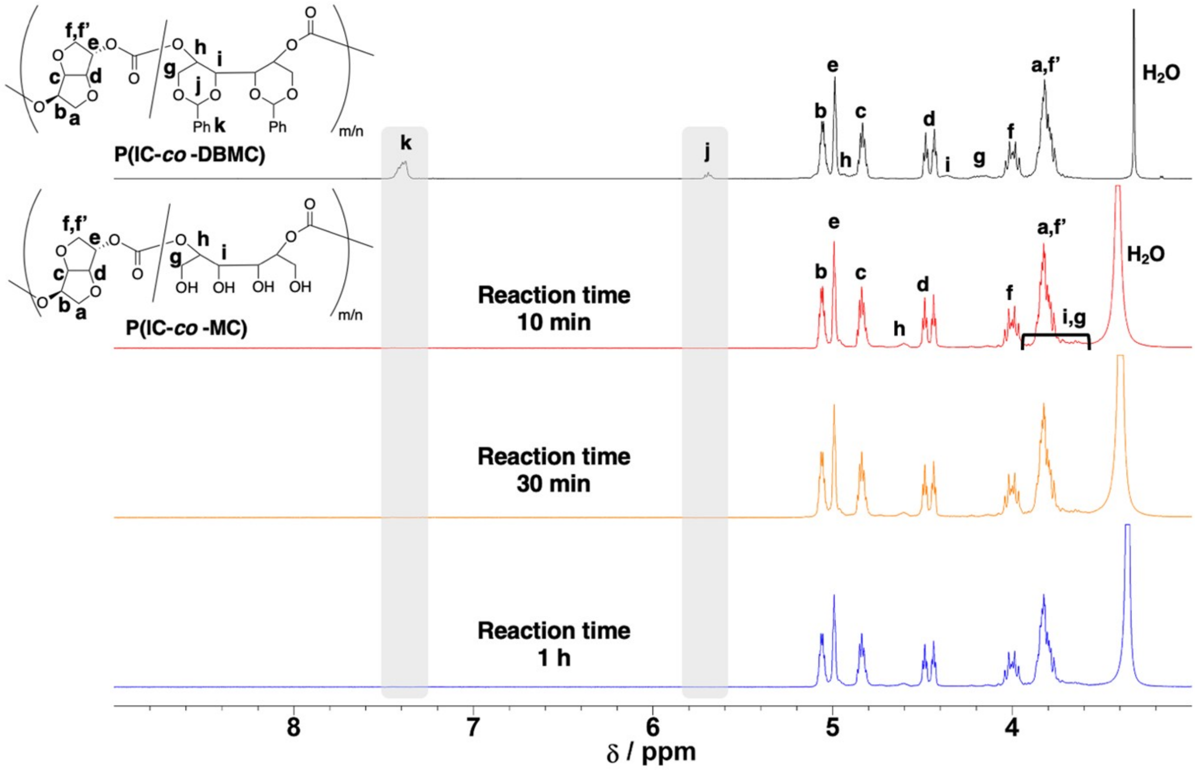


Figure S7. ^{1}H NMR spectra of **P(IC-*co*-DBMC)** and **P(IC-*co*-MC)** after each deprotection time (500 MHz, 25 °C, DMSO-d_6)

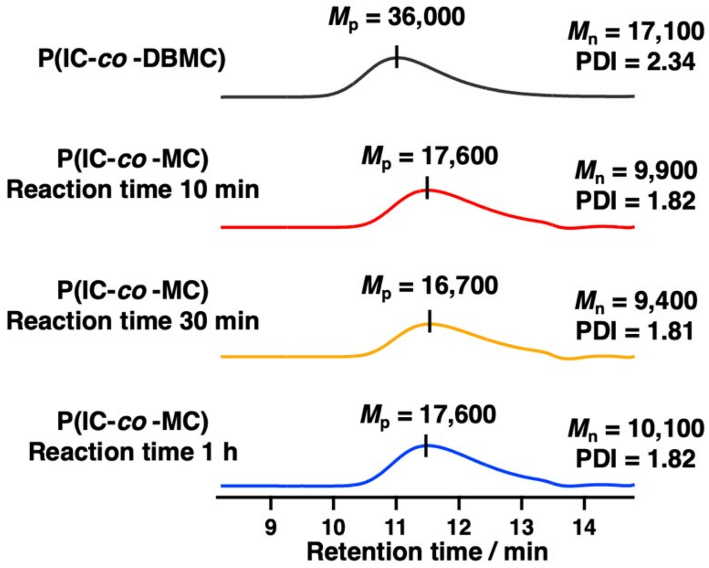


Figure S8. GPC profiles of **P(IC-*co*-DBMC)** and **P(IC-*co*-MC)** after each deprotection reaction time (eluent: DMF; detector: RI; polystyrene standard).

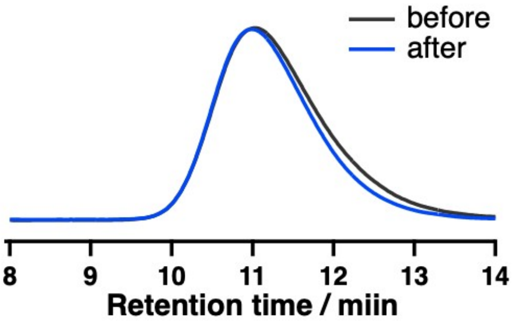


Figure S9. GPC profiles of **P(IC-*co*-DBMC)** (black) and the product after treating **P(IC-*co*-DBMC)-5** with acetic acid (blue) (eluent: DMF; detector: RI; polystyrene standard). The change in large retention time region contributed to the elution of small molecular weight component during the reprecipitation purification.

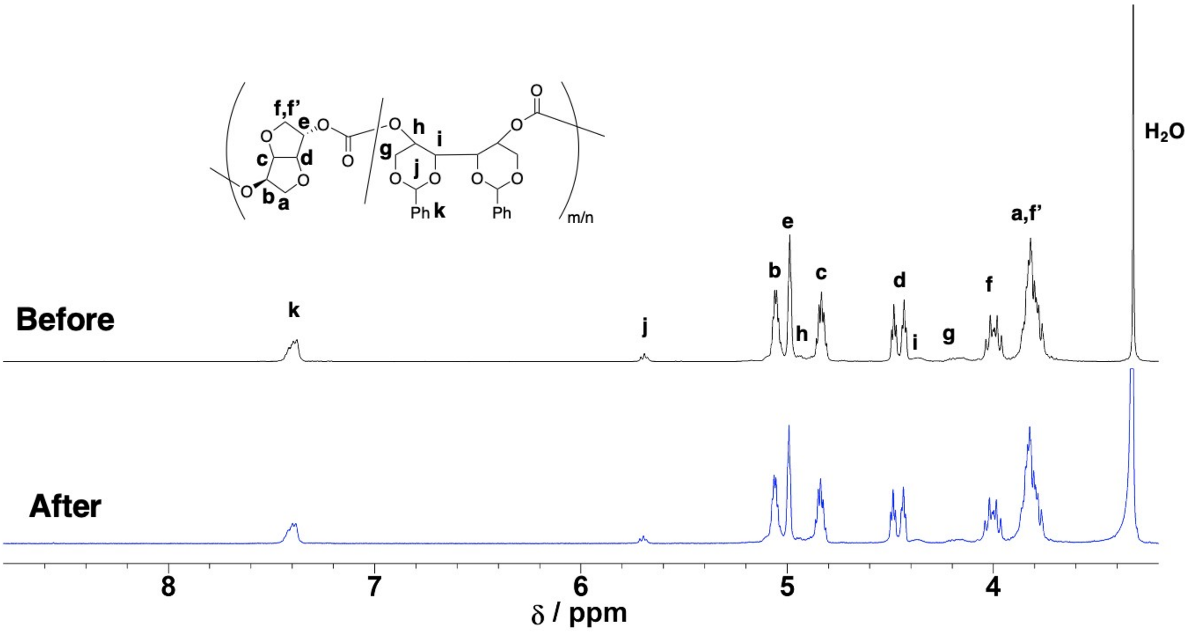


Figure S10. ^{1}H NMR spectra of **P(IC-*co*-DBMC)** and the product after treating **P(IC-*co*-DBMC)** with acetic acid (blue) (500 MHz, 25 °C, DMSO-d_6).

2.2. Thermal stability of ISB-based PCs

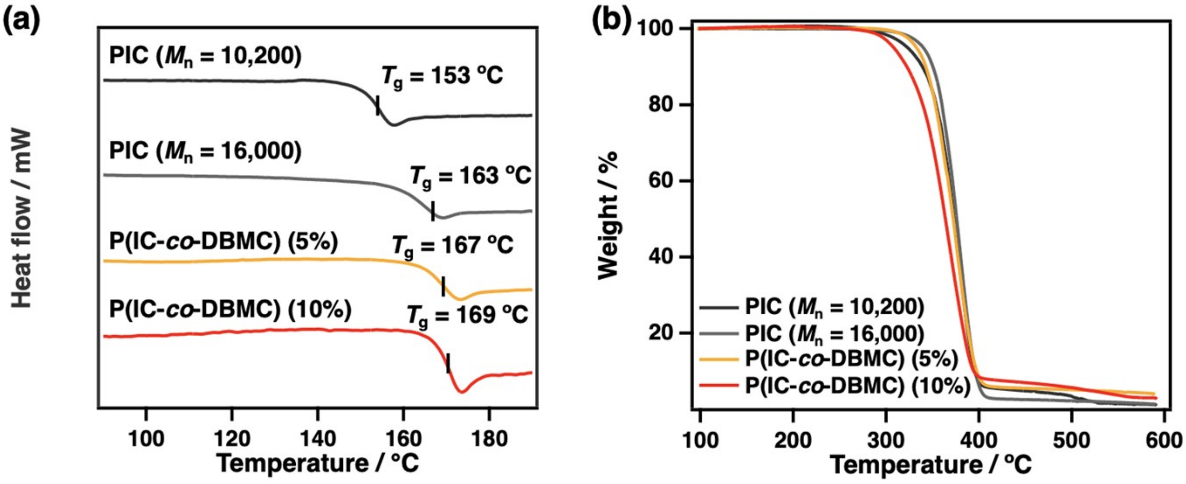


Figure S11. DSC and TGA traces of PIC and **P(IC-*co*-DBMC)** with different copolymerization ratio.

Table S2. Grass transition temperature (T_g) and 5% weight loss temperature ($T_{d\text{-}5\%}$) of PIC, and **P(IC-*co*-DBMC)** with different copolymerization ratio

Sample	M_n (PDI) [a]	T_g / °C [b]	$T_{d\text{-}5\%}$ / °C [c]
PIC	10200 (1.69)	153	323
PIC	16000 (1.79)	163	340
P(IC-*co*-DBMC) Copolymerization ratio 5%	17100 (2.34)	167	333
P(IC-*co*-DBMC) Copolymerization ratio 10%	15800 (2.06)	169	308

a) Determined by GPC (eluent: DMF; detector: RI; calibration: polystyrene standards)., b) Determined by DSC; The DSC data were given on the basis of the second heating at a heating rate of 10 °C/min, c) Determined by TGA; The TGA data were given at a heating rate of 10 °C/min.

2.3. Modification of **P(IC-*co*-MC)**

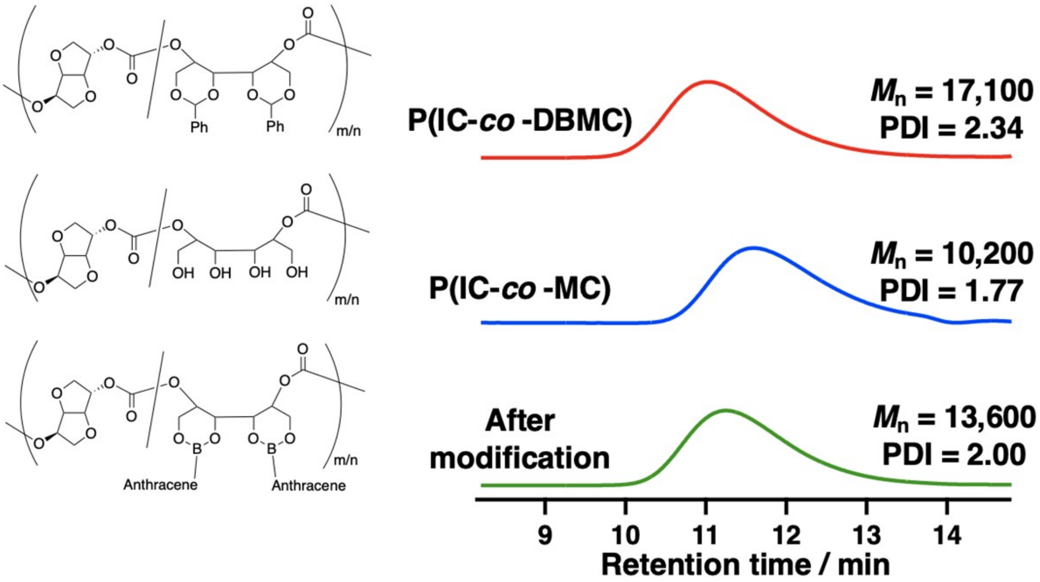


Figure S12. GPC profiles of **P(IC-*co*-DBMC)** (red), **P(IC-*co*-MC)** (bule) and **P(IC-*co*-MC)** modified with 2-anthraceneboronic acid (green) (eluent: DMF; detector: RI; polystyrene standard).

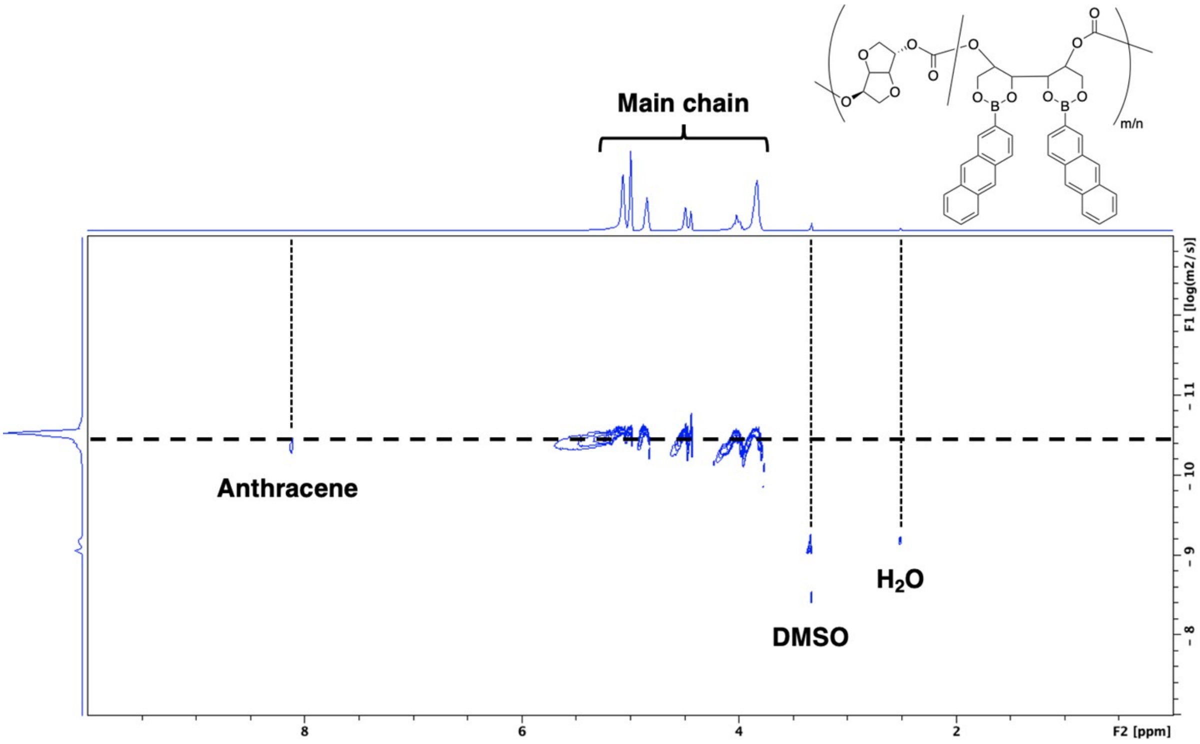


Figure S13. ^{1}H DOSY spectrum of **P(IC-*co*-MC)** modified with 2-anthraceneboronic acid (500 MHz, 25 °C, DMSO-d_6).

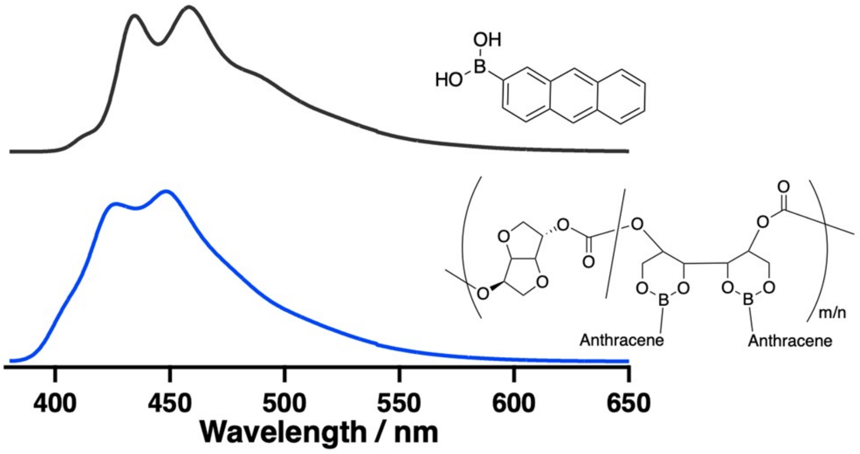


Figure S14. Solid state fluorescence spectra of **P(IC-*co*-MC)** and **P(IC-*co*-MC)** modified with 2-anthraceneboronic acid (excitation wavelength: 365 nm).

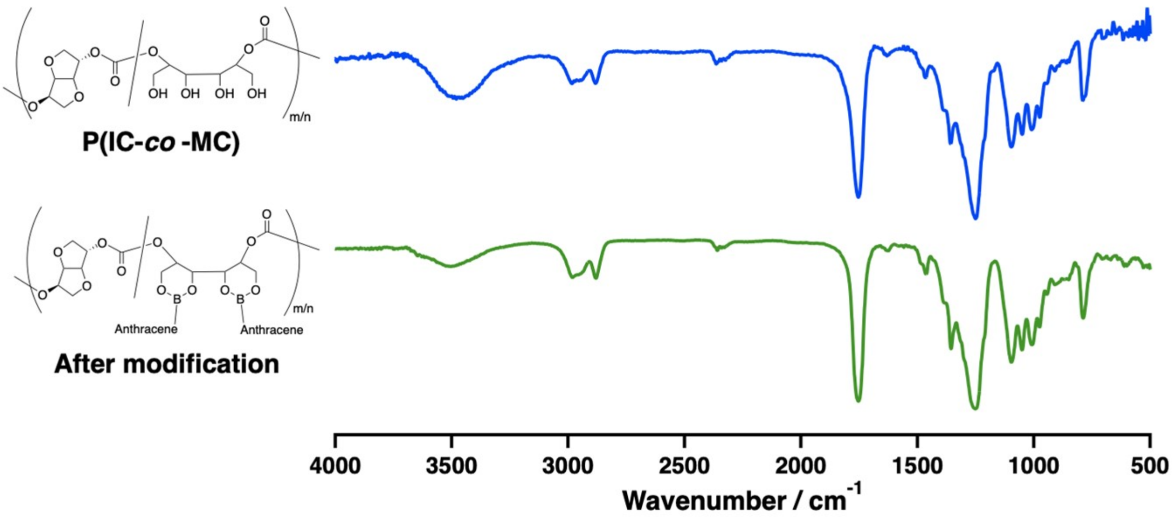


Figure S15. FT-IR spectra of d **P(IC-*co*-MC)** (blue) and **P(IC-*co*-MC)** modified with 2-anthraceneboronic acid (KBr)

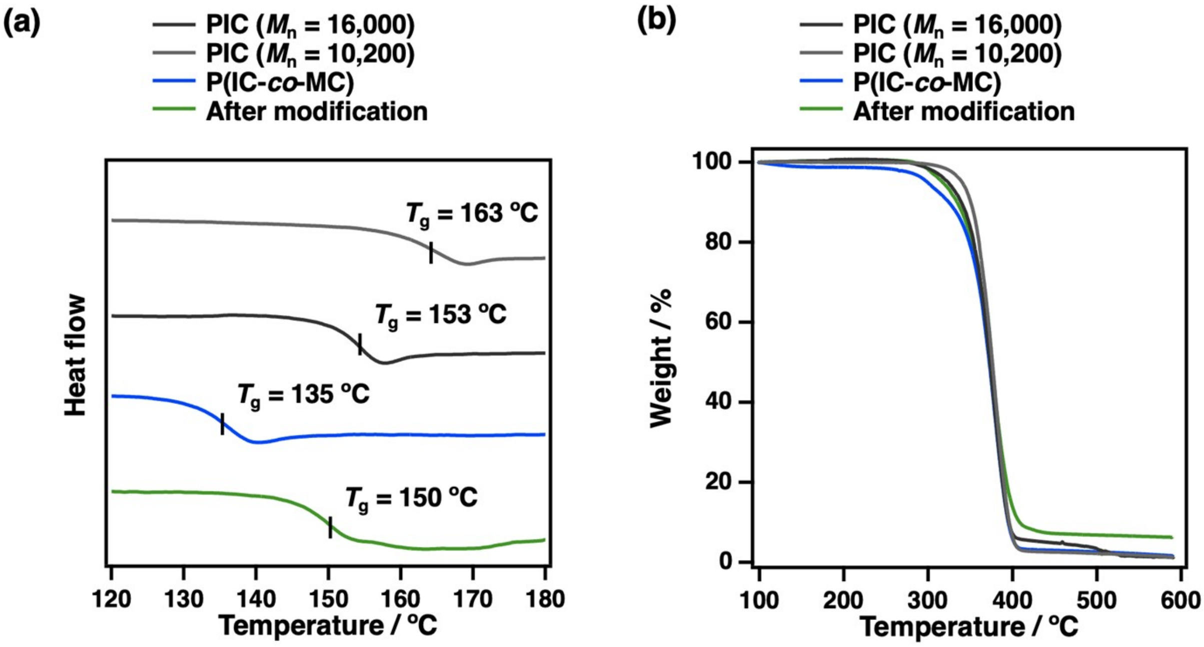
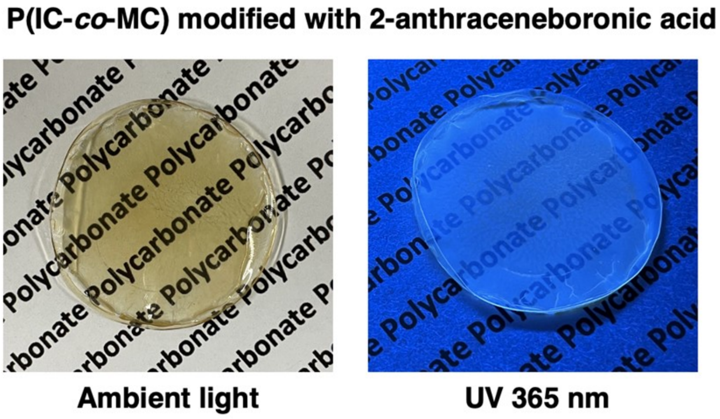


Figure S16. DSC and TGA traces of (a) PIC, **P(IC-*co*-MC)**, **P(IC-*co*-MC)** modified with 2-anthraceneboronic acid.

Table S3. Grass transition temperature (T_g) and 5% weight loss temperature ($T_{d\text{-}5\%}$) of PIC, **P(IC-*co*-MC)** and **P(IC-*co*-MC)** modified with 2-anthraceneboronic acid

Sample	M_n (PDI) [a]	T_g / °C [b]	$T_{d\text{-}5\%}$ / °C [c]
PIC	16,000 (1.79)	163	340
PIC	10,200 (1.69)	153	323
P(IC-*co*-MC)	10,200 (1.77)	135	299
Modified **P(IC-*co*-MC)**	13,600 (1.77)	150	317

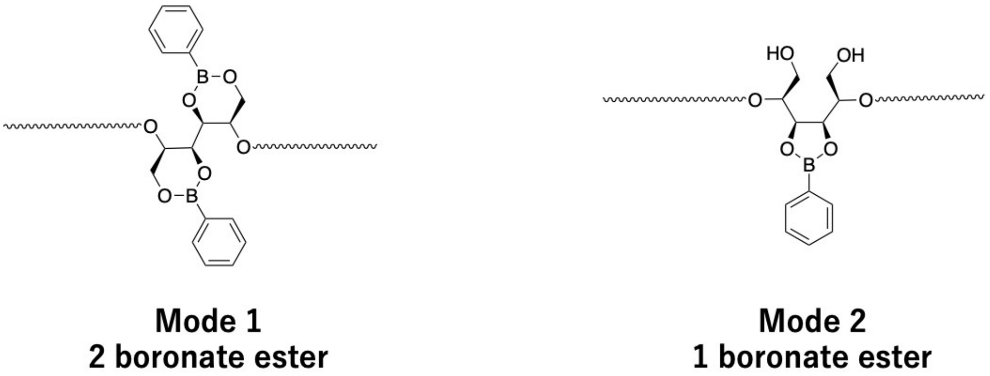
a) Determined by GPC (eluent: DMF; detector: RI; calibration: polystyrene standards)., b) Determined by DSC; The DSC data were given on the basis of the second heating at a heating rate of 10 °C/min, c) Determined by TGA; The TGA data were given at a heating rate of 10 °C/min.



Ambient light

UV 365 nm

Figure S17. Photographs of film of **P(IC-*co*-MC)** modified with 2-anthraceneboronic acid prepared by solvent-cast method from chloroform solution.



Mode 1
2 boronate ester

Mode 2
1 boronate ester

Figure S18. Conceivable boronate esters formation mode in the **P(IC-*co*-MC**) main chain.

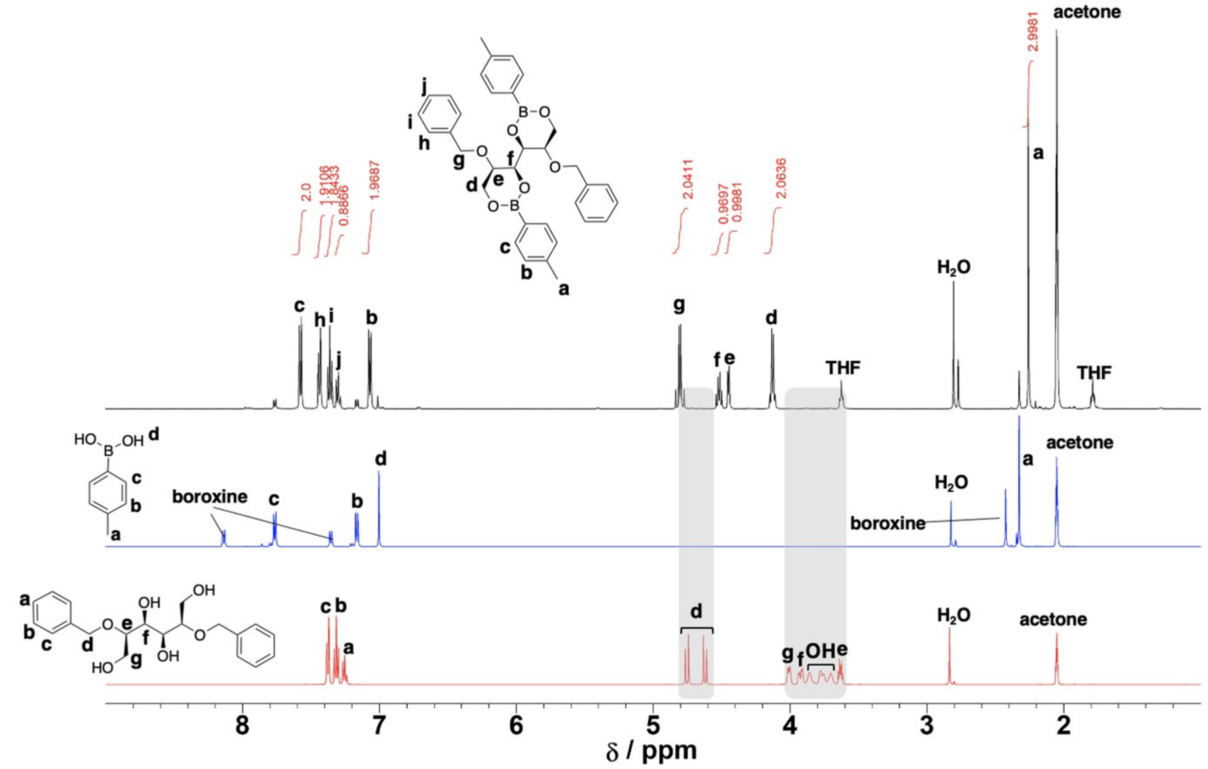


Figure S19. ^{1}H NMR spectrum of the product of the reaction between model compounds and 4-methylphenylboronic acid (500 MHz, 25 °C, DMSO-d_6).

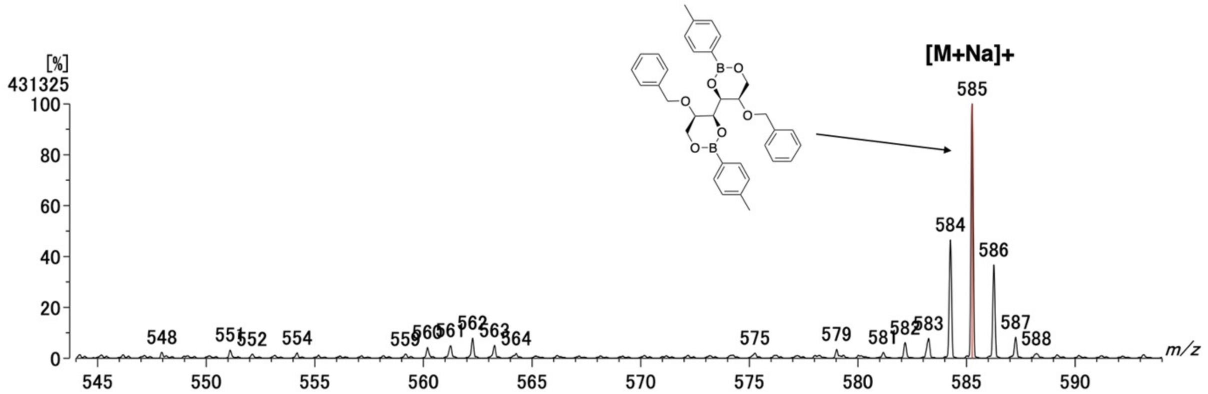


Figure S20. FAB-MS spectrum for the product of the reaction between model compounds and 4-methylphenylboronica acid (matrix: NBA+Na). The product was calculated for $C_{34}H_{36}O_6B_2$ [M+Na]+ 585.2607 and found 585.2606.

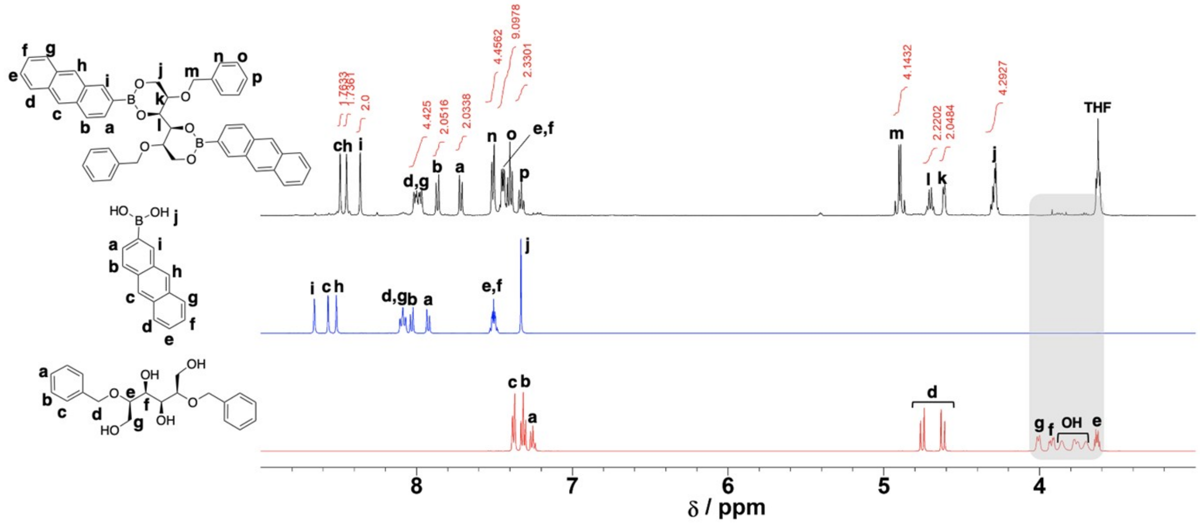


Figure S21. ^{1}H NMR spectrum of the product of the reaction between model compounds and 2-anthraceneboronic acid (500 MHz, 25 °C, DMSO-d_6).

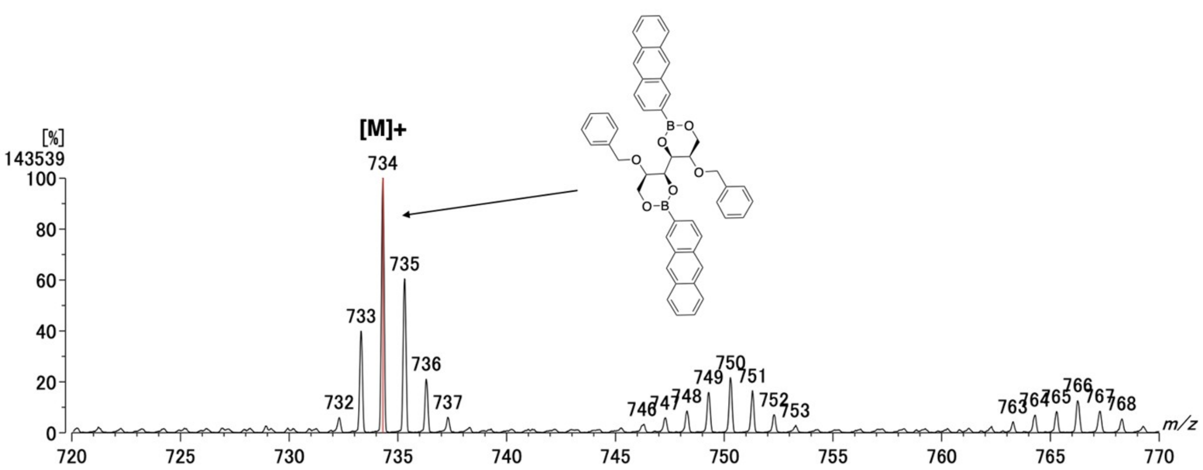


Figure S22. FAB-MS spectrum for the product of the reaction between model compounds and 2-anthraceneboronic acid (matrix: NBA). The product was calculated for $C_{48}H_{40}O_6B_2$ [M]+ 734.3027 and found at 734.3028.

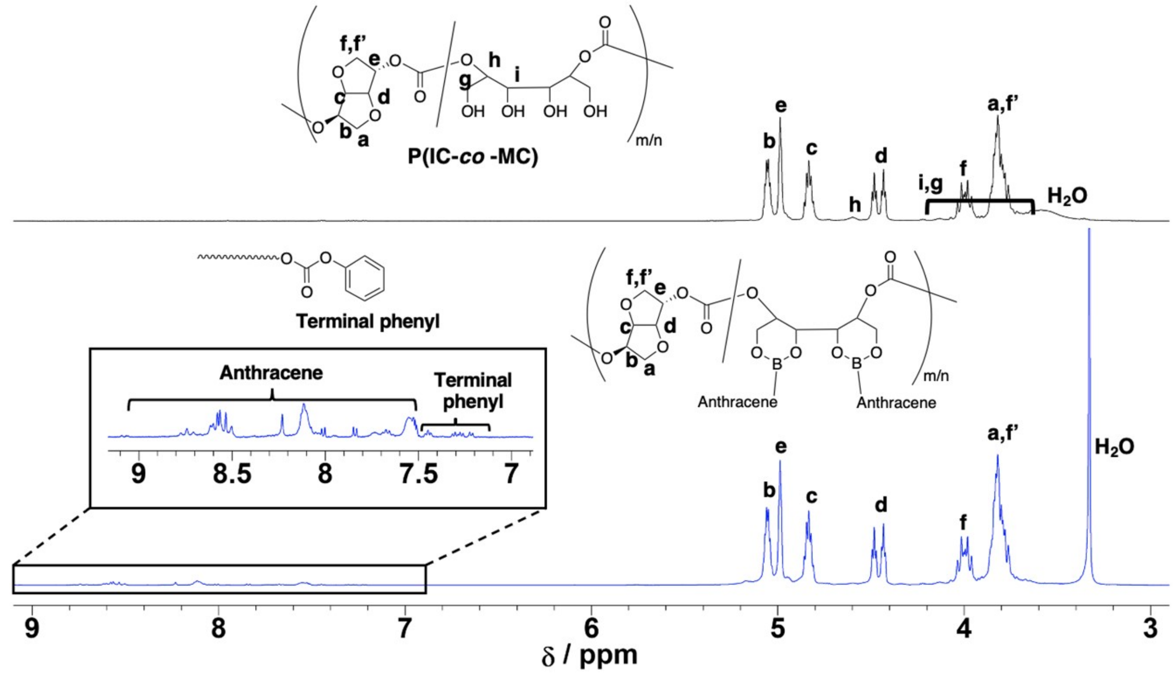


Figure S23. ^{1}H NMR spectra of **P(IC-*co*-MC)** and **P(IC-*co*-MC)** modified with 2-anthraceneboronic acid (500 MHz, 25 °C, DMSO-d_6).

2.4. Ammonolysis of **P(IC-*co*-MC)**

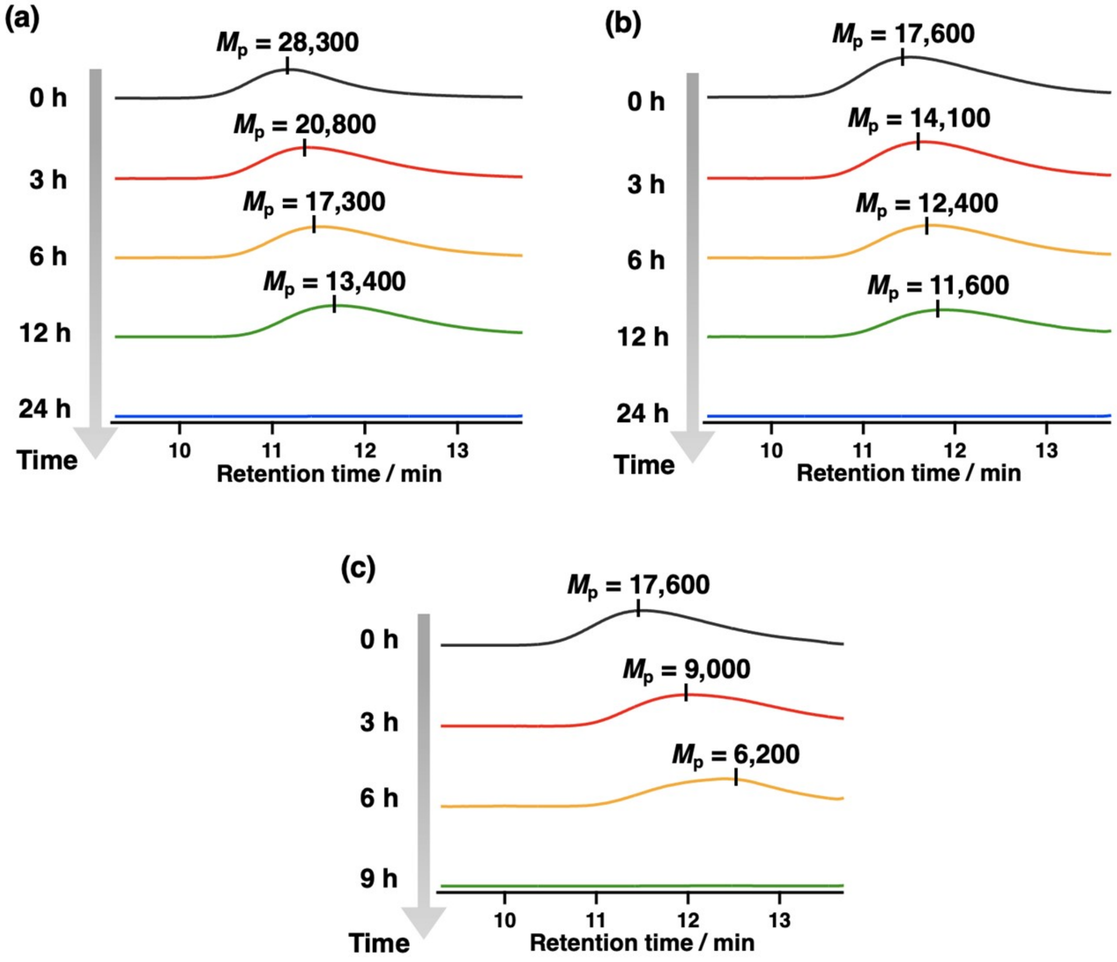


Figure S24. GPC profiles of the degradation product of (a) PIC (M_n = 16,000), (b) PIC (M_n = 10,200) and (c) **P(IC-*co*-MC)** (eluent: DMF; detector: RI; polystyrene standard).

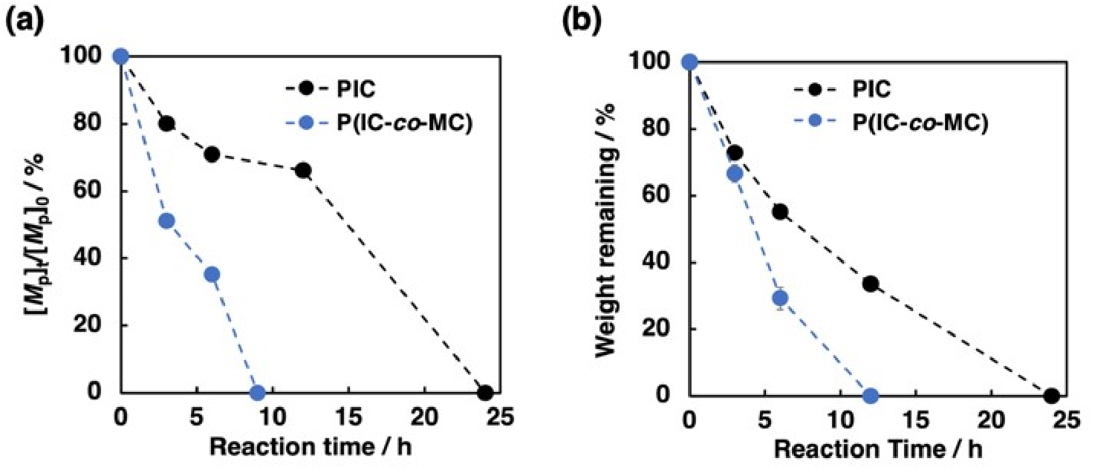


Figure S25. (a) $[M_p]_t/[M_p]_0$ (residual polymer ratio) and (b) weight of the remaining degradation products of PIC (black) and **P(IC-*co*-MC)** (M_n = 10200, PDI = 1.69, blue) during ammonolysis.

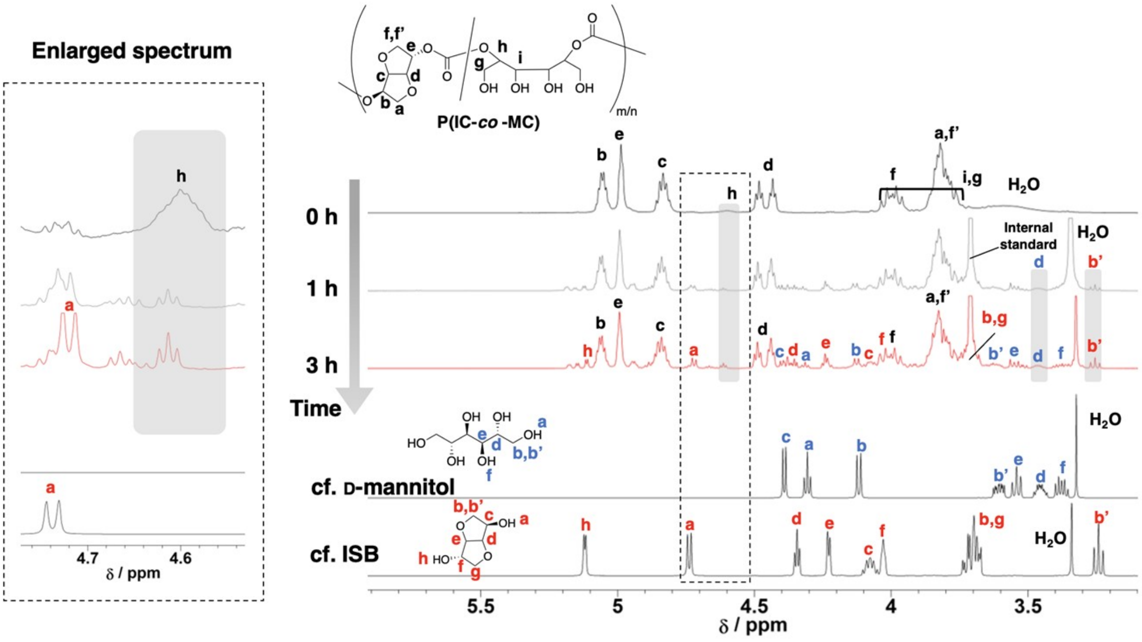


Figure S26. ^{1}H NMR spectrum of the degradation products of **P(IC-*co*-MC)** during the ammonolysis and enlarged spectra around 4.65 ppm (500 MHz, 25 °C, DMSO-d_6).

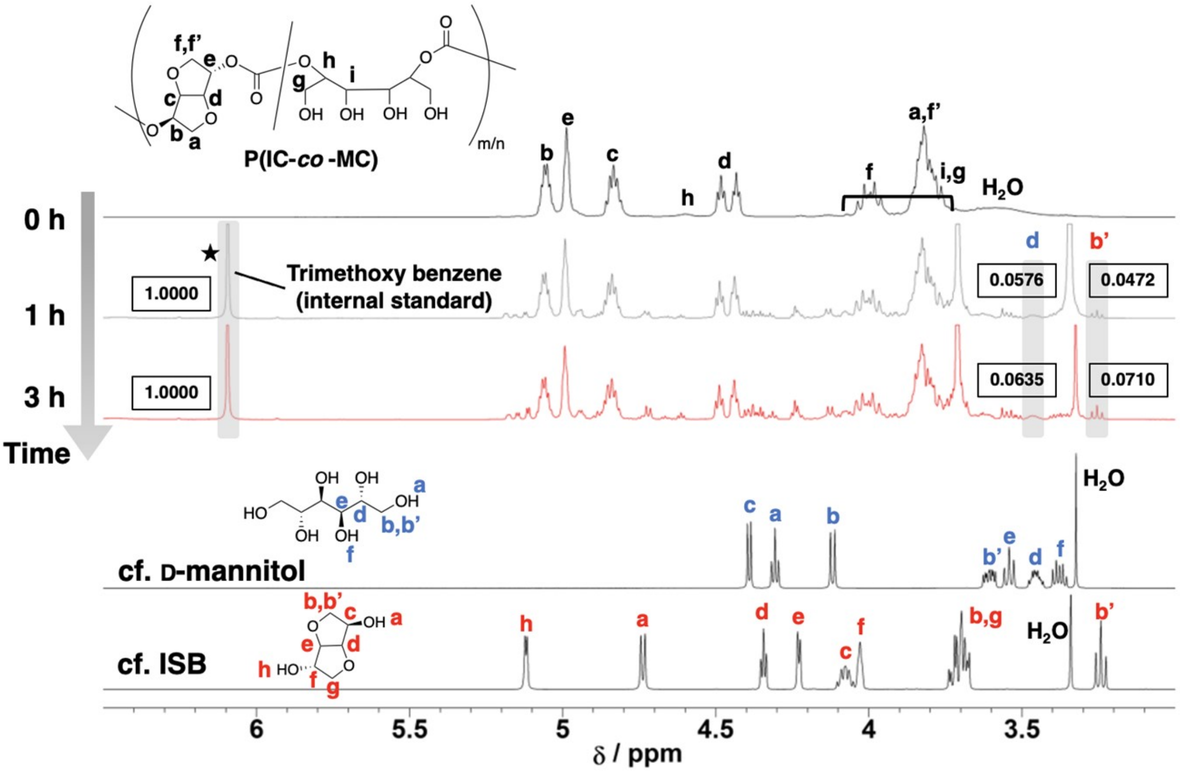


Figure S27. ^{1}H NMR spectrum of the degradation products of **P(IC-*co*-MC)** with trimethoxybenzene as an internal standard during the ammonolysis (500 MHz, 25 °C, DMSO-d_6). The boxed numbers in the spectrum are the integration ratio.

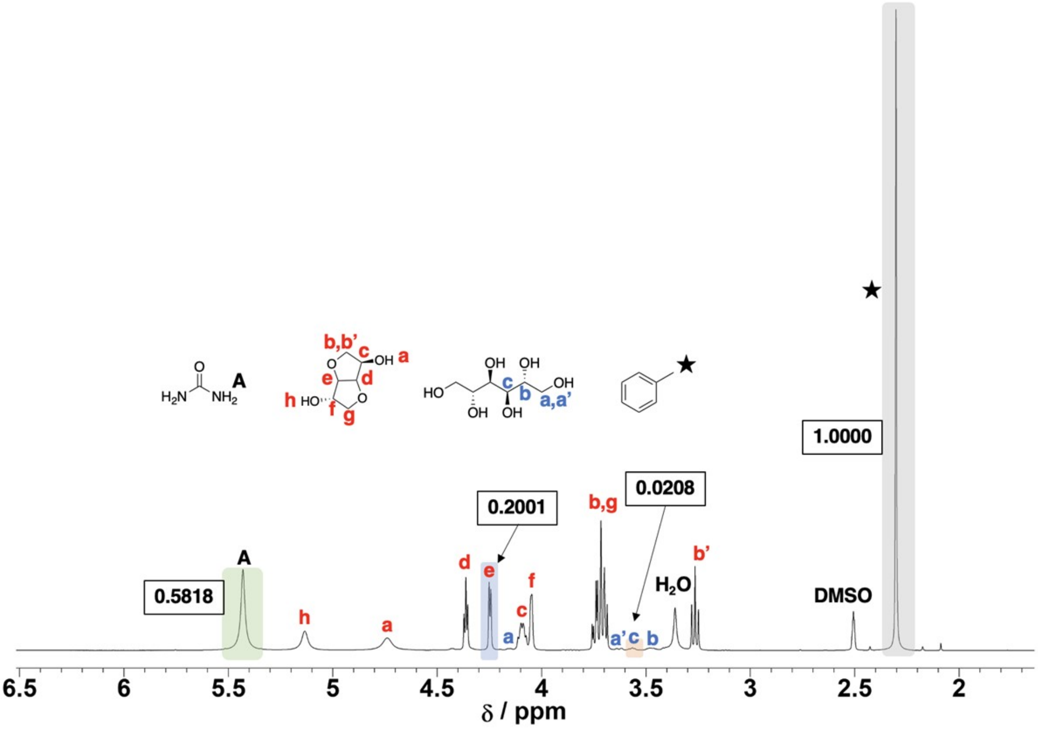


Figure S28. ^{1}H NMR spectrum of the degradation products of **P(IC-*co*-MC)** after 9 h at 90 °C with toluene as an internal standard (500 MHz, 25 °C, DMSO-d_6). The boxed numbers in the spectrum are the integration ratio.

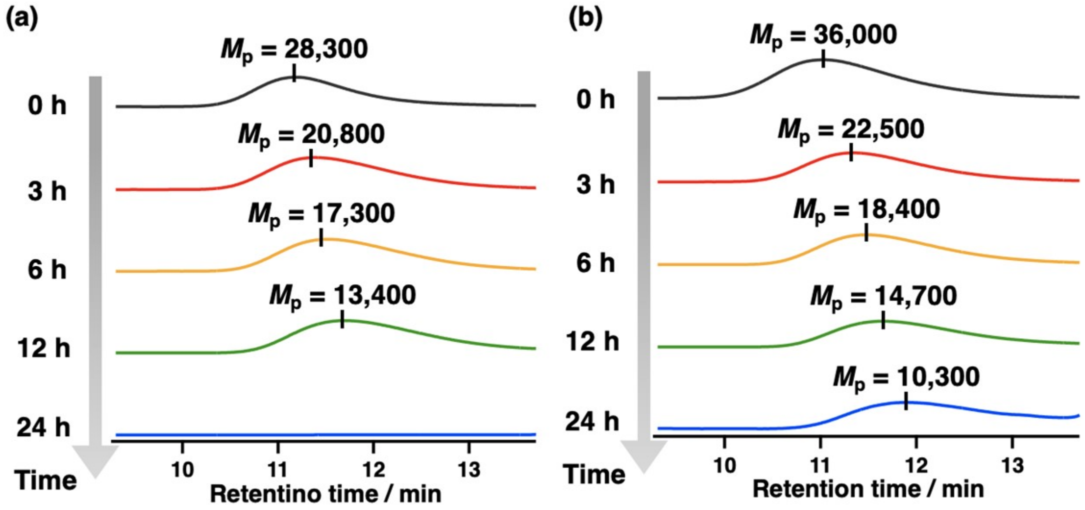


Figure S29. (a) GPC profiles of the degradation products of PIC and (b) **P(IC-*co*-DBMC)** during the ammonolysis (eluent: DMF; detector: RI; polystyrene standard).

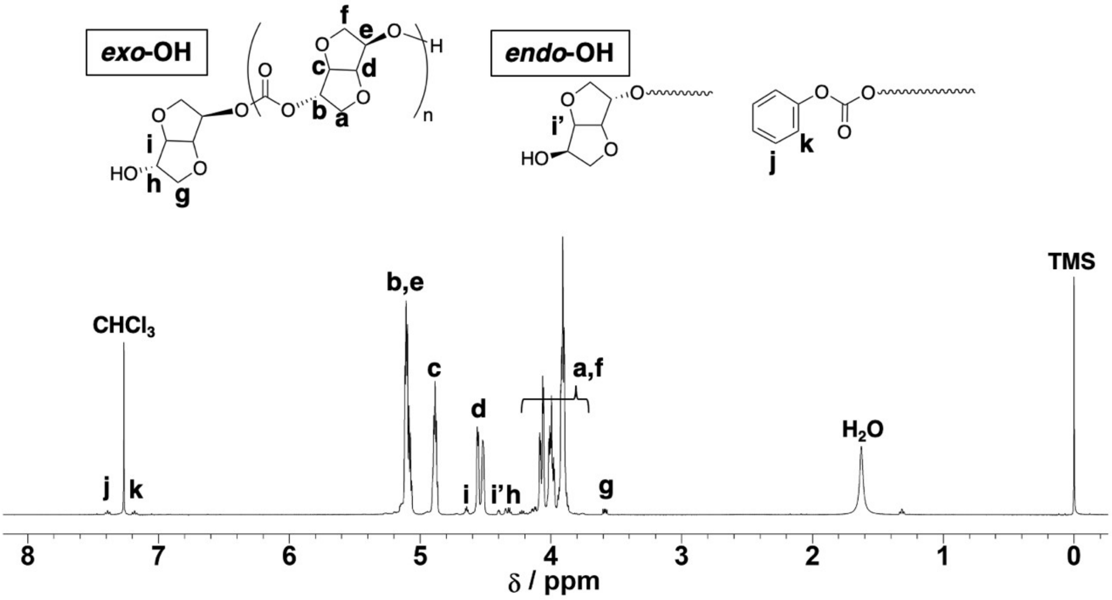


Figure S30. ^{1}H NMR spectrum of PIC (500 MHz, 25 °C, DMSO-d_6).

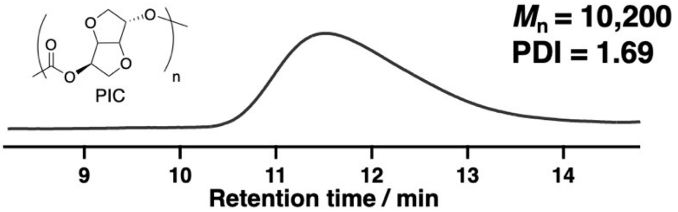


Figure S31. GPC profile of PIC (eluent: DMF; detector: RI; polystyrene standard).

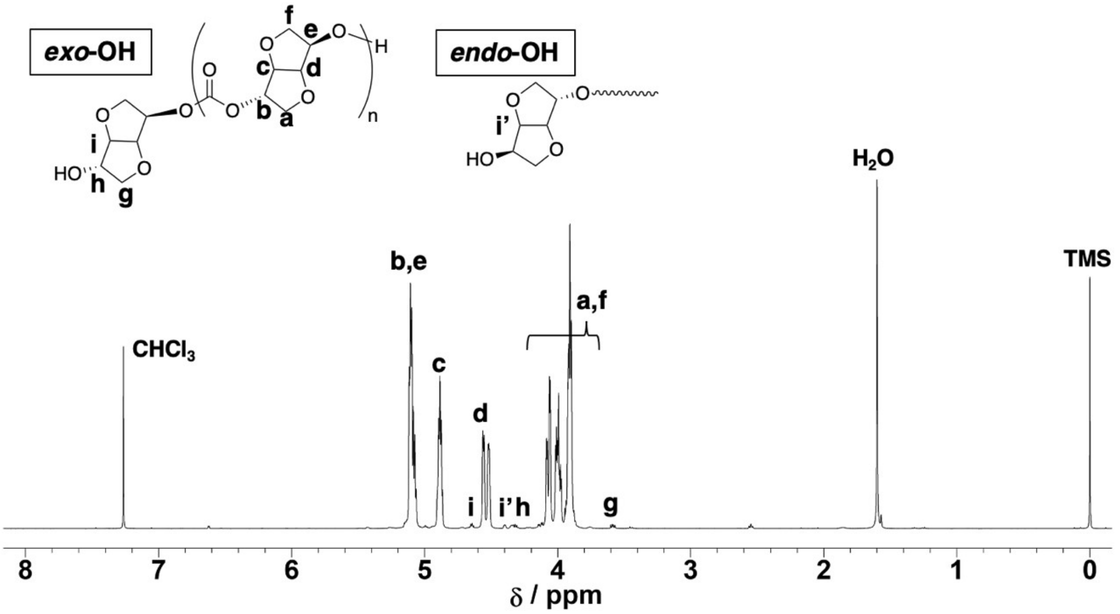


Figure S32. ^{1}H NMR spectrum of PIC (500 MHz, 25 °C, DMSO-d_6).

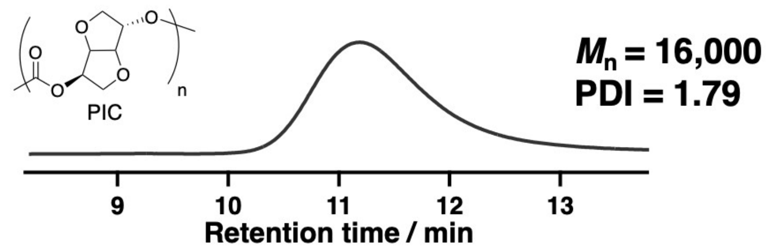


Figure S33. GPC profile of PIC (eluent: DMF; detector: RI; polystyrene standard).