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Synthesis and Properties of Biomass-Based Polymethacrylate Comprising Chitin-Derived 2-Acetamide-2-Deoxyisosorbide as a Repeating Unit

Yasuhito Koyama,[1,] Takuya Sagawa,[2] Kazufumi Kohno,[3] Kento Sato,[4] Hirokazu Kobayashi,[4,5] and Atsushi Fukuoka[3]*

[1]*Department of Pharmaceutical Engineering, Toyama Prefectural University, 5180 Kurokawa, Imizu, Toyama 939-0398, Japan*

[2]*Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science, 6-3-1 Niijuku, Katsushika-ku, Tokyo 125-8585, Japan*

[3]*Institute for Catalysis, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan*

[4]*Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-Ku, Tokyo 153-8902, Japan*

[5]*Komaba Institute for Science, Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-Ku, Tokyo 153-8902, Japan*

*E-mail: ykoyama@pu-toyama.ac.jp

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Abstract

Synthesis and applications of biobased polymers have been extensively studied in order to reduce the use of petroleum-based polymers and likewise environmental load. Several biobased polymers have been produced on the commercial large scale to date. However, the lineup of biobased high performance polymers with transparency and high glass transition temperature is inadequate and their development is a critical issue. In this paper, we design a new biobased polymethacrylate comprising rigid *cis*-fused bicyclic 2-acetamide-2-deoxyisosorbide (ADI) as a repeating unit. We have recently invented catalytic transformation systems from chitin as a marine biomass to ADI as a new nitrogen-containing platform chemical. The ADI-based polymethacrylate is synthesized via free radical polymerization of the methacrylic acid ester of ADI initiated by $(NH_4)_2S_2O_8$ and TMEDA in DMSO-H_2O mixed solvent. The molecular weight and its dispersity are estimated by a size exclusion chromatography on the basis of polymethylmethacrylate standards. The UV-vis spectroscopy demonstrates the high transparency of the polymer at visible wavelength region. The DSC analysis of the polymer clarifies the remarkably high glass transition temperature, compared with that of polymethylmethacrylate. The thermal decomposition temperature of the polymer is also evaluated by TGA analysis. On the basis of the favorable properties of the ADI-based polymer, the present study proposes one of nitrogen-containing biobased polymers useful for real-world applications.

INTRODUCTION

From the viewpoint of sustainable development goals as the overall aim,[1,2] biomass is gaining attention as a renewable alternative to petroleum-based resources for use as raw materials in chemicals and plastics.[3-9] If we can leverage non-edible biomass that is being discarded around the world, it would be possible to reduce the use of petroleum resources and contribute to a carbon-neutral society. A number of biobased polymers have been developed to date and several polymers such as poly(lactic acid)[10] and poly(butylene adipate-*co*-terephthalate)[11] have been produced on the commercial large scale. However, there still remains challenging to develop a series of transparent biobased polymers with high glass transition temperature (T_g).[12] The very few successful examples have been achieved by the use of isosorbide as a repeating unit of polymer. Isosorbide is a *cis*-fused bicyclic diol, which can be derived from cellulose as a glucose-based polysaccharide.[13] The representative members of isosorbide-based polymers are as follows: poly(ethylene-*co*-isosorbide)terephthalate,[14,15] poly(isosorbide oxalate),[16] poly(isosorbide carbonate),[17] and poly(alkanoyl isosorbide methacrylate).[18-23] The incorporation of rigid isosorbide skeletons into polymer endows the polymer with high T_g. The skeletal characteristics of aliphatic isosorbide tends to suppress the coloration of the polymers during industrial production and processing. On the other hand, glucano-δ-lactone has a *cis*-fused bicyclic framework similar to isosorbide, which has also been exploited as the component of high performance polymers.[24,25]

We are intrigued by the creation of new biobased polymers using chitin as a raw material. Chitin is the second most abundant polysaccharide found in nature.[26] The polymer skeleton comprises *N*-acetylglucosamine units. Although chitin seems to be a fascinating candidate as a resource for nitrogen-containing platform chemicals and plastics, little is known about effective chemical transformations for chitin compared to cellulose.[27,28] Chitin forms strong interchain hydrogen bonds to adopt thermodynamically stable aggregates. Therefore, it is extremely difficult to disentangle chitin from its aggregate into a single strand. Considering

such backgrounds, we have recently invented two catalytic transformation systems in the conversion processes from chitin to 2-acetamide-2-deoxyisosorbide (ADI) via the formation of 2-acetamide-2-deoxysorbitol (ADS) (Figure 1). The first is a mechanochemical system for catalytic chitin hydrolysis.[29-34] This method uses mechanical grinding with a ball mill, where mechanical stress is applied to chitin chains for activating glycosidic bonds.[35-38] A carbon catalyst with weak acid sites such as carboxy groups facilitates to hydrolyze the glycosidic bonds, leading to the scission of chitin chain.[29] The second is the catalytic dehydrative cyclization of ADS to give ADI as a *cis*-fused bicyclic structure analogous to those of isosorbide and glucano-δ-lactone.[39-41] While a further optimization of the reaction conditions is needed on the large scale synthesis of ADI from chitin, these achievements motivate us to perform the researches on the synthesis and characterization of ADI-based polymers. The simple route to prepare the polymer from ADI should be a radical chain polymerization of ADI-containing vinyl monomer (Figure 1c). Esterification of ADI with a (meth)acrylic acid derivative would give the corresponding vinyl monomer. Subsequent free radical polymerization could give the vinyl polymer comprising ADI side groups.

Herein, we describe the synthesis and properties of biomass-based polymethacrylate comprising ADI side groups. The methacrylate consisting of ADI skeleton was synthesized as a new monomer. Free radical polymerizations of the monomer to afford the corresponding polymethacrylate were investigated to evaluate the effects of initiator and solvent on the polymerization. It turned out that the polymethacrylate containing ADI side groups shows high T_g (168 °C) and high transparency at visible wavelength region, which appears to be attributed to rigid aliphatic ADI skeletons. We discuss the effects of amide functionality of the polymer on the properties through the comparison with those of isosorbide-based polymethacrylate. It is also noteworthy that this paper includes an alternative route for synthesizing ADI from a commercially available feedstock to supply the monomer on a gram scale before establishing a practical chitin conversion.

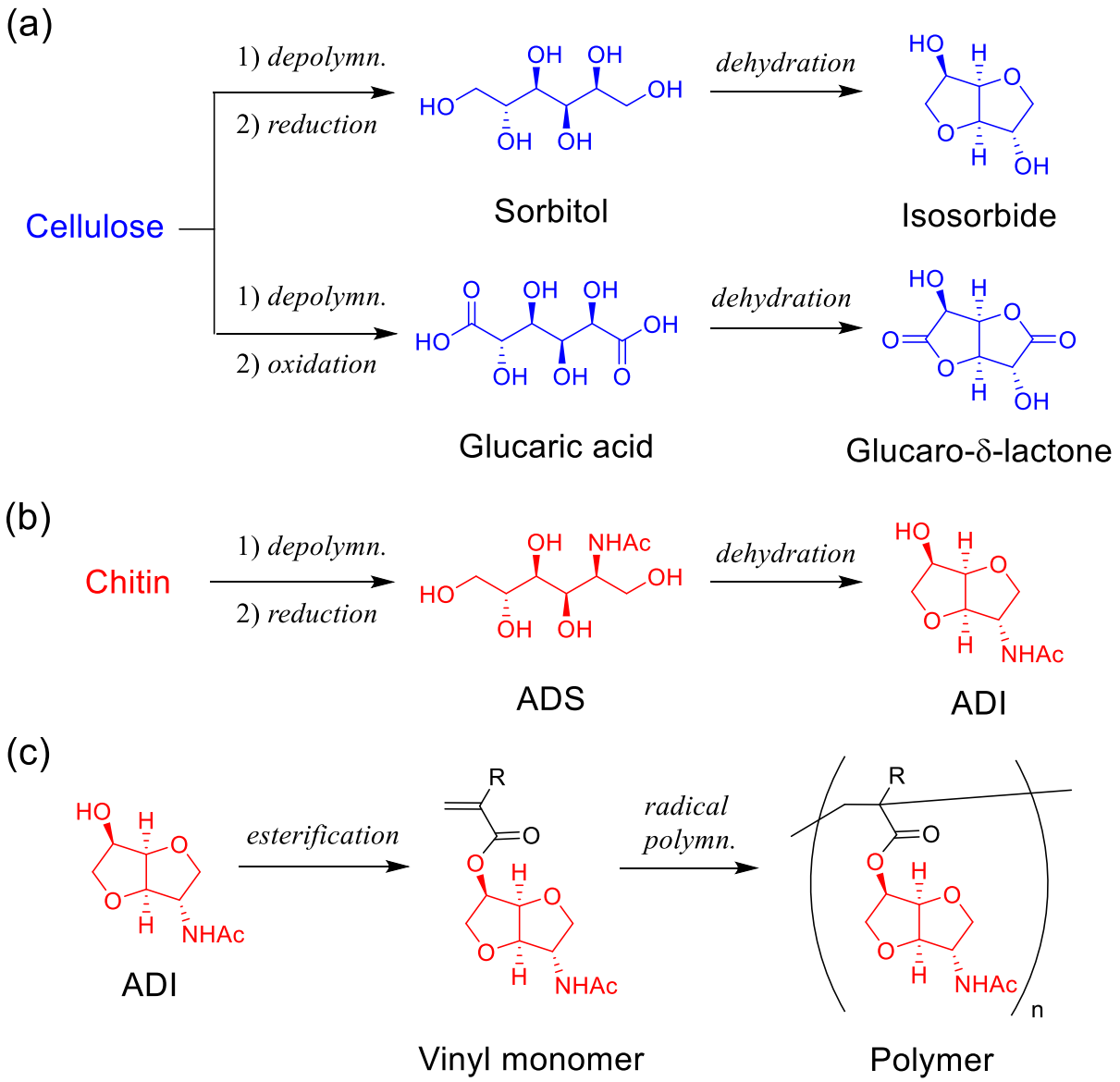


Figure 1. (a) Biorefinery from (a) cellulose and (b) chitin to give the corresponding *cis*-fused bicyclic compounds as platform chemicals and (c) synthetic strategy to produce biobased polymers comprising chitin-derived ADI as a repeating unit.

EXPERIMENTAL

General Methods

Materials: Isomannide (Tokyo Chemical Industry, Co. Ltd., Tokyo, Japan), *p*-toluenesulfonyl chloride (Tokyo Chemical Industry, Co. Ltd., Tokyo, Japan), pyridine (Kanto Chemical Co.

Inc., Tokyo, Japan), sodium azide (Tokyo Chemical Industry, Co. Ltd., Tokyo, Japan), *N*,*N*-dimethylformamide super dehydrated (Fujifilm Wako Pure Chemical Corp., Osaka, Japan), 10% palladium on carbon (Sigma-Aldrich Co. LLC., St. Louis, USA), methanol (Kishida Chem. Co. Ltd., Osaka, Japan), triphenylphosphine (PPh_3, Tokyo Chemical Industry, Co. Ltd., Tokyo, Japan), tetrahydrofuran (THF, Kanto Chemical Co. Inc., Tokyo, Japan), acetic anhydride (Kanto Chemical Co. Inc., Tokyo, Japan), triethylamine (Nacalai Tesque Inc., Kyoto, Japan), dichloromethane (Kanto Chemical Co. Inc., Tokyo, Japan), methacryloyl chloride (Tokyo Chemical Industry, Co. Ltd., Tokyo, Japan), dimethyl sulfoxide super dehydrated (DMSO, Fujifilm Wako Pure Chemical Corp., Osaka, Japan), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Fujifilm Wako Pure Chemical Corp., Osaka, Japan), 2,2'-azobis(isobutyronitrile) (AIBN, Tokyo Chemical Industry, Co. Ltd., Tokyo, Japan), ammonium persulfate (Nacalai Tesque Inc., Kyoto, Japan), and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA, Tokyo Chemical Industry, Co. Ltd., Tokyo, Japan) were used as obtained. The other chemicals and solvents were used without further purification.

Measurements: The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL ECZ400R spectrometer (JEOL Co. Ltd., Tokyo, Japan) using $CDCl_3$, CD_3OD, or DMSO-d_6 as a solvent, and calibrated using residual undeuterated solvent and tetramethylsilane as internal standards. FT-IR spectra via an attenuated total reflection (ATR) method were measured using an IR Spirit spectrometer (Shimadzu Co. Ltd., Kyoto, Japan). MALDI-TOF mass spectra were recorded on a JMS-S3000 SpiralTOF-plus mass spectrometer (JEOL Co. Ltd., Tokyo, Japan) using 2,5-dihydroxybenzoic acid (DHBA) as a matrix. The analyzer was operated in a positive spiral mode. Specific rotation values were measured using a polarimeter MCP 150 (Anton Paar OptoTec GmbH, Ostfildern-Scharnhausen, Germany). Size exclusion chromatography (SEC) analyses were performed using a chromatographic system comprising a Shimadzu LC-20AT pump (Shimadzu Co. Ltd., Kyoto, Japan), a Shimadzu SPD-20A UV

detector, and a Shimadzu RID-20A RI detector with a gel column (Inertsil WP300 Diol, GL Sciences Inc., Tokyo, Japan) using DMSO as an eluent (flow rate: 1.0 mL/min, temperature: 25 °C) on the basis of polymethylmethacrylate (PMMA) standards. UV-vis spectra were recorded on a JASCO V-750ST spectrophotometer (JASCO Co. Ltd., Tokyo, Japan) using a glass plate for a polymer cast film or 0.1 cm path quartz cell for a polymer solution with a temperature controller (ETCS-761, JASCO Co. Ltd., Tokyo, Japan). Differential scanning calorimetry (DSC) was performed using a DSC-60 plus instrument (Shimadzu Co. Ltd., Kyoto, Japan) under a N_2 atmosphere (flow rate: 50 mL/min). Thermogravimetric analysis (TGA) was carried out on a TGA-50 thermogravimetric analyzer (Shimadzu Co. Ltd., Kyoto, Japan) controlled by a TA-60 WS system (Shimadzu Co. Ltd., Kyoto, Japan) under N_2 atmosphere (flow rate: 50 mL/min). The sample was preheated at 90 °C for 10 min before the TGA measurement.

Synthetic Procedures

Synthesis of **1**:[42] *p*-Toluenesulfonyl chloride (21.5 g, 0.113 mol) was added to a stirred solution of isomannide (15.0 g, 0.103 mol) in pyridine (90 mL) at room temperature. The mixture was warmed to 50 °C, stirred for 1 d at the same temperature, cooled to room temperature, and diluted with $CHCl_3$. The organic layer was sequentially washed with 1 M aqueous HCl (300 mL), water, and sat. aq. $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude was purified by silica gel column chromatography (eluent: hexane-EtOAc = 1:1) to give **1** (14.1 g) as white solids in 46% yield: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.83 (1H, d, *J* = 8.4 Hz, Ar), 7.35 (1H, d, *J* = 8.4 Hz, Ar), 4.91 (1H, td, *J* = 7.2, 4.8 Hz, CH), 4.50 (1H, t, *J* = 4.8 Hz, CH), 4.43 (1H, t, *J* = 4.8 Hz, CH), 4.29 (1H, quin, *J* = 7.2 Hz, CH), 4.03 (1H, dd, *J* = 9.2, 6.4 Hz, CH_2), 3.96 (1H, dd, *J* = 9.2, 6.4 Hz, CH_2), 3.79 (1H, dd, *J* = 9.2, 7.6 Hz, CH_2), 3.55 (1H, dd, *J* = 9.2, 7.6 Hz, CH_2), 2.46 (3H, s, CH_3) ppm.

Synthesis of **2**:[42] To a solution of **1** (5.02 g, 0.017 mol) in DMF (46 mL) was added NaN_3 (3.26 g, 0.050 mol) at room temperature. The mixture was warmed to 140 °C, stirred for 19 h at the same temperature, and cooled to room temperature. Excess sodium azide was removed by filtration. To the filtrate was added water. The products were extracted with EtOAc three times. The combined organic layer was washed with water (× 2) and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. To the crude were added a mixture of hexane-EtOAc (1:1, 100 mL) and silica gel (20 g). The mixture was stirred for 10 min at room temperature and filtered. The filtrate was concentrated in vacuo to give **2** (1.73 g) with a small amount of DMF. The obtained **2** was used for the next step without further purification: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 4.63 (1H, brt, *J* = 4.0 Hz, CH), 4.48 (1H, brd, *J* = 4.0 Hz, CH), 4.33 (1H, quin, *J* = 5.6 Hz, CH), 4.10-4.06 (2H, m, CH, CH_2), 3.97 (1H, ddd, *J* =10.0, 4.0, 1.2 Hz, CH_2), 3.88 (1H, ddd, *J* = 9.6, 5.6, 1.2 Hz, CH_2), 3.61 (1H, ddd, *J* = 9.6, 5.6, 1.2 Hz, CH_2), 2.55 (1H, dd, *J* = 5.6, 1.2 Hz, OH) ppm.

Synthesis of **3**: 10% Palladium on carbon (Pd/C, 109 mg) was added to a glass flask. To the flask cooled at 0 °C were slowly added MeOH (33 mL) and then a solution of **2** (2.17 g, 12.7 mmol) in MeOH (30 mL). The mixture was stirred under H_2 atmosphere at room temperature for 43 h and filtered through a celite pad. The filtrate was concentrated in vacuo to give **3** (1.94 g) as a crude. The purity of **3** was estimated by ^{1}H NMR spectroscopy to be 90%: ^{1}H NMR (400 MHz, CD_3OD, 25 °C) δ 4.62 (1H, dd, *J* = 6.0, 4.4 Hz, CH), 4.44 (1H, brd, *J* = 4.4 Hz, CH), 4.27 (1H, q, *J* = 6.0 Hz, CH), 4.03 (1H, dd, *J* = 10.0, 4.4 Hz, CH_2), 3.87 (1H, brd, *J* = 10.0 Hz, CH_2), 3.82 (1H, dd, *J* = 9.2, 6.0 Hz, CH_2), 3.65 (1H, brd, *J* = 4.4 Hz, CH), 3.57 (1H, dd, *J* = 9.2, 6.0 Hz, CH_2) ppm.

Treatment of **2** with PPh_3 in the presence of water also gave **3**: To a solution of **2** (0.047 mol) in THF (200 mL) were added PPh_3 (18.4 g, 0.070 mol) and water (10.1 mL) at room temperature.

The mixture was warmed to 60 °C, stirred for 2 h, cooled to room temperature, and concentrated in vacuo. The conversion of the crude was estimated by ^{1}H NMR spectroscopy to be quantitative. After the azeotropic removal of humidity using toluene, the crude was used for the next acetylation reaction without further purification.

Synthesis of **4**:[39] The crude **3** from the reaction using PPh_3 and water was dissolved in MeOH (200 mL). The mixture was cooled to 0 °C. Ac_2O (8.84 mL, 0.094 mol) was added to the mixture. After stirring at room temperature for 20 h, SiO_2 (160 g) was added to the mixture. The mixture was concentrated in vacuo. The obtained residue was purified by silica gel column chromatography (eluent: $CHCl_3$ → $CHCl_3$: MeOH = 9:1) to give **4** (7.07 g) as white solids in 81% for 2 steps: $[\alpha]_D^{25}$ +56.0° (c. 1.00, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 5.57 (1H, br, NH), 4.56 (1H, dd, *J* = 5.6, 4.6 Hz, CH), 4.51-4.47 (1H, m, CH), 4.41 (1H, brd, *J* = 4.6 Hz, CH), 4.30 (1H, ddt, *J* = 6.8, 6.0, 5.6 Hz, CH), 3.99 (1H, dd, *J* = 10.0, 4.4 Hz, CH_2), 3.89 (1H, brd, *J* = 10.0 Hz, CH_2), 3.86 (1H, dd, *J* = 9.6, 6.0 Hz, CH_2), 3.63 (1H, dd, *J* = 9.6, 5.6 Hz, CH_2), 2.54 (1H, d, *J* = 6.8 Hz, OH), 2.00 (3H, s, Ac) ppm.

Synthesis of **5**: To a solution of **4** (177.4 mg, 0.948 mmol) in CH_2Cl_2 (9.5 mL) were added pyridine (153.0 μL, 1.90 mmol) and methacryloyl chloride (183.4 μL, 1.90 mmol) at 0 °C. The mixture was warmed to room temperature, stirred for 19 h, and concentrated in vacuo. The crude was purified by silica gel column chromatography (eluent: hexane : EtOAc = 1:1 → EtOAc → EtOAc : MeOH = 9:1) to give **5** (157.8 mg) as a colorless amorphous in 65% yield: $[\alpha]_D^{25}$ +31.4° (c. 1.00, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 6.61 (1H, s, olefin), 5.62 (1H, t, *J* = 1.2 Hz, olefin), 5.57 (1H, br, NH), 5.21 (1H, td, *J* = 5.6, 3.6 Hz, CH), 4.81 (1H, t, *J* = 5.6 Hz, CH), 4.48 (1H, dd, *J* = 7.6, 3.6 Hz, CH), 4.38 (1H, d, *J* = 3.6 Hz, CH), 3.96 (1H, dd, *J* = 10.4, 3.6 Hz, CH_2), 3.93-3.87 (2H, m, CH_2), 3.78 (1H, brd, *J* = 9.6 Hz, CH_2), 1.98 (3H, s,

Ac), 1.97 (3H, brs, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 170.2, 166.6, 135.5, 126.2, 86.9, 80.4, 74.1, 72.8, 70.9, 56.2, 22.8, 18.1 ppm; IR (ATR) υ 3276 (NH), 1720 (C=O), 1652 (amide I), 1545 (amide II) cm^{-1}; MALDI-TOF MS (matrix: DHBA) calc'd for $C_{12}H_{18}NO_5^+$ $[M+H]^+$ 256.12, found 256.15.

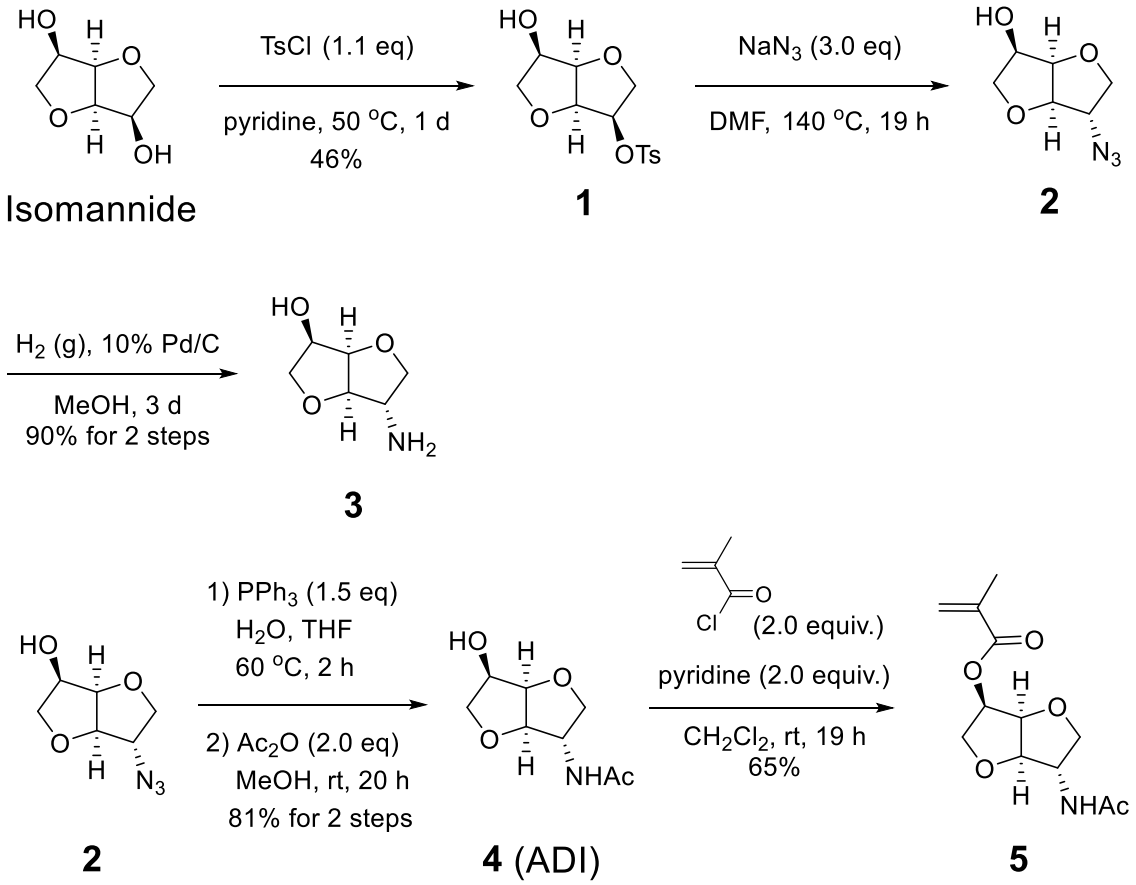
Typical procedure for the radical polymerization of **5** to give **6**: To a solution of **5** (234.6 mg, 0.919 mmol) in DMSO (0.30 mL) was added a solution of ammonium persulfate (2.1 mg, 9.19 μmol) in water (0.60 mL). The mixture was degassed by frozen-pump-thaw cycling technique and the atmosphere was replaced to an argon. TMEDA (10.7 μL, 64.3 μmol) was added to the mixture. The mixture was stirred for 1 d at room temperature and poured into acetone (50 mL) to give precipitates. The precipitates were collected by filtration and repeatedly washed with acetone. The residue was dried in vacuo to give **6** (91.7 mg) as an acetone-insoluble part in 39% yield. The filtrate was concentrated in vacuo to give a crude (161.8 mg) as an acetone-soluble part. Through the ^1H NMR spectroscopic analysis, it was found that the crude mainly consists of **6** (99%) with a small amount of unreacted **5** (1%).

Polymer **6** as an acetone-insoluble part: T_g 168 °C; T_{d5} 196 °C; T_{d10} 235 °C; ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ 8.14 (1H, br, NH), 4.95 (1H, br, CH), 4.65 (1H, br, CH), 4.29 (1H, br, CH), 4.12 (1H, br, CH), 3.90-3.60 (4H, m, CH_2), 1.82 (3H, m, CH_3), 1.10-0.76 (2H, m, CH_2) ppm; IR (ATR) υ 3287 (NH), 1725 (C=O), 1656 (amide I), 1547 (amide II) cm^{-1}.

RESULTS & DISCUSSION

ADI-based methacrylate **5** was prepared via 5 steps from commercially available isomannide (Scheme 1 and Figures S1-S8). Isomannide was tosylated with TsCl in pyridine at 50 °C to give mono-tosylate **1** in 46% yield according to the literature.[42] Nucleophilic substitution of **1** with NaN_3 in DMF at 140 °C proceeded with inversion at the stereogenic

center to yield azide **2**. Subsequent hydrogenolysis of **2** in MeOH in the presence of Pd/C under H_2 atmosphere afforded amine **3** in 90% yield for 2 steps. We also performed Staudinger reaction for the reduction of **2** to give **3**.[39] Treatment of **2** with PPh_3 in THF in the presence of water gave **3** in a quantitative yield. After azeotropic removal of the solvent using toluene, the crude was used for the next acetylation reaction without further purification. The crude **3** was acetylated in MeOH to give **4** (ADI) in 81% yield for 2 steps. The spectral data of the obtained **4** was in good agreement with the reported data (Figure S4). Further treatment of **4** with methacryloyl chloride and pyridine afforded methacrylate **5** as a monomer. When Et_3N was used as a base in place of pyridine, a significant amount of methacrylamide was formed as a byproduct. The structure of **5** was determined with ^1H NMR, ^{13}C NMR, IR, and MALDI-TOF mass spectra (Figures S5-S8).

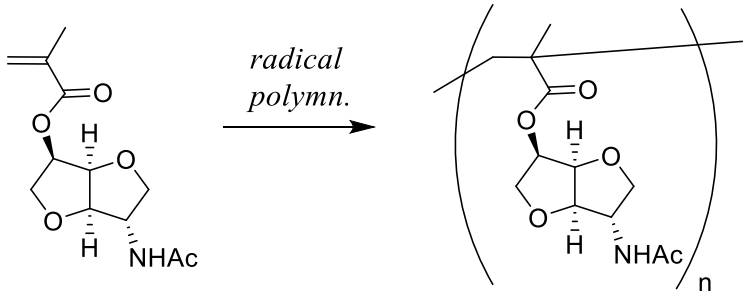


Scheme 1. Synthesis of ADI-based methacrylate **5**.

With the monomer **5** in hand, we performed the free radical polymerization of **5**. The results are summarized in Table 1. At first, we used V-70, having a half-life of ca. 10 h at 30 °C, as an azo polymerization initiator at a low temperature (Table 1, entry 1). The polymerization of **5** was performed by using 5 mol% of V-70 in DMF (2.0 M) at room temperature. After 1 d, the conversion of **5** was estimated by taking an aliquot of the mixture to be 41% yield. Because we found that the polymer **6** was hardly soluble in acetone, the reaction mixture was poured into acetone to remove unreacted **5**, reagent, and solvent. The precipitates were collected by filtration to give **6** as an acetone-insoluble part. Figures 2 and S9 show the ^{1}H NMR spectra of **5** and **6**. The ^{1}H NMR spectrum of **6** shows the presence of ADI side groups and the polymethacrylate main chain and the absence of olefinic proton signals originating from **5**, indicating the formation of **6** as a polymethacrylate comprising ADI side groups. The IR spectrum of **6** showed the characteristic absorption signal for the ester carbonyl group at 1725 cm^{-1} and amide I and II peaks at 1652 and 1545 cm^{-1}, respectively (Figure S10), also supporting that the polymer involves ADI skeletons as the side groups. The weight-average molecular weight (M_w) and its dispersity (M_w/M_n) were estimated by SEC (eluent: DMSO) on the basis of PMMA standards to be 2,500 Da for M_w and 3.0 for M_w/M_n (Figure S13). To improve the yield and the M_w, we investigated the effects of radical initiator on the polymerization. Using AIBN at 60 °C (Table 1, entries 2 and 3), the reaction in DMF afforded 60% conversion of **5** and the formation of low molecular weight polymer (M_w 900 Da), whereas that in DMSO led to better conversion (93%) and higher M_w (5,000 Da) than those in DMF. However, the polymer prepared in DMSO was colored (Figure S12), although the reason for coloration is not clear. Finally, we found the optimal polymerization condition using a redox initiator based on the combination of $(NH_4)_2S_2O_8$ and TMEDA in DMSO-H_2O mixed solvent. As shown in entry 4, the reaction conditions using 1.0 mol% of $(NH_4)_2S_2O_8$ and 7.0 mol% of TMEDA in DMSO-H_2O (1:2) at room temperature provided almost quantitative conversion of **5** (99%) to give a

colorless polymer with a good M_w value (46,000 Da). Both the low temperature polymerization and the addition of water would make the polymerization efficient.[43] As part of the structural analysis, we estimated the tacticity of the obtained polymer based on the derivation to PMMA and the details are included in the supporting information (Scheme S1 and Figure S14).

Table 1. Effects of solvent and initiator on the radical polymerization of **5**.



5 **6**

Entry	Initiator (mol%)	Solvent	Temp. & Time	Conversion of **5** (%)	M_w (Da)[a]	M_w/M_n [a]
1	V-70 (5)	DMF	rt, 1 d	41	2,500	3.0
2	AIBN (1)	DMF	60 °C, 1 d	60	900	1.3
3	AIBN (1)	DMSO	60 °C, 1 d	93	5,000	6.4
4	$(NH_4)_2S_2O_8$ (1) TMEDA (7)	DMSO-H_2O (1:2)	rt, 1 d	99	46,000	1.3

[a] Estimated by SEC using acetone-insoluble part on the basis of PMMA standards.

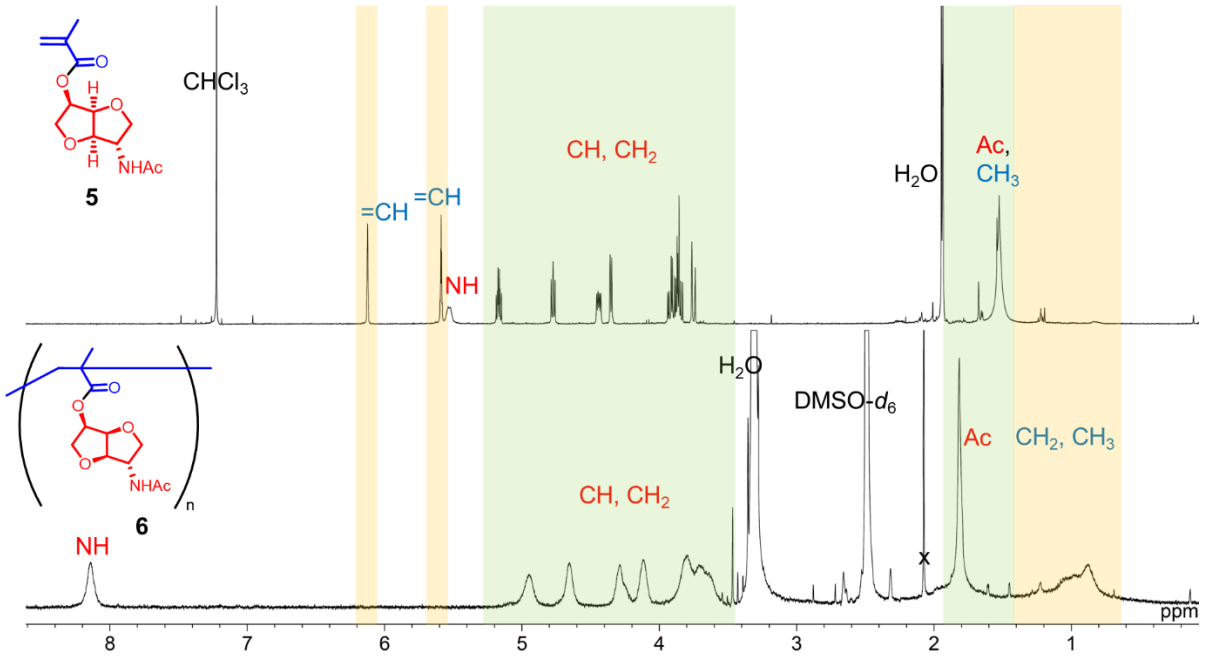


Figure 2. ^{1}H NMR spectra of **5** in $CDCl_3$ and **6** in DMSO-d_6 (400 MHz, 25 °C). x: acetone.

To know the transparency of **6** in a visible wavelength region, we evaluated the transparency of a cast film and DMSO solution of **6** (Figures 3 and S11). The cast film of **6** was prepared by casting the solution of **6** in MeOH on a glass plate and air-dried. We measured UV-vis spectrum of the sample at 300-650 nm (Figure 3). The spectrum indicates that the cast film shows >95% transparency at 400-650 nm, which seems to be comparable to that of PMMA as an optical polymer.[44] The UV-vis spectrum of a solution of **6** in DMSO (100 μM, 25 °C) shows >99% transparency at 260-650 nm (Figure S11).

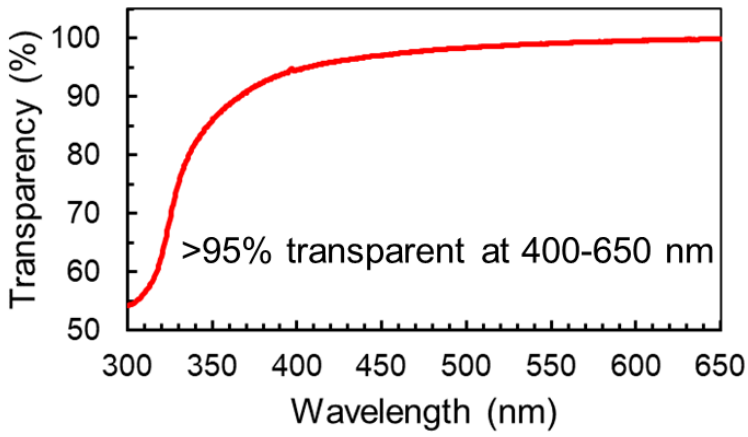


Figure 3. Transparency of a cast film of **6** (thickness: 40 μm).

The thermal properties of **6** were evaluated by TGA and DSC analyses (Figure 4). TGA profile of **6** indicates that 5% and 10% weight-loss temperatures (T_{d5} and T_{d10}) were 196 and 235 °C, respectively (Figure 4a). Because it has been reported that the T_{d5} values of isosorbide-based polymethacrylate and the acetylated one are 238 and 228 °C, respectively (Figure 4c), the weight loss of **6** upon heating could start from the degradation of acetamide moieties. The glass transition temperature (T_g) of **6** was estimated by DSC analysis to be 168 °C (Figure 4b), which is remarkably higher than those of PMMA (105 °C) or biobased high T_g polymers such as poly(D-glucose carbonate) (106-123 °C)[45] and poly(vanillin methacrylate) (120 °C).[46] The T_g value of **6** is almost same as hydroxyl group-containing **7** and higher than hydrogen bond-free **8** that is structurally similar to **6** (Figure 4c).[20] The results imply that interchain hydrogen bonds may contribute on the increase in T_g.

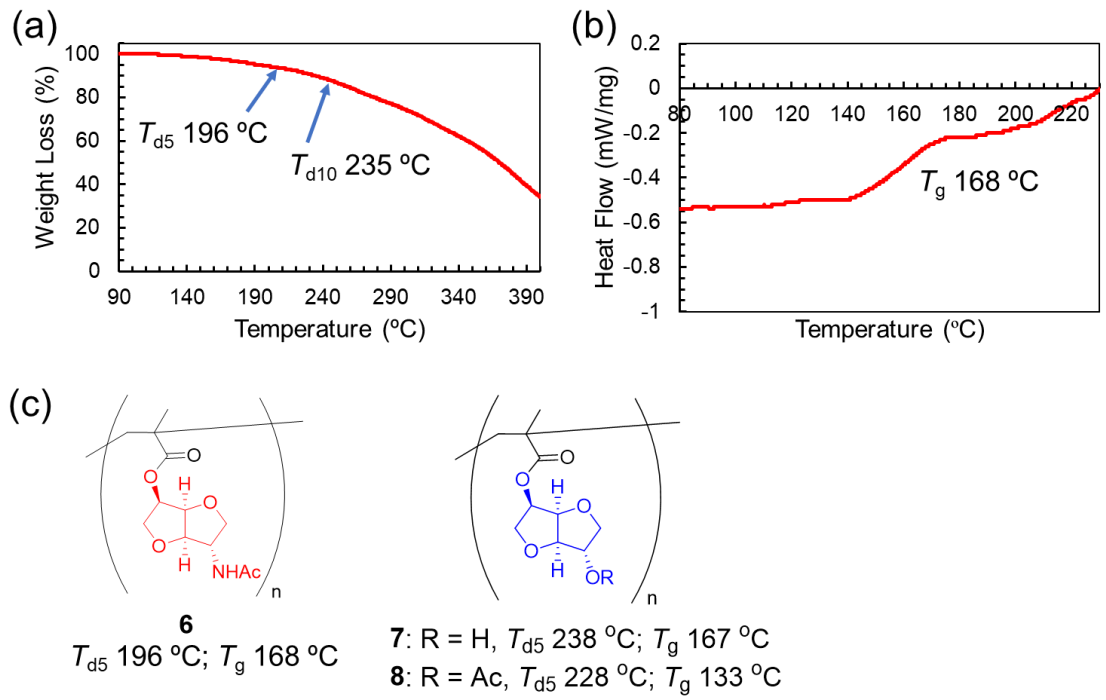


Figure 4. (a) TGA and (b) DSC profiles of **6** (entry 5 in Table 1) and (c) effects of the polymer functionality on thermal properties.

CONCLUSION

We investigated the synthesis and properties of biobased polymethacrylate comprising chitin-derived ADI side groups. The polymer was synthesized via free radical polymerization of newly developed ADI-based methacrylate in the presence of $(NH_4)_2S_2O_8$ and TMEDA. The use of DMSO-H_2O mixed solvent for the polymerization gave the optimal results in terms of high yield, high M_w, and a decrease in the coloration of the polymer. This polymerization investigation is exploratory and we conducted a simple free radical polymerization with industrial applications in mind. By applying controlled radical polymerization technique such as reversible addition/fragmentation chain transfer polymerization (RAFT), atom transfer radical polymerization (ATRP), or nitroxide-mediated polymerization (NMP) to this system, it could allow to control the molecular weight. Since DMSO as the optimized reaction solvent is harmful, we need to find a safer solvent in future. The UV-vis spectrum of the polymer was measured to evaluate that the polymer shows >95% transparency at 400-650 nm, indicating the

applicability of the polymer to optical materials. The TGA analysis of the polymer indicates that the T_{d5} is somewhat lower than those of isosorbide-based polymethacrylates. The DSC profile of the polymer suggests that the T_g is almost same or higher than those of isosorbide-based polymethacrylates, indicating the special role of amide of **6** on the increase in T_g. We envision that the polymer has great potential as the biobased substitute of nitrogen-containing commercial polymers such as polyamides and polymethacryl amides. The mechanical properties of the polymer are currently being evaluated in our laboratory. The present results could unveil not only the high performance of ADI-based polymethacrylate but also the usefulness of chitin as a raw material for the creation of biobased polymers. Because it has been reported that methacrylic acid is preparable via a biobased route,[47] the synthesis of ADI-based polymethacrylate entirely from biomass is our important future work.

SUPPORTING INFORMATION

Supporting Information is available from the Wiley Online Library or from the author.

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CONFLICT OF INTEREST

The authors hereby declare that they have no conflict of interest.

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A polymethacrylate comprising chitin-derived 2-acetamide-2-deoxyisosorbide (ADI) as a repeating unit is developed as a new biobased high performance polymer. The UV-vis spectrum of the polymer indicates high transparency at 400-650 nm. The DSC analysis suggests that the polymer shows high T_g at 168 °C, similar to those of isosorbide-based polymethacrylates.

Keywords: biomass, chitin, 2-acetamide-2-deoxyisosorbide, polymethacrylate, biobased plastics, optical materials

Y. Koyama*, T. Sagawa, K. Kohno, K. Sato, H. Kobayashi, A. Fukuoka

Title

Synthesis and Properties of Biomass-Based Polymethacrylate Comprising Chitin-Derived 2-Acetamide-2-Deoxyisosorbide as a Repeating Unit

ToC figure