

Dissertation Abstract

Synthesis and characterization of polysaccharide derivatives using ionic liquids catalyzed transesterification reactions

イオン液体触媒エステル交換反応による多糖誘導体の合成と
キャラクターゼーション

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Abstract

In this dissertation, the scalability and recyclability were evaluated for the catalytic transesterifications of polysaccharides with the Im-II (EmimOAc) serving as both a solvent and an organocatalyst. The synthesis and characterization of various polysaccharide derivatives from cellulose, xylan, dextrin, pullulan, rice husk and coconut fiber using EmimOAc or EmimOAc/DMSO catalyzed TER were conducted.

The results show that the EmimOAc was recycled for four times without an obvious decrease in catalytic activity and the recovery rate of the EmimOAc reached sufficiently high (at least, 96 wt %). The applicability of the EmimOAc catalyzed transesterifications was expanded to gram-scale reaction with various materials (avicel, pulps, rayon, xylan, dextrin and pullulan), affording polysaccharide esters with practically perfect conversions of the starting hydroxyl groups. Structural determinations of the obtained products by FT-IR and ^1H NMR measurements confirmed the successful synthesis of polysaccharide derivatives bearing acetyl, butyryl, pivaloyl and benzoyl groups, respectively. The kinetic evolution of the TER of polysaccharides in EmimOAc was investigated. These investigations indicated that the EmimOAc-mediated polysaccharide modification reactions were quantitatively proceeded. Furthermore, the thermal properties and solubility of the obtained polysaccharide derivatives were characterized presenting significant improvements after TER. The $M_{n,\text{SEC}}$ and M_w/M_n were determined by the SEC measurements, which indicated the Im-II-catalyzed TER was the mild reaction without any polysaccharide decompositions. Finally, this homogeneous system composed EmimOAc, DMSO and IPA could be applied eco-friendly and efficiently to synthesize polysaccharide acetates from raw lignocellulosic biomass.

1. The objectives of the research

The objectives of my research are to synthesize and characterize a wide range of polysaccharide derivatives by using the EmimOAc and EmimOAc/DMSO catalyzed TER. First of all, the scalability and recyclability were evaluated for the catalytic transesterifications of cellulose with imidazolium-based ionic liquid (Im-ILs) such as EmimOAc serving as both a solvent and an organocatalyst. In addition, the syntheses and characterizations of a large variety of polysaccharide derivatives such as CA, cellulose butyrate (CBu), cellulose pivalate (CPiv), cellulose benzoate (CBn), cellulose acetate pivalate (CAPiv), xylan acetate (XA), xylan butyrate (XBu), dextrin acetate (DA), dextrin butyrate (DBu), pullulan acetate (PuA) and pullulan butyrate (PuBu) will be presented. The kinetic evolution of TER of polysaccharides in EmimOAc by changing the amount of IPA, reaction time and temperature. Furthermore, the application of this methodology to directly acetylate the polysaccharides within rice husk and coconut fiber raw biomasses. Finally, the thermal property and the solubility behavior of synthesized polysaccharide derivatives were investigated.

2. Methods

Materials: 1-Ethyl-3-methylimidazolium acetate (EmimOAc; 95 %), dichloromethane, methanol, chloroform, deuterated NMR solvents (DMSO-*d*₆, CDCl₃-*d*, Acetone-*d*) were purchased from Kanto Chemical Co., Inc., and used without further purification. For ester reagents, the isopropenyl acetate (IPA) (99%) was available from the Sigma-Aldrich Chemicals Co., vinyl butyrate (VBu), vinyl pivalate (VPiv) and vinyl benzoate (VBn) were purchased from Tokyo Chemical Industry Co., Ltd, Japan and used as received. As cellulose sources, Avicel PH-101 and filter paper (whatman) were purchased from Sigma-Aldrich Chemicals Co, pulp A, B, C and rayon were kindly offered by DAICEL Chemical Industries Ltd, Japan, xylan and pullulan were purchased from Tokyo Chemical Industry Co., Ltd, Japan, dextrin was purchased from Nacalai, Kyoto,

Japan, rice husk and coconut fiber obtained from Vietnam. All other chemicals such as dimethyl sulfoxide (anhydrous >99.9%), benzoyl chloride were available and used without further purification unless otherwise stated.

Characterization methods: The FT-IR spectra were observed by a Thermo Fisher Scientific Nicolet iS10 equipped with an ATR unit. All the ¹H NMR spectra were recorded by JEOL 400 and 600 MHz FT-NMR spectrometers. The Degree of substitution (DS) values of polysaccharide derivatives were determined by ¹H NMR measurements of the polysaccharide derivatives and that were obtained by the reaction of these derivatives with an excess amount of benzoyl chloride. The DS values of CA, CBu, CPiv and CAPiv, PuA, PuBu, of DA and DBu were calculated using the following equation (1) the DS values of XA and XBu were determined by the followed equation (2):

$$(1) \quad DS = \frac{\text{peak area (CH3)}/3}{\text{peak area (CH3)}/3 + \text{peak area (7.0~8.5ppm)}/5} \times 3$$

$$(2) \quad DS = \frac{\text{peak area (CH3)}/3}{\text{peak area (CH3)}/3 + \text{peak area (7.0~8.5ppm)}/5} \times 2$$

Thermogravimetric analysis (TGA) was performed on a DTG-60AH instrument (Shimadzu) with a heating rate of 10°C/min under nitrogen atmosphere. The decomposition temperature (T_d) was determined as the onset temperature of decline in the TGA chart. Size exclusion chromatography (SEC) measurements for xylan, dextrin, and pullulan derivatives were performed at 40°C using Prominence gel permeation chromatography (GPC) system. The number average molecular weight ($M_{n,SEC}$) and polydispersity (M_w/M_n) were determined by the RI based on polystyrene standards (PStQuick A and PStQuick C). In the solubility check, ten milligram of the obtained products were dissolved in various organic solvents. The solubility behavior was observed.

3. Experiment/analysis

3.1 Recycling and reusing EmimOAc for the cellulose modification reactions in EmimOAc/DMSO mixed solvent systems

In order to make the reported cellulose modification protocol greener and more practical, we first turned our attention to a recyclability and reusability of employed Im-ILs. Therefore, the first purpose in this work was to test whether or not employed Im-ILs could be recycled and reused for the cellulose modification reactions in the Im-ILs. To be precise, the cellulose modification reaction was conducted in EmimOAc/DMSO mixed solvent with isopropenyl acetate (IPA) being an ester donating reagent and EmimOAc being a cellulose solvent and an organocatalyst for transesterification. The initial cellulose modification condition of [EmimOAc]/[DMSO]/[IPA] was set to be 4.0/4.4/3.7 with cellulose concentration being 1.0 wt %. The TER was conducted for 18 hours under Ar atmosphere at 80 °C. After the CA was isolated by a simple reprecipitation into MeOH, the resultant MeOH layer was subject to evaporation and subsequently high vacuum distillation. This gave the employed EmimOAc in 99.2 wt % recovery ratio (run 1, Table 1). As shown in the ¹H NMR spectrum of the recovered EmimOAc, a slight amount of impurity was observed. Though a precise decomposition mechanism has been unclear, this phenomenon could be correlated with a rather acidic C2 proton. Since EmimOAc features a strongly basic acetate anion, instinctive nucleophilic attack of acetate anion to the C2 proton would be inevitable but could lead to a decomposition reaction. In spite of the confirmed impurity most probably owing to the decomposition during the reaction and/or purification steps, the recovered EmimOAc was then used for the next cellulose modification reaction without any cautions. As shown in run 2 (Table 1), CA was produced with high DS value of 2.96 and good recyclability of the EmimOAc (98.1 %). This procedure was successfully iterated at least four times without any difficulties and a decrease in catalytic activities (runs 3 ~ 5, Table 1). Thus, although unknown impurities have been generated in the

employed EmimOAc through the iterated reaction and purification steps, the EmimOAc was revealed to be recyclable and reusable in the cellulose modification reaction for at least 3 times.

Table 1. Recycling EmimOAc in the cellulose modification reactions in EmimOAc/DMSO mixed solvent systems

Run	EmimOAc	DS values	Recovery rate of EmimOAc [wt %]	$M_{n,SEC}$	M_w/M_n
1	Fresh	2.95	99.2	31,700	3.58
2	Recycle 1	2.96	98.1	32,200	4.33
3	Recycle 2	2.87	96.2	33,200	3.43
4	Recycle 3	2.88	96.8	31,500	3.33
5	Recycle 4	2.86	97.7	29,900	5.69

3.2 Scaling up and expanding the polysaccharide source for the organocatalytic transesterifications in EmimOAc/DMSO mixed solvent systems.

In order to provide a robust and reliable synthetic protocol, scalability of the reaction system should be addressed because a large scale synthesis might face difficulties owing to a difference in reaction scale itself. Along with the scalability of the reaction system, the polysaccharide source should be considered because polysaccharides are naturally occurring polymers and thus can be obtained from a range of natural sources. First, scaling-up of our previously reported protocol with standard cellulose of avicel was targeted as shown in run 5 (Table 1). The reaction scale was increased by 20 times, corresponding to the scale shift from 120 mg to 2.4 g without any optimization and special caution. As expected, the organocatalytic transesterification of cellulose was successfully achieved on gram scale, demonstrating that the reported synthetic protocol is indeed reliable and robust. In addition to avicel, pulps and rayon were examined as the cellulose source (runs 6 ~ 9, Table 2) where pulps based cellulose is known

to show higher molecular weight than that of avicel. Regardless of the employed cellulose source, the synthetic protocol realized facile conversion of cellulose into CA with high DS values (~ 2.9).

Table 2. A large scale polysaccharide modification reactions

Run	polysaccharide (source)	DS values	$M_{n,SEC}$	M_w/M_n
6	Cellulose (avicel)	2.88	40,600	2.95
7	Cellulose (Rayon)	2.86	40,300	2.60
8	Cellulose (Pulp C)	2.91	125,200	1.87
9	Cellulose (Pulp B)	2.94	211,400	3.70
10	Cellulose (Pulp A)	2.96	517,600	2.02
37	Xylan	1.88	<i>n. d.</i> ^d	<i>n. d.</i> ^d
57	Dextrin	2.94	11,400	1.97
65	Pullulan	2.99	129,900	8.76

Encouraged by the robustness of the organocatalytic transesterification, we finally aimed to expand our synthetic portfolio to other polysaccharides such as xylan, dextrin, and pullulan were subject to the organocatalytic transesterification, essentially affording polysaccharide based polymeric materials. In the same manner as the cellulose modification reaction, organocatalytic TER of xylan, dextrin, and pullulan afforded corresponding polysaccharide esters with essentially high DS values (runs 37, 57, 65, Table 2)

3.3 Synthesis of cellulose derivatives by using EmimOAc or EmimOAc/DMSO with various ester donating reagents

The TER of cellulose using homogeneous system composed EmimOAc as both solvent and catalyst or mixed solvent of EmimOAc and DMSO with a range of esterification reagents such as IPA, VBu, VPiv and VBn without using additional catalysts and corrosive chemicals were successfully accomplished affording cellulose derivatives. The structural characterization of the obtained

cellulose derivatives were clearly confirmed by FT-IR and ¹H NMR analyses indicated that CA, CBU, CPiv, CBn and CAPiv with high DS values were successfully and rapidly synthesized.

3.4 The kinetic evolution of the TER of polysaccharides

In order to provide a detailed structural insight into the obtained these polysaccharide derivatives. The detailed kinetic evolution of TER of polysaccharides in EmimOAc was investigated. DA reached the highest DS of 2.66 (conversion rate of 88.7%), while XA showed the lowest DS of 1.39 ($DS_{max}=2$, conversion rate of 69.5%) compared with CA and PuA with the same conversion rate of 85% for 5 minutes after the reaction initiation. The DS values or the conversion rate of these polysaccharide derivatives slightly increased and reached by 1.88 (94%, XA), 2.93 (97.7%, DA), 2.94 (98%, PuA) compared with CA (2.88, 96%) for 60 minutes, respectively. The effect of the IPA concentration to the OH groups ratios and reaction temperature within 1 hour to further confirm the high reactivity of the TER of dextrin in EmimOAc was also investigated. The TER of dextrin with different IPA concentration by using EmimOAc successfully proceeded. The DS values of dextrin acetate peaked at 2.38 (Run 47) and significantly increased to 2.90 (Run 53) with [IPA]/[OH] being from 1 to 12. The TER of dextrin did not successfully proceeded at 40°C (Run 38) and 50°C (Run 39) for 1h, but after 24 hours at 40°C the reaction occurred to result in the obtained product with DS 2.64, while at 50°C within 4h the achieved product has a DS of 2.75. The reaction efficiently carried out at 60°C (Run 40) to obtain the DS of 2.84, the DS values continuously peaked by 2.89 and 2.93 at 70°C (Run 41) and 80°C (Run 55), respectively.

3.5 Thermal property:

The thermal stability of polysaccharide derivatives was determined by TGA measurement. At 50% weight loss, the decomposition temperature of CA (Run 6-11, 368-379°C), CBn (Run 12, 373°C), CPiv (Run 13, 381°C), CAPiv

(Run 14, 377°C), and CBU (Run 15, 384°C) were compared with cellulose (332°C), the decomposition temperature values of XA (342°C, Run 32), XBU (356°C, Run 36) compared with native xylan (305°C), DA (375°C, Run 55), DBU (377°C, Run 56), compared with native dextrin (323°C), PuA (384°C, Run 62), PuBU (382°C, Run 64) compared with native pullulan (324°C). These results indicated that the thermal stability of these polysaccharide derivatives could be improved by 36-60°C after transesterification. The TGA curves of RH and CF indicated a minor weight loss due to the water desorption, which was not clear in the PAs from 40 to 150°C. This is pointed that PAs are more hydrophobic than that of RH and CF. At 50% weight loss, the decomposition temperature of PAs isolated from RH (Run 66, 374°C) and CF (Run 68, 373°C) is higher by 7-8°C compared to raw biomass (366°C). The high thermal decomposition temperatures of the polysaccharide derivatives could possibly be due to the disappearance of the hydroxyl groups after esterification.

3.6 Solubility:

The solubility behavior of polysaccharide derivatives in organic solvents such as DMSO, chloroform (CHCl₃), dichloromethane (CH₂Cl₂) and acetone was investigated. All the obtained cellulose derivatives dissolve in CHCl₃, DMSO and CH₂Cl₂ at room temperature. Acetone showed lower soluble ability with cellulose derivatives compares to the other solvents. DA (Run 55), DBU (Run 56) and PuBU (Run 64) showed an excellent solubility dissolving completely in all used solvents. All these polysaccharide derivatives could be dissolved in DMSO. However, XA (Run 32) and PuA (Run 62) showed poor soluble activity, and did not dissolve or partly dissolve in CHCl₃, acetone and CH₂Cl₂. All PAs (from rice husk and coconut fiber) revealed good solubility in CH₂Cl₂, whereas these samples are poor or not soluble in acetone. The PAs obtained from both RH and CF by using recycled EmimOAc (Run 67, 69) dissolve in DMSO while the obtained PAs by using fresh EmimOAc show a partly solubility in this solvent.

4. Conclusion

The synthesis and characterization of a series of polysaccharide derivatives using ionic liquid catalyzed transesterification reactions were successfully investigated and developed. The EmimOAc shows an excellent solvent and organocatalyst for TER of a range of polysaccharides including cellulose materials, xylan, dextrin, pullulan and lignocellulosic biomass with different esterification reagents such as IPA, VBu, VPiv and VBn. The homogeneous system consisted of mixed solvent of EmimOAc and DMSO catalyzed transesterification was revealed to show not only robustness on gram-scale (2.4g) synthesis but also sufficient green nature with high recyclability (at least 96 wt%) and recover for 4 times without an obvious decrease in catalytic activity. The structural characterization of the obtained polysaccharide derivatives were clearly confirmed by FT-IR and ^1H NMR analyses. The $M_{n,\text{SEC}}$ and M_w/M_n were determined by the SEC measurements, which indicated the Im-IL-catalyzed TER was the mild reaction without any polysaccharide decompositions. The kinetic evolution of the TER of polysaccharides in EmimOAc was investigated indicating that polysaccharide derivatives with high DS values were achieved rapidly and smoothly. Finally, the thermal stability and the solubility behavior of polysaccharide derivatives in commercial organic solvents were significantly improved after transesterification reactions.

学位論文審査報告書（甲）

1. 学位論文題目（外国語の場合は和訳を付けること。）

Synthesis and characterization of polysaccharide derivatives using ionic liquids catalyzed transesterifications

イオン液体触媒エステル交換反応による多糖誘導体の合成とキャラクタリゼーション

2. 論文提出者 (1) 所属 自然システム学専攻

(2) 氏名 Nguyen Van Quy (ぐえん ばん うい)

3. 審査結果の要旨（600～650 字）

天然物由来の高分子であるセルロースは地球上で最も多量に生産・蓄積されているバイオマスであり、セルロースエステルなどは液晶光学フィルムや分離膜など、広範な分野に応用可能である。しかしながら、セルロースは一般的な有機溶媒には不溶であり、現在は酢酸溶媒中で、硫酸を触媒、無水酢酸をエステル化剤とする不均一系で行われている。

このような背景のもと、学位申請者である Quy 氏は、イオン液体 1-ethyl-3-methylimidazolium acetate (EmimOAc) がセルロースを溶解する溶媒としての機能のみならず、エステル交換反応の有機分子触媒としての機能がある性質を利用した反応プロセスの最適化を行なった。使用するイオン液体やエステル化剤の少量化、イオン液体のリサイクルプロセスなどを構築した。また、セルロース以外の多糖、例えばキシロース、プルランおよびデキストリンなどのエステル交換反応にも適用可能であることを見出した。また、籾殻やココナツ椰子のファイバーにも本手法が適用可能であることを実証し、イオン液体有機分子触媒によるエステル交換反応が汎用的に有効利用できることを見出した。

これらの結果は、従来のエステル交換反応に変わる新規のプロセスを構築できることを示しており、その工学的意義は極めて高く、博士（工学）に値するものと判断された。

4. 審査結果 (1) 判定 (いずれかに○印) 合格 ・ 不合格

(2) 授与学位 博士（工学）