Synthesis of Cellulose Acetate-*graft*-Poly(propylene carbonate) from CO_2-based Polycarbonate and Cellulose Acetate

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Abstract: Poly(propylene carbonate) (PPC), which can be prepared by the alternating copolymerization of propylene oxide (PO) with carbon dioxide (CO_2), has attracted considerable attention due to its biodegradability, biocompatibility, oxygen-barrier property, and ion-conductivity. However, there are some inherent disadvantages, such as its low thermal stability and limited mechanical strength. Therefore, combination of PPC with other polymers has been investigated to improve its properties and develop PPC-based polymer materials. In light of this background, we designed the graft copolymer, cellulose acetate-*graft*-PPC with a cellulose acetate (CA) main chain and PPC side chains. CA is a high-performance thermoplastic with excellent mechanical strength as well as biodegradability. Therefore, CA-*graft*-PPC would be endowed with complementary properties derived from both components. The designed graft copolymer was synthesized via a grafting-to approach. First, the PPC with a terminal alkynyl group (PPC–C≡CH) was synthesized by the immortal PO/CO_2 alternating copolymerization using 4-ethynylbenzoic acid as a chain transfer agent (CTA). PPC–C≡CH with number-average molecular weight (M_n) of 3,900–36,600 was successfully obtained by changing the monomer and CTA feed ratios. Then, the resulting PPC–C≡CH was grafted onto CA through copper-catalyzed azide–alkyne cycloaddition (CuAAC). The reaction of PPC–C≡CH (M_n = 5,600, 7,000, 15,600, or 36,600) with azide-functionalized CA (the degree of substitution of CA by azide groups = 0.156 or 0.248) successfully proceeded with CuBr/Cu as catalysts, affording the desired CA-*graft*-PPC with the degree of substitution of CA by PPC of 0.149–0.235. The resulting graft copolymers exhibit higher thermal decomposition temperature compared with PPC.

Keywords: carbon dioxide; cellulose acetate; click reaction; graft copolymer; poly(propylene carbonate)

1. Introduction

The alternating copolymerization of epoxides with carbon dioxide (CO_2) has gained a continuous interest since the first report in 1969[1)] because it can utilize abundant, renewable, and non-toxic CO_2 as a raw material[2,3)]. Extensive efforts have been devoted to the development of catalyst systems with enhanced activity[4-6)] as well as improved selectivity toward either polycarbonates or cyclic carbonates[7-9)]. Recent reviews have also highlighted emerging trends in epoxide/CO_2 copolymerization, including bimetallic catalytic systems and boron-based organocatalysts[10-12)]. These advances have expanded the monomer scope of the copolymerization[13,14)] and diversified the structures and functionalities of the resulting polycarbonates[15-17)].

A wide range of epoxides have been employed in the copolymerization, affording the corresponding aliphatic polycarbonates. Poly(propylene carbonate) (PPC) is a prototypical aliphatic polycarbonate obtained by using propylene oxide[18,19)]. PPC shows attractive properties, such as biodegradability[20,21)], biocompatibility[22,23)], oxygen-barrier property[24)], and ion-conductivity[25-27)]. Owing to these properties, PPC finds its potential applications in adhesives, packaging, polymer electrolyte, and biomedical field. However, PPC has some inherent disadvantages, including relatively low thermostability and poor mechanical property. Therefore, considerable efforts have been made to enhance its properties and broaden its applications.

Combination of PPC with other polymers seems to be a promising avenue to modify and enrich PPC's properties.

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Polymer blending has been frequently employed to achieve physical modification of PPC[28,29]. A variety of polymer blends have been investigated by using starch[30], starch derivatives[31-34], cellulose[35-37], poly(butylene succinate)[38-40], poly(lactic acid)[41-44], thermoplastic polyurethane[45,46], poly(methyl methacrylate) (PMMA)[47-49], and so on[50-52]. The effects of additives, such as succinic anhydride[53,54], polymeric materials[55-57], plant oil-derived compounds[58-60], and corn stover[61], on the miscibility and mechanical properties of these polymer blends have also been widely investigated. Furthermore, the use of additives to introduce specific functionalities into polymer blends has also been studied[62,63]. Block and graft copolymer approaches have also been studied to improve the properties of CO_2-derived aliphatic polycarbonates[64,65]. For instance, several research groups, including ours, reported the synthesis of PPC-based block copolymers containing poly(cyclohexene carbonate)[66], PMMA[67,68], polystyrene[67-69], poly(vinyl acetate)[70], polyester[71-73], poly(amino acid)[74], and polycycloalkene[75,76] blocks. Graft copolymers with PPC chains have been also investigated. Honda and Sugimoto reported the synthesis of the brush polymer with PPC side chains through the PO/CO_2 copolymerization using poly(acrylic acid) as a macroinitiator[77]. Graft copolymers with a PPC main chains have also been synthesized by controlled radical polymerization of styrene and methacrylate monomers[78-80].

Cellulose is the most abundant polysaccharide on earth. Owing to attractive properties including biocompatibility, biodegradability, high strength, and high thermal stability, cellulose and its derivatives have been applied in various fields[81]. Despite these advantages, cellulose also has certain limitations such as poor solubility (in both organic and aqueous solvents), poor crease resistance, low dimensional stability, and lack of thermoplasticity. Therefore, chemical modification of cellulose has been developed to extend its range of industrial applications[82,83]. Among the previously reported strategies, the polymer grafting has been considered as one of the most effective approaches to modify the chemical and physical properties of cellulose and to increase its functionality[84,85]. For instance, "grafting-from[86,87] and "grafting-on[88] methods have been applied to synthesize cellulose-based graft copolymers with vinyl polymer, polyester, and polyether side chains.

In this context, we report herein the preparation of the graft copolymer consisting of a cellulose acetate (CA) main chain and PPC side chains. We anticipated that the graft copolymer exhibits complementary advantages derived from both PPC and CA. The PPC with an alkynyl terminal group (PPC–C≡CH) were designed to graft the PPC chain onto CA by copper-catalyzed azide–alkyne cycloaddition (CuAAC), one of the most widely used click reactions[89-92]. PPC–C≡CH was successfully prepared by immortal copolymerization of PO with CO_2 in the presence of 4-ethynylbenzoic acid as a chain transfer agent. The CuAAC between PPC–C≡CH and azide-functionalized CA (CA–N_3) was found to afford the target graft copolymer. The resulting graft copolymer shows higher thermal properties compared to PPC.

2. Materials and Methods

2.1. Materials

All chemicals and solvents used for preparing cobalt complexes and polymers were purchased from commercial suppliers, such as Kanto Chemical Co., Inc., Tokyo Chemical Industry Co., Ltd., and Sigma-Aldrich Co. LLC and used without further purification unless otherwise specified. Carbon dioxide (>99.990%) was purchased from Showa Denko Gas Products Co., LTD. Propylene oxide was dried over CaH_2 and distilled under argon. Cobalt complex 1 and 4-ethynylbenzoic acid were prepared according to the literature[93-95].

NMR spectra were recorded in $CDCl_3$ on a JEOL–ECX400 spectrometer. Chemical shifts are reported in ppm relative to the internal standard signal (0 ppm for Me_4Si in $CDCl_3$). Size-exclusion-chromatography (SEC) analyses for estimating molecular weight were carried with two columns (Shodex K-804L) using chloroform as an eluent at 40 °C at 1 mL/min. The molecular weight was calibrated against standard polystyrene samples. Matrix-assisted laser desorption/ionization time-of-flight (MALDI–TOF) mass spectra are taken with Bruker Daltonics Autoflex Speed mass spectrometer. Samples were prepared by mixing the copolymer (5 mg/mL in THF), a matrix (2-[(2E)-3-(4-tert-butylphenyl)-2-methylpropenylidene]malononitrile (DCTB), 10 mg/mL in THF), and a cationizing agent (sodium trifluoroacetate, 0.10 M) in the weight ratio of 5/5/1[96]. Thermogravimetric analysis (TGA) was performed on a Rigaku Thermo plus EVO2 apparatus. Differential scanning calorimetry (DSC) measurements were performed on a SII DSC−6000 apparatus. Heating rate in the second heating run was 10 °C per minute.

2.2. Methods

2.2.1. Preparation of [Ph_3P=N=PPh_3]Z (Z = 4-ethynylbenzoate)

The titled compound was synthesized following the method described in the literature[93]. A 100-mL round-bottomed flask was charged with NaOH (0.15 g, 3.8 mmol), 4-ethynylbenzoic acid (0.46 g, 3.1 mmol) and distilled H_2O (13 mL). The mixture was stirred until all solid materials were dissolved. After adding [Ph_3P=N=PPh_3]Cl (0.30 g, 0.53 mmol) and CH_2Cl_2 (30 mL), the resulting mixture was stirred for 15 min. The organic layer was separated, and then NaOH (0.15 g, 3.7 mmol) and 4-ethynylbenzoic acid (0.46 g, 3.1 mmol) were added to the

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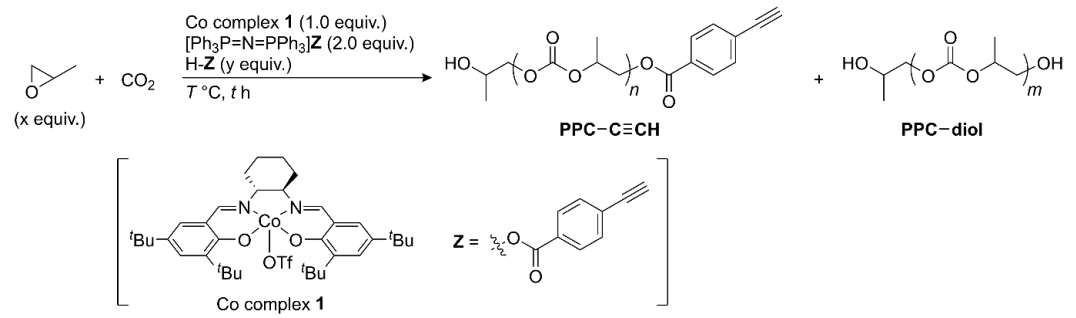

Fig. 1: Synthesis of the alkynyl-terminated PPC

Table 1: Copolymerization conditions and results for the synthesis of alkynyl-terminated PPC[a]

entry	x (equiv.)	y (equiv.)	CO_2 (MPa)	*T* (°C)	*t* (h)	yield (%)	M_n	M_w/M_n
1	2,000	10	1.5	25	5	71	7,900	1.16
2	2,000	15	1.5	25	5	56	6,900	1.13
3	2,000	20	1.5	25	5	63	5,700	1.12
4	2,000	40	1.5	25	24	55	3,900	1.13
5	4,000	20	2.9	30	24	93	15,600	1.13
6	16,000	20	2.5	30	24	47	36,600	1.22

[a]*Each entry represents the result of a single experiment.*

organic layer. The resulting mixture was stirred for 15 min and concentrated under reduced pressure. The resulting oily material was dissolved in CH_2Cl_2, and the solution was poured into diethyl ether under argon at −20 °C. The resulting precipitation was collected by filtration and dried under reduced pressure to afforded $[Ph_3P=N=PPh_3]Z$ as a colorless solid (0.32 g, 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.2, 2H), 7.68–7.63 (m, 6H), 7.49–7.40 (m, 24H), 7.36 (d, J = 8.2 Hz, 2H).

2.2.2. Representative procedure for the PO/CO_2 alternating copolymerization (Table 1, entry 2)

A 50-mL autoclave was charged with propylene oxide (2.0 mL, 29 mmol), cobalt complex **1** (11 mg, 14 μmol), $[Ph_3P=N=PPh_3]Z$ (21 mg, 30 μmol), and 4-ethynylbenzoic acid (32 mg, 0.22 mmol) under argon atmosphere. After CO_2 (1.5 MPa) was introduced, the reaction mixture was stirred at 25 °C for 5 h. The CO_2 pressure was released, and then the polymerization mixture was diluted with $CHCl_3$. The reaction was quenched with MeOH/aqueous HCl. To the resulting mixture was added phenanthrene as an internal standard. After dissolving phenanthrene with stirring, a small aliquot of the resulting mixture was picked up, concentrated under reduced pressure, and analyzed by ^{1}H NMR spectroscopy to determine the NMR yield of the copolymer [comparison of signal area ratio of –C*H*(CH_3)CH_2– of **PPC–C≡CH** and Ar-H of phenanthrene]. The remaining solution was concentrated under reduced pressure. The crude residue was dissolved in $CHCl_3$, and the resulting solution was poured into MeOH to precipitate the copolymer. The resulting precipitate was collected and dried under reduced pressure to give PPC–C≡CH (1.5 g, 56% yield). The resulting PPC–C≡CH was analyzed by SEC and MALDI–TOF MS. The amount of the terminal alkynyl group per unit weight of the obtained PPC–C≡CH was estimated by ^{1}H NMR spectrum of PPC–C≡CH with phenanthrene as an internal standard.

2.2.3. Preparation of azide-functionalized CA (CA–N_3)

CA–N_3 was prepared according to the literature[97]. CA with a molecular weight of approximately 40,000 and DC_{acetyl} of 2.44, which was purchased from FUJIFILM Wako Pure Chemical Corporation, was used. The degree of substitution of CA by azide groups (DS_{azide}) was estimated based on ^{1}H NMR data of the resulting CA–N_3 according the literature[97].

2.2.4. Representative procedure for grafting of CA–N_3 with PPC–CCH (CA-*graft*-PPC)

A 200-mL three-necked flask was charged with CA–N_3 (0.50 g, corresponding to 1.8 mmol of glycosidic rings and 0.28 mmol of azide groups), PPC–C≡CH (3.2 g, 0.34 mmol of a terminal alkyne group), and DMSO (30 mL) under argon atmosphere. The resulting mixture was degassed by three freeze-pump-thaw cycles. To the mixture was added CuBr (45 mg, 0.31 mmol) and copper powder (12 mg, 0.19 mmol) under argon atmosphere, and the resulting mixture was stirred for 24 h at room temperature. The reaction mixture was poured into ethanol containing PMDETA (0.58 mL, 2.8 mmol) to give the crude residue. The resulting crude residue was dissolved in $CHCl_3$, and the resulting solution was poured into EtOH. This reprecipitation procedure was performed one more to give CA-*graft*-PPC-1. Then, the obtained CA-*graft*-PPC-1 was dissolved in $CHCl_3$, and the resulting solution was poured into toluene. This reprecipitation procedure was conducted two more times. The resulting precipitate was

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collected and dried under reduced pressure to give CA-*graft*-PPC-2 (1.6 g). The obtained CA-*graft*-PPC-2 was analyzed by ^{1}H NMR spectroscopy, SEC, DSC, and TGA. The degree of substitution of CA by the PPC grafts (DS_{PPC}) was calculated from equation (1),

$$DS_{PPC} = \frac{I_i / 2}{I_a / 3} \times 2.44 \qquad (1)$$

where I_i was the area of the signal corresponding to Hi (the benzoate unit from PPC) and I_a was the area of the signal corresponding to Ha (the acetyl group on CA) (Figure 4b).

3. Results and Discussion

3.1. Preparation of PPC with an alkynyl terminal group

In order to prepare the PPC with alkynyl terminal group (**PPC–C≡CH**), the copolymerization of propylene oxide (PO) with CO_2 (1.5 MPa) was carried out with cobalt complex **1**[98] in the presence of $[Ph_3P{=}N{=}PPh_3]Z$ (Z = 4-ethynylbenzoate) as a co-catalyst (2.0 equivalents to **1**) and 4-ethynylbenzoic acid as a chain transfer agent (CTA) (Figure 1).

The triflate anion on the cobalt center of **1** is not expected to initiate the copolymerization owing to its low nucleophilicity. Therefore, we anticipated that the 4-ethynylbenzoate anion from the co-catalyst and CTA initiate the copolymerization to afford the desired **PPC–C≡CH** selectively. The PO/CO_2 copolymerization results are summarized in Table 1. When using 2,000 equivalents of PO and 10 equivalents of 4-ethynylbenzoic acid to **1** (25 °C, 5 h), the PPC was obtained in 71% yield (entry 1). Increase in the amount of 4-ethynylbenzoic acid gave the PPC with lower molecular weight while maintaining narrow molecular-weight distribution (entries 2–4). These results strongly suggest that immortal polymerization proceeded efficiently[99-101]. A higher PO feed ratio gave PPC with a higher molecular weight (entries 5 and 6).

The ^{1}H NMR spectrum of the PPC samples recovered from the polymerization solution by reprecipitation shows that the resulting PPC does not contain the ether linkage. Therefore, the copolymerization proceeded in an almost completely alternating manner. In addition, characteristic signals corresponding to the aromatic protons of the 4-ethynylbonzoate terminal group (8.0 and 7.5 ppm) are observed in the ^{1}H NMR spectrum of the purified PPC (Figure 2a; signal a (3.26 ppm for the terminal ethynyl proton, signals b (7.56 ppm) and c (8.0 ppm) for the aromatic protons of the terminal 4-ethynylbenzoate group, signal d (4.3–4.1 ppm) for the methylene protons of PPC, signal e (5.1 ppm) for the methine proton of PPC, and signal f (1.34 ppm) for the methyl protons of PPC). In the MALDI–TOF mass spectrum of the resulting PPC, a series of signals with a regular interval of 102.0 (repeating unit) were observed (Figure 2b). The m/z value of each signal corresponds with [145.0 (4-ethynylbenzoate, initiating group) + 102.0n (repeating unit) + 59.1 ($CH_2CHMeOH$, terminal group) + 23.0 (Na^+ ion)]. These NMR and mass data clearly indicate the formation of the desired PPC–C≡CH. The SEC trace of the obtained PPC was found to be bimodal. The lower- and higher-molecular-weight portions correspond to PPC–C≡CH and PPC–diol (PPC with hydroxy groups at both chain ends), respectively. PPC–diol[99] is known to form via the chain transfer to water contaminants followed by subsequent copolymerization. Because PPC–diol does not possess an alkynyl terminal group, it cannot undergo the CuAAC and is not expected to interfere with it. Therefore, we used the mixture of PPC–C≡CH and PPC–diol without further purification in the next grafting step.

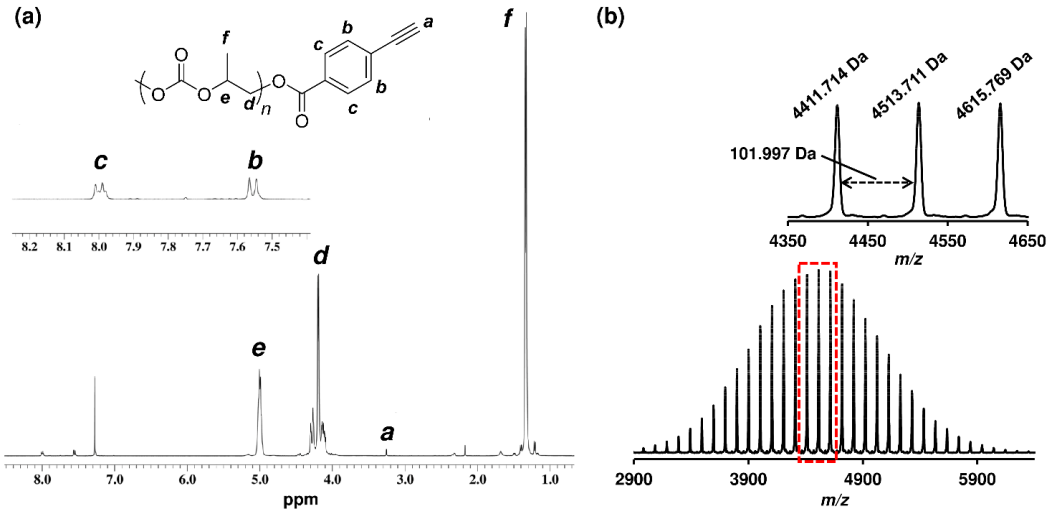

Fig. 2: (a) ^{1}H NMR (in $CDCl_3$) and (b) MALDI–TOF MS spectra of PPC–C≡CH (Table 1, entry 2)

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3.2. Grafting of PPC onto CA

With **PPC–C≡CH** in hand, we investigated the grafting of PPC onto CA (Figure 3 and Table 2). First, we conducted CuAAC between the azide-functionalized CA (**CA–N_3**) with DS_{azide} of 0.156 and PPC with M_n of 7,000 (a mixture of **PPC–C≡CH** and **PPC–diol**) in the presence of CuBr and Cu as catalysts (Table 2, entry 1). The amount of the alkynyl group was set to 1.2 equivalents relative to the azide groups. The reaction product was preliminarily purified by reprecipitation using ethanol as a poor solvent. The SEC analysis of the resulting precipitate (**CA-*graft*-PPC-1**) revealed that **CA-*graft*-PPC-1** contained higher-molecular-weight components compared to the parent **CA–N_3** and **PPC–C≡CH** as well as unreacted PPC, indicating successful grafting (Figure 4a). Therefore, **CA-*graft*-PPC-1** was further purified by reprecipitation with toluene as a poor solvent. The SEC trace of the resulting precipitate (**CA-*graft*-PPC-2**) demonstrated the complete removal of the parent PPC. The ^{1}H NMR spectrum of **CA-*graft*-PPC-2** showed the typical signals assigned to PPC and CA, especially those at 5.0 ppm from the methine proton of PPC and those around 2.0 ppm from acetyl group of CA (Figure 4b; signal a (2.1–1.9 ppm) for the acetyl protons of the CA segment, broad signals b (2.4–2.3 ppm), c, d, e (1.7–1.5 ppm), and f (3.3 ppm) for the methylene protons between the triazine and carbonyl group, signal g (7.92 ppm) for the aromatic proton of the triazine group, signals h (7.9 ppm) and I (8.09 ppm) for aromatic protons of the benzoate group, signal j (4.3–4.1 ppm) for the methylene protons of PPC, signal k (5.1 ppm) for the methine proton to PPC, signal l (1.34 ppm) for the methyl protons of PPC, and broad signals 1–6 (5.2–3.4 ppm) for the protons on the sugar moieties). In addition, the covalent linkage of PPC onto CA was confirmed by the appearance of the triazole signals at 7.9 ppm and the lower-field shift of phenylene protons of the benzoate unit. These results clearly indicate the formation of the desired graft copolymer. The DS_{PPC} was estimated to be 0.154 from the ^{1}H NMR data. Therefore, the CuAAC enabled an almost quantitative grafting rate (≥99%). The CuAAC-mediated grafting by using **PPC–C≡CH** with lower and higher molecular weight (M_n = 5,600, 15,600 or 36,600) and **CA–N_3** with higher DS_{azide} (0.248) also proceeded efficiently to yield the corresponding CA-*graft*-PPC (Table 2, entries 2–5). Within the scope of our experiments, the grafting rate, that is the efficiency of the CuAAC tends to be almost independent on the PPC molecular weight and DS_{azide} of CA.

3.3. Thermal degradation properties of CA-*graft*-PPC

Thermal degradation property of the resulting graft copolymers was evaluated by TGA. The weight loss observed around 100 °C is considered to be due to residual water that could not be completely removed. Each CA-*graft*-PPC showed two-stage thermal decomposition (Figure 5). The first-stage decomposition started at ≈250 °C, which would be attributed to thermal degradation of the PPC side chain. It should be noted that the first-stage decomposition temperatures are slightly higher (15–20 °C) than that of the parent PPC. In the literature, intermolecular hydrogen-bonding is indicated to form between the

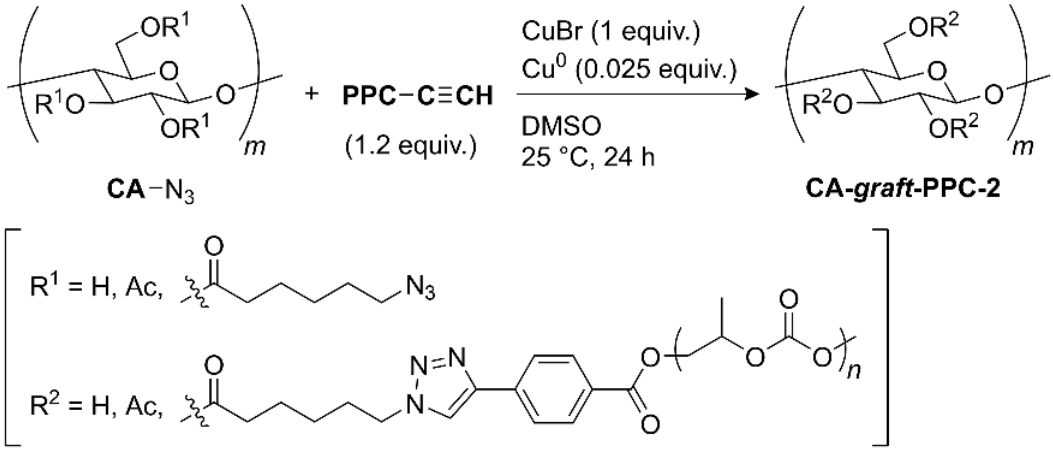

Fig. 3: Synthesis of CA-*graft*-PPC-2 via CuAAC

Table 2: Results of CuAAC between CA–N_3 and PPC–C≡CH[a]

entry	DS_{azide}	M_n (PPC)	DS_{PPC}	grafting rate (%)
1	0.156	7,000	0.154	≥99
2	0.156	15,600	0.155	>99
3	0.248	15,600	0.235	99
4	0.156	5,600	0.152	97
5	0.156	36,600	0.149	96

[a]*Each entry represents the result of a single experiment.*

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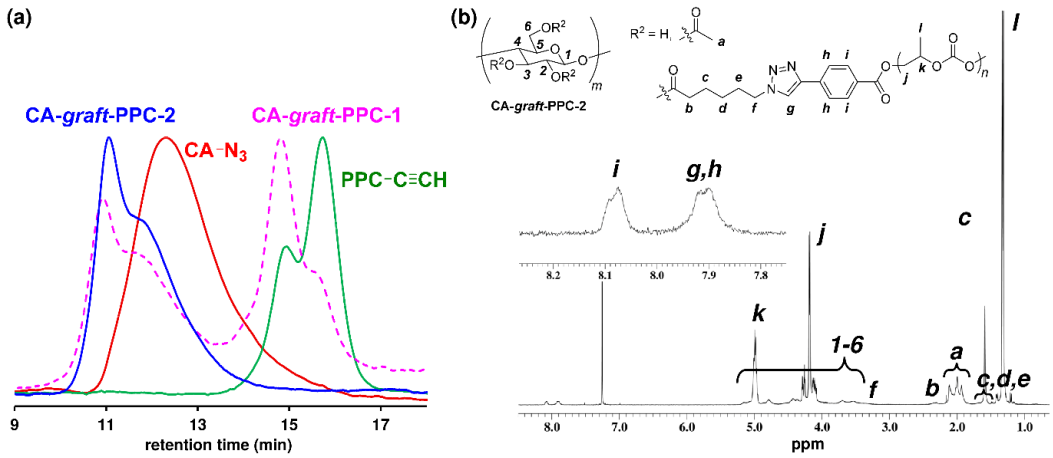
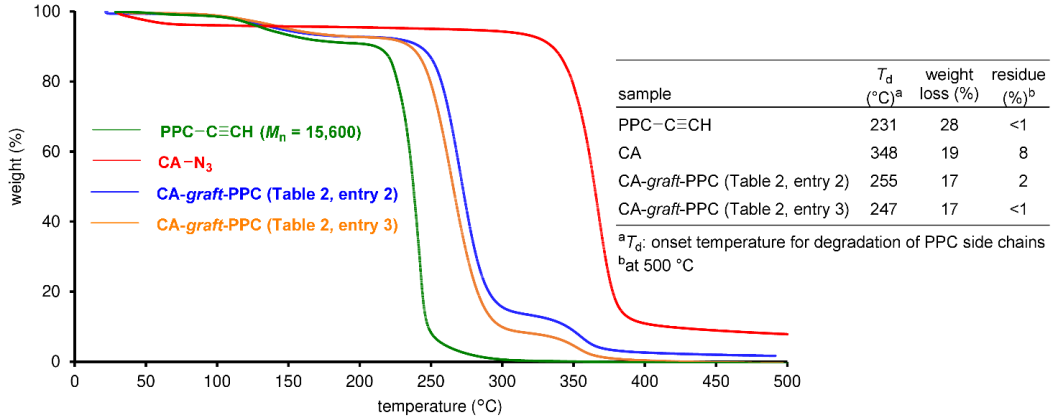


Fig. 4: (a) SEC traces [two columns (Shodex K-804L) using chloroform as an eluent at 40 °C at 1 mL/min. The molecular weight was calibrated against standard polystyrene samples.] and (b) ^{1}H NMR spectrum of CA-*graft*-PPC-2 (Table 2, entry 1)



sample	T_d (°C)[a]	weight loss (%)	residue (%)[b]
PPC−C≡CH	231	28	<1
CA	348	19	8
CA-*graft*-PPC (Table 2, entry 2)	255	17	2
CA-*graft*-PPC (Table 2, entry 3)	247	17	<1

[a] T_d: onset temperature for degradation of PPC side chains
[b] at 500 °C

Fig. 5: TGA analysis of CA-*graft*-PPC

hydroxy end groups of PPC and the carbonyl groups of CA in the PPC/CA blend based on FT-IR analysis[102]. In addition, such hydrogen bonding suppresses the back-biting degradation process of PPC, resulting in higher thermal degradation temperature of PPC. Therefore, the higher decomposition temperature observed in this study is possibly attributed to the hydrogen bonding between the terminal hydroxy groups of PPC and the carbonyl groups of CA, while FT-IR analysis was not conducted. In addition, we consider that not only the acetyl groups but also the ester groups (adjacent to methylene proton b) and the nitrogen atoms of the triazole rings may act as hydrogen-bond acceptors. CA-*graft*-PPC with less PPC graft chains demonstrated slightly higher decomposition temperature (T_d = 255 °C) than that with more PPC graft chains (T_d = 247 °C). The second-stage decomposition started at ≈340 °C, which should be derived from the thermal decomposition of the CA main chain. The glass transition temperature (T_g) of the resulting graft copolymers was found to be 20 °C (Table 2, entry 2) and 17 °C (Table 2, entry 3), as determined by DSC (Figure S5). The T_g of CA has been reported to be 160–180 °C), which is much higher than that of that of PPC (25–45 °C)[19]. Although our DSC measurement did not detect the glass transition behavior of the CA segment in the graft copolymers as well as the parent CA, the CA segment has less effect on the grass transition behavior of the PPC side chains.

3.4. Mechanical properties of CA-*graft*-PPC

Most of the graft copolymers prepared in this study were too brittle to prepare self-standing specimens. On the other hand, specimens suitable for tensile test could be prepared for the graft copolymer incorporating low-molecular-weight PPC (Table 2, entry 4). Preliminary tensile test results revealed a significant improvement in tensile strength (48 MPa) compared with PPC (Figure S6). In contrast, the elongation at break (9%) and tensile strength were lower than those of CA.

4. Conclusion

PPC with an alkynyl terminal group was successfully synthesized through immortal PO/CO_2 copolymerization with the cobalt complex as a catalyst and 4-ethynylbenzoic acid as a CTA. The obtained PPC was found to be grafted onto azide-functionalized CA by using CuAAC. The CA-

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graft-PPC showed higher thermal decomposition temperature than the parent PPC. As described in the Introduction, several PPC-containing graft copolymers have previously been reported, including poly(acrylic acid)-*graft*-PPC[77], PPC-*graft*-polystyrene[78], poly(cyclohexene carbonate)-*graft*-PPC[79], and PPC-*graft*-poly(PEOMA)[80]. Compared with these previously reported graft copolymers, the graft copolymer developed in this study is characterized by its synthesis via a grafting-onto approach using CuAAC chemistry. In addition, the combination with CA, a representative biomass-derived material, is another notable feature of this work. This strategy would be expected to be applicable not only to cellulose acetate but also to various other polysaccharides, enabling the development of a wide variety of PPC-based graft copolymers.

Author Contributions

Conceptualization, K.N.; validation, K.S., A.I., and K.N.; formal analysis, K.S., A.I., and K.N.; investigation, K.S., A.I., and K.N.; data curation, K.S., A.I., and K.N.; writing—original draft preparation, K.S. A.I.; writing—review and editing, K.N.; supervision, K.N.; project administration, K.N.; funding acquisition, K.N. All authors have read and agreed to the published version of the manuscript.

Conflict of Interests

The authors declare no conflicts of interest.

Data availability

All data supporting the findings of this study are available within the paper and its Supplementary Information.

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