Dissertation

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

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Abstract

During several decades, people have been using fossil resources including coal, gas and oil to generate energy and produce chemicals and materials. The use of fossil resources results in greenhouse gas emission and climate change. Moreover, fossil resources will not last forever, they will be depleted and not enough for all our needs in the future. Therefore, environmental protections and energy security become main global concerns. Biomass, a non-fossil and renewable resource of biological origin has been investigated to produce bioenergy and bio-based chemicals and materials to replace the employment of fossil resources. This process is defined as biorefinery. Isolated from renewable resources - biomass, naturally occurring polysaccharides have been hooked much concern to produce greener chemical products to replace the petroleum-based polymers. However, the numerous strong hydrogen-bonding networks in the polymeric chains of natural polysaccharides limit their solubility, processability, and feasibility. These problems cause many difficulties to apply them as materials. To solve these problems, many effective chemical methods and solvent systems have been developed and reported. Recently, Takahashi and co-workers reported that dual functionalities of the ionic liquid, 1-ethyl-3-methylimidazolium acetate (EmimOAc), had an effective and quick direct transesterification reactions of microcrystalline cellulose with isopropenyl acetate as a green process of cellulose modification. From this work, the limitation for the ability of EmimOAc-mediated cellulose modification is interesting. In this dissertation, the scalability and recyclability were evaluated for the catalytic transesterifications of polysaccharides with EmimOAc serving as both a solvent and an organocatalyst. The synthesis and characterization of a wide range of polysaccharide derivatives from various starting compounds such as cellulose, xylan, dextrin and pullulan using EmimOAc catalyzed transesterification reactions were conducted to address the limitations of its reaction system by addition of co-solvent dimethyl

sulfoxide (DMSO), and apply this effective methodology to directly acetylate the polysaccharides within rice husk and coconut fiber raw biomasses, which are abundant agricultural residues in Vietnam.

For the organocatalytic transesterifications with EmimOAc as a solvent and an organocatalyst, 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 %). In order to show the applicability of the EmimOAc catalyzed transesterifications, the above-mentioned EmimOAc-catalyzed polymer modification was expanded to gram-scale reaction with various polysaccharide sources such as avicel, pulps, rayon, xylan, pullulan, and dextrin affording corresponding polysaccharide esters with practically perfect conversions of the starting hydroxyl groups. Structural determinations of the obtained polysaccharide derivatives by FT-IR and ^{1}H NMR measurements were confirmed the successful syntheses of polysaccharide derivatives bearing acetyl, butyryl, pivaloyl and benzoyl groups, respectively. The degree of substitution of the obtained polysaccharide derivatives were determined by ^{1}H NMR measurements that were obtained by the further benzoylation reaction and other reported calculation methods. The kinetic evolution of the TER of polysaccharides in EmimOAc was investigated by changing the amount of isopropenyl acetate (IPA), reaction time and temperature. These investigations indicated that the EmimOAc-mediated polysaccharide modification reactions were quantitatively proceeded. Furthermore, the thermal properties of the obtained polysaccharide derivatives were characterized by TGA measurement and solubility behavior observation presenting significant improvements after TER. Size exclusion chromatography measurements for polysaccharide derivatives were performed at 40°C using Prominence gel permeation chromatography system. The number average molecular weight ($M_{\mathrm{n,SEC}}$) and polydispersity ($M_\mathrm{w}/M_\mathrm{n}$) were determined by the RI based on polystyrene

standards. The $M_{n,SEC}$ and M_w/M_n indicated the Im-IL-catalyzed TER was the mild reaction without any polysaccharide decompositions. Finally, this homogeneous system composed EmimOAc, DMSO and IPA could apply eco-friendly and efficiently to synthesize polysaccharide acetates from raw lignocellulosic biomass.

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Abbreviations

AGU	anhydroglucose unit
CA	cellulose aceate
CAPiv	cellulose acetate pivalate
CBu	cellulose butyrate
CBn	cellulose benzoate
CF	coconut fiber
CPiv	cellulose pivalate
DMAc	*N*,*N*-dimethyl acetamide
DMF	*N*,*N*-dimethyl formamide
DMI	1,3-dimethy-2-imidazolidinone
DMSO	dimethyl sulfoxide
DMSO-d_6	deuterated dimethyl sulfoxide
DP	degree of polymerization
DS	degree of substitution
DA	dextrin acetate
DBu	dextrin butyrate
EmimOAc	1-ethyl-3-methylimidazolium acetate
FT-IR	fourier - transform infrared spectroscopy
g	gram
h	hour
ILs	ionic liquids
L	liter
LiCl	lithium chloride
M	molar (mol/L)
PuA	pullulan acetate
PuBu	pullulan butyrate
PAs	polysaccharide acetates

min	minute
mL	milliliter
mg	milligram
NMR	nuclear magnetic resonance
RH	rice husk
RTILs	room temperature ionic liquids
SEC	size exclusion chromatography
TBAF	tetrabutylammonium fluoride trihydrate
TER	transesterification reactions
TFAA	trifluoroacetic anhydride
TGA	thermogravimetric analysis
XA	xylan acetate
XBu	xylan butyrate
XU	anhydroxylose unit

Chapter 1: General introduction

1.1 Natural polysaccharides as the sustainable resources instead of fossil fuel

The human life has become more and more comfortable and convenient because of the development of science and technology, especially in the field of polymer materials. Polymers have being applied widely in various aspects of human life including food industry, textile, health care, transportation, construction, pharmaceutical industry.[1] However, during several centuries, human activities based on fossil resources such as coal, gas and oil to generate energy and produce chemical products such as polymeric materials.[2] The employment of fossil resources results in the accumulation of greenhouse gas and climate change significantly. Moreover, fossil resources will not last forever, they will be depleted and not enough to supply all our demands in the future. Therefore, for the sustainability of global economic development, environmental protections and energy security are main global interests.[3] Looking for alternative and sustainable resources to produce fuels, chemicals and materials by using greener technologies needs to be investigated. Recently, biomass, a non-fossil and renewable resource of biological origin has been employed to convert into bioenergy and bio-based chemicals and materials to replace the use of non-biodegradable petroleum-based polymers due to their eco-friendly properties. This process is defined as biorefinery[4] (Figure 1.1). Natural polysaccharides such as cellulose, xylan, pullulan, dextran, dextrin and chitin are interesting kinds of biological polymers with the functionality of polysaccharide structures combined with reactive groups.[5] However, the numerous complex hydrogen-bonding networks within the polymeric chains of natural polysaccharides lead to the limitations of solubility, processability, and feasibility that are difficult to use them as materials.[6]

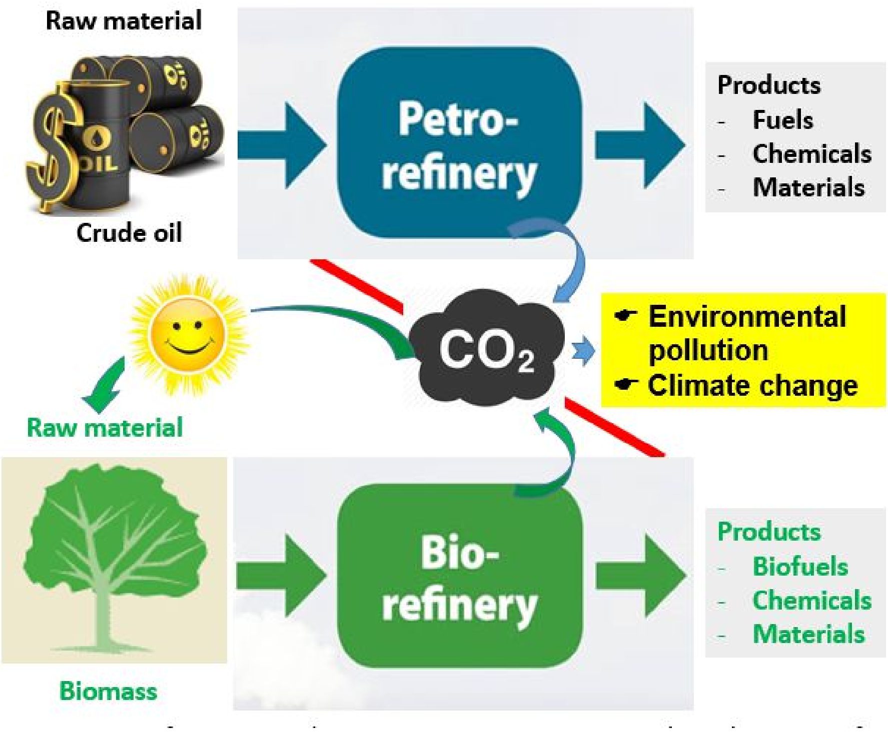
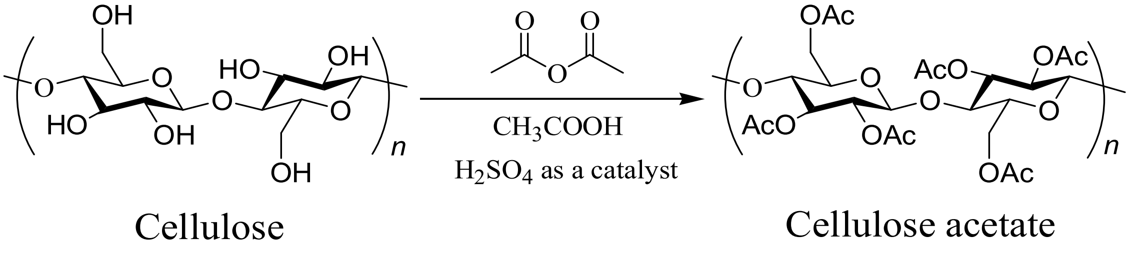


Figure 1.1 Biorefinery is an alternative green process to replace the petrorefinery

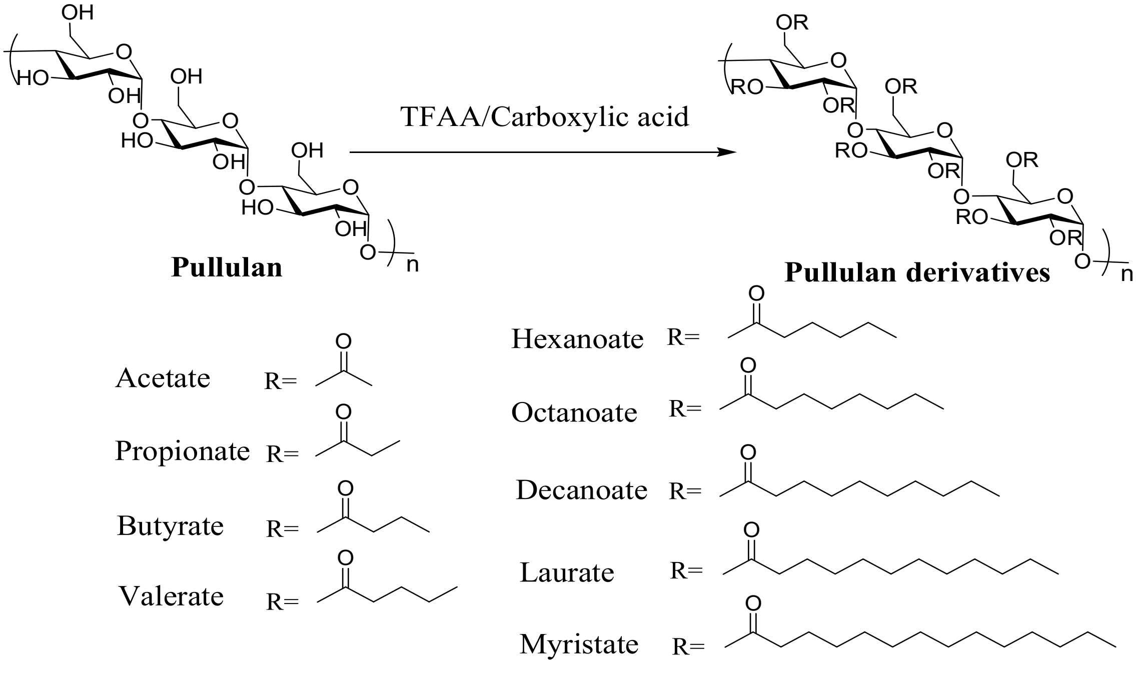
Esterification is an effective chemical modification method of polysaccharides to achieve thermoplastic polymeric materials.[7-9] Traditionally, cellulose acetate (CA) is produced by acetylating the hydroxyl groups in cellulose with acetic acid and acetic anhydride using sulfuric acid as a catalyst.[10] Other heterogeneous or homogeneous methods have been developed to synthesize CA (Scheme 1.1).[11, 12]

Scheme 1.1 Schematic representation of CA in acetic acid/anhydride/catalyst of H_2SO_4



The obtained xylan derivatives had potential applications to produce biodegradable plastics, resins, films and its blends.[13-17] Low solubility or completely insoluble in water pullulan derivatives can be modified by chemical methods.[18] In 2015, Iwata et al.[19] reported that fully substituted pullulan esters with carbon number of acyl group (n) of 2-14 were conducted in carboxylic acid/trifluoroacetic anhydride (TFAA) system (Scheme 1.2).

Scheme 1.2 Schematic representation of pullulan derivatives in carboxylic acid/trifluoroacetic anhydride (TFAA) system



Stearic acid dextrin ester was synthesized by using lipase as a catalyst.[20] Lignocellulosic biomass refers to inedible and the most abundant plant material in the planet with the chemical components of 45-55% cellulose, 25-35% hemicellulose and 20-30% lignin. It has been investigated as a promising potential resource to obtain chemicals, energy and various materials because of its renewable and biodegradable characteristics.[21-23]

1.2 Ionic liquids of the alternative solvent for green chemistry

Ionic liquids (ILs) are groups of imidazolium, pyridinium or halide/halogenoaluminate low-melting-point molten salts, that change into liquid phase around room temperature.[24] ILs have specific characteristics such as a negligible vapor pressure, excellent thermal stabilities, and controllable physicochemical properties, and recently, ILs have attracted much attention.[25] The researches related to biomolecules such as naturally occurring polysaccharides by using ILs have been increased because ILs structures have specific affinities for polysaccharides.[26] ILs were investigated as green solvents for dissolution biopolymers instead of the use of volatile organic. In 2002, Rogers and co-workers comprehensively confirmed that the 1-butyl-3-methylimidazolium chloride (BmimCl) significantly dissolved cellulose in high concentrations under mild conditions (Table 1.1).[27] Since then, ILs were mainly used to homogeneously derivatize, modify, and regenerate cellulose and other polysaccharides.[28-31]

Table 1.1 Solubility of dissolving pulp cellulose in ionic liquids

Ionic liquid	Method	Solubility (wt%)
[C_4mim]Cl	Heat 100°C, 70°C	10, 3
[C_4mim]Cl	Heat 80°C + sonication	5
[C_4mim]Cl	Microwave heating 3-5-pulses	25, clear viscous solution
[C_4mim]Br	Microwave	5-7
[C_4mim]SCN	Microwave	5-7
[C_4mim][BF_4]	Microwave	Insoluble
[C_4mim][PF_6]	Microwave	Insoluble
[C_6mim]Cl	Heat 100°C	5
[C_8mim]Cl	Heat 100°C	Slightly soluble

1.3 Effective co-solvent of dimethyl sulfoxide together with ionic liquids

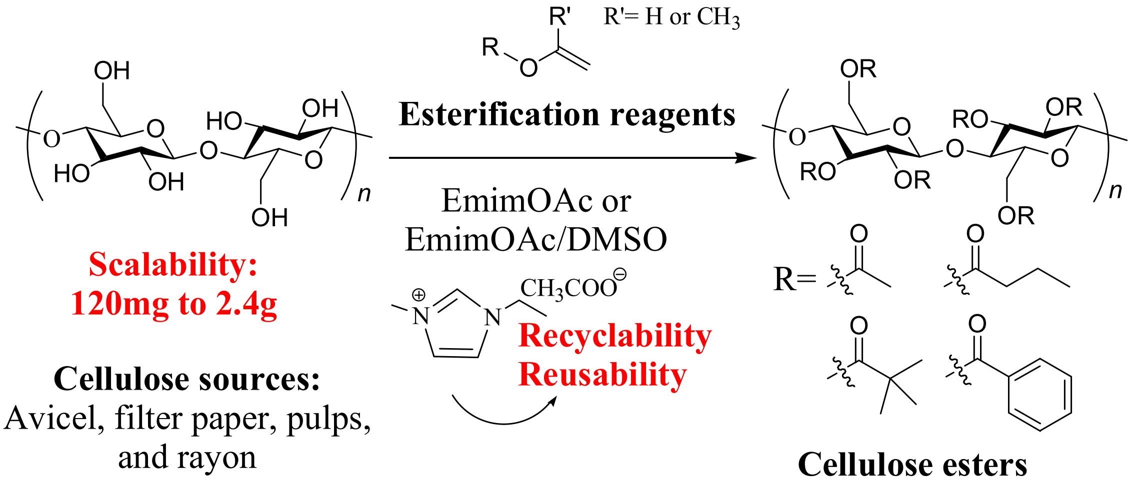
ILs have been used as solvents for polysaccharide modifications. However, some disadvantages were found because of high viscosity of the ILs and the corresponding polysaccharide solution, and limited miscibility of the ILs with hydrophobic reagents. These limitations may result in a non-uniform and irreproducible reaction products. These problems can be addressed by adding co-solvents to polysaccharide/ILs solutions. For example, the employment of varied co-solvents in ternary systems (cellulose/IL/co-solvent) has studied and the results indicated that DMSO was the most suitable co-solvent compared with the others.[32]

1.4 Objective and outline of the thesis

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 and apply this effective methodology to directly acetylate the polysaccharides within rice husk (RH) and coconut fiber (CF) raw biomasses. An outline for this dissertation is presented as follows:

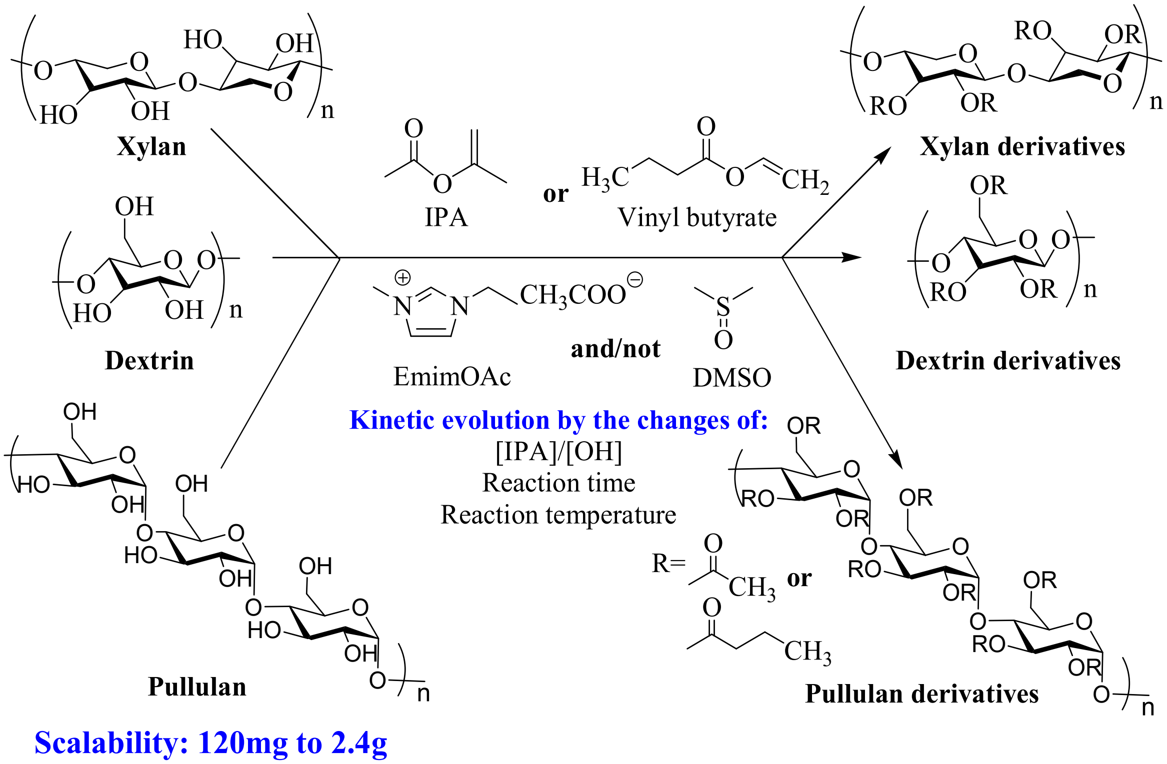
Chapter 2 will present a brief review of cellulose structure and chemical modification methods. The summarization of chapter 2 is depicted in Scheme 1.3. The scalability and recyclability were evaluated for the catalytic transesterifications of cellulose with imidazolium-based ionic liquid (Im-ILs) such as EmimOAc serving as both a solvent and an organocatalyst. Then describe the syntheses of a variety of cellulose derivatives such as CA, cellulose butyrate (CBu), cellulose pivalate (CPiv), cellulose benzoate (CBn) and cellulose acetate pivalate (CAPiv).

Scheme 1.3 The schematic representation of chapter 2



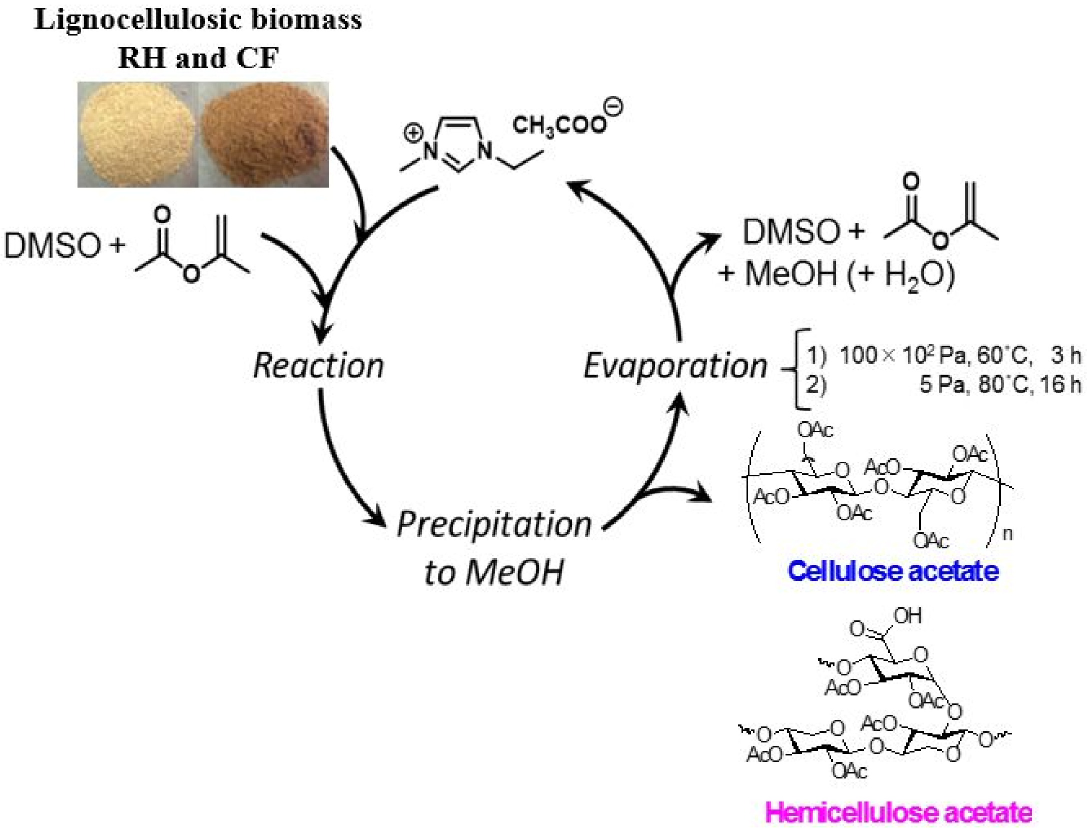
In Chapter 3, the syntheses and characterizations of other polysaccharides derivatives including xylan, pullulan and dextrin will be presented and summarized in Scheme 1.4. The structural polysaccharide derivatives, the kinetic evolution of TER of polysaccharides in EmimOAc by changing the amount of IPA, reaction time and temperature, the thermal property and the solubility behavior of polysaccharide derivatives were investigated.

Scheme 1.4 The schematic representation of chapter 3



Chapter 4 will discuss the application of the TER using recyclable EmimOAc and co-solvent DMSO to directly acetylate polysaccharides from raw lignocellulosic biomass (Scheme 1.5). The structures of polysaccharide acetates (PAs) including cellulose acetate (CA) and hemicellulose acetate (HA) isolated from RH and CF were confirmed by FT-IR and ^{1}HNMR measurements. The characterizations of the obtained PAs such as thermal property, solubility and the comparison of the efficiency the TER by using fresh EmimOAc and recycled EmimOAc was also investigated.

Scheme 1.5 The schematic representation of chapter 4



Chapter 5 is a summary of this dissertation and suggest some possibility for the future work of the ionic liquid catalyzed modification of cellulose and other reactions.

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Chapter 2: Recyclable and Scalable Organocatalytic Tranesterification of cellulose in a mixed solvent of EmimOAc and DMSO

In this chapter, scalability and recyclability were evaluated for the catalytic transesterifications of cellulose with imidazolium-based ionic liquid (Im-ILs) serving as both a solvent and an organocatalyst. For the organocatalytic transesterifications with 1-ethyl-3-methylimidazorium acetate (EmimOAc) as a solvent and an organocatalyst, 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 %). In order to show the applicability of the Im-IL catalyzed transesterifications, the above-mentioned EmimOAc-catalyzed polymer modification was expanded to gram-scale reaction with various cellulose sources such as avicel, pulps, and rayon, affording corresponding cellulose esters with practically perfect conversions of the starting hydroxyl groups. The TER of a series of cellulose materials using homogeneous system composed EmimOAc or EmimOAc/DMSO with IPA/VBu/VPiv/VBn as donating ester reagents without using additional catalysts and corrosive chemicals were successfully accomplished affording cellulose derivatives. The structural characterizations of the obtained products were confirmed by FT-IR and ^{1}H NMR analyses indicated that CA, CBu, CPiv, CBn and CAPiv with high DS values were successfully synthesized in short reaction time. SEC measurements indicated that the obtained products had no decomposed compound during the EmimOAc-catalyszed TER.

2.1 Introduction

Nowadays, environmental protection and energy security are dominant themes for the world. Human activities, by over-exploitation of fossil fuels such as oil, coal and natural gas have leaded to the shortage of resources, accumulation of greenhouse gas and global warming. The need has dramatically arisen to find renewable and sustainable resources to replace the use of fossil resources which will not enough to offer all our needs.[1] Lignocellulosic biomass has been investigated as a promising potential and important alternative to produce fuels, bio-based chemicals, energy and various materials because of its non-fossil renewable and biodegradable properties.[2-4] Cellulose is one of the most abundant lignocellulosic resources and widely presented in photosynthetic organisms such as plants, bacteria, algae, invertebrates, and even amoeba.[5, 6] It is estimated that about 56.8 × 10^9 tons of elemental carbon is produced annually by terrestrial plants via photosynthesis around the world.[7] Cellulose has extensive inter-/intra-molecular hydrogen-bonding network of crystalline structure which consists of a linear chain of up to 10000 β-1,4-linked D-glucopyranose units (Figure. 2.1). However, cellulose shows some disadvantages such as poor solubility in conventional solvents, high hydrophilicity, and lack of thermalplasticity, thus limiting its wider application as bio-based polymers.[8] These difficulties can be addressed by chemical modification, and the production of cellulose derivatives has attracted significant concerns.[9] Chemical esterification is an effective method was used to modify cellulose,[10] and CA is one of the most commercially important cellulose derivatives and has been applied in many fields such as fibers, plastic, film, cigarette filter, dialyzer, and coating industry.[11, 12] Global production of CA is estimated to be 1.5 billion pounds a year. Traditionally, CA is produced by acetylating the hydroxyl groups in cellulose with acetic acid and acetic anhydride

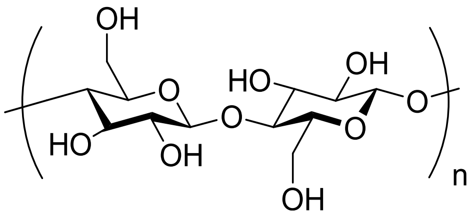
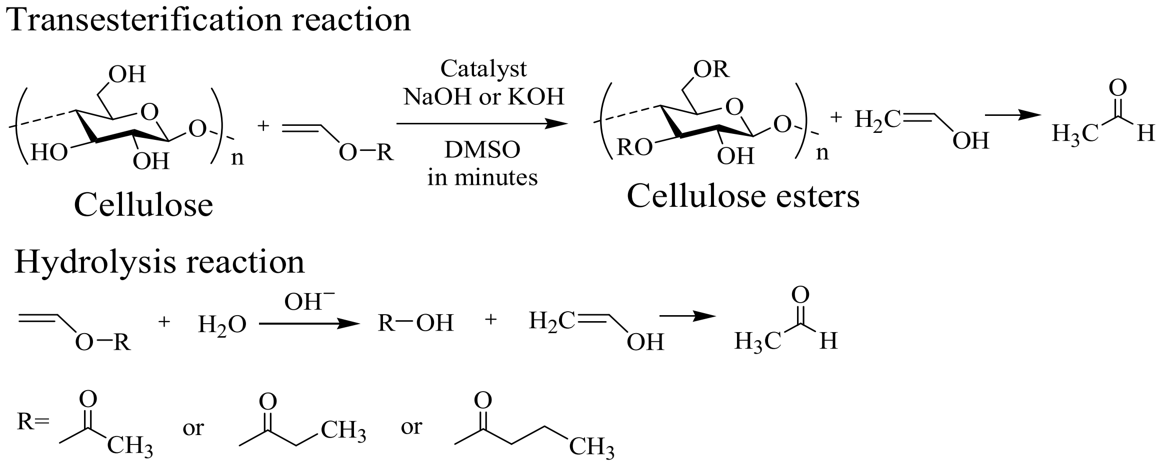


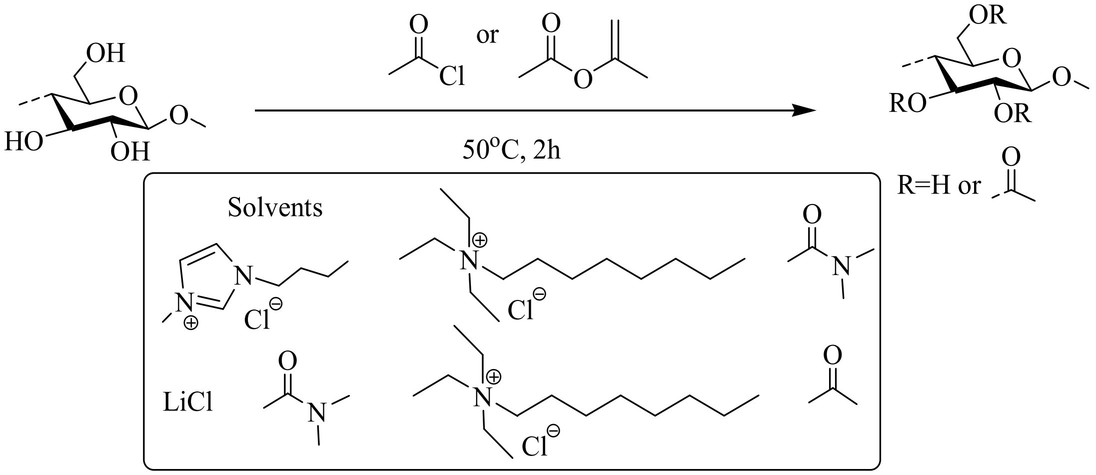
Figure 2.1 Structure of cellulose

using sulfuric acid as a catalyst.[13] Other heterogeneous or homogeneous methods have been developed to synthesize CA such as *N,N*-carbonyldiimidazole, dialkylcarbodiimide, iminium chloride, ring-opening esterification and transesterification.[14, 15] The transesterification of cellulose with acetic anhydride or vinyl acetate in dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF/$3H_2O$) was carried out and obtained in high yield.[16, 17] CA was also prepared by using other solvents such as *N*-ethyl-pyridinium chloride,[18] *N,N*-dimethylacetamide (DMAc)/Lithium chloride (LiCl),[19, 20] 1,3-dimethy-2-imidazolidinone (DMI)/LiCl, DMSO under the catalysis of NaOH or KOH (Scheme 2.1),[21] and DMSO with 1,8-diazabicyclo [5,4,0] undec-7-ene (DBU) catalyzed per-O-acetylation.[22] Scheme 2.2 presents the acetylation of cellulose in new solvent triethyloctylammonium chloride ($N_{2228}Cl$) combination with acetone and DMAc/pyridine.[23] However, the use of these solvents having various disadvantages such as environmental problems, side reactions, difficult recycling and high cost because of the requirement of activation before dissolution and instability.[24]

Scheme 2.1 Transesterification and hydrolysis reaction of vinyl esters under the catalyst of NaOH or KOH in DMSO



Scheme 2.2 Schematic representation of homogeneous acetylation of in new solvent triethyloctylammonium chloride ($N_{2228}Cl$) combination with acetone and DMAc/pyridine.[23]



Recently, the room temperature ionic liquids (RTILs) have been defined as low-melting-point molten salts[25] and they have received significant attentions as promising green solvents[26] for dissolution of cellulose[27, 28] due to their attractive properties such as a negligible vapor pressure, non-flammability, excellent thermal stability, controllable physical and chemical characterictics,[29] and allowed efficient and homogeneous synthesis of cellulose esters. The homogeneous system consisted of 1-allyl-3-methylimidazolium chloride (AmimCl) and acetic anhydride without a catalyst was used to obtained CA with DS values from 0.94 to 2.74 by different reaction conditions.[30] The acetylation of cellulose was carried out using Zn-based acidic ILs featuring Zn^{2+} as a Lewis acid.[31]

During the past decades, emergence of metal-free catalysts, the so-called organocatalysts, has emerged in the chemical sciences.[32-37] With the rapid growth of organocatalysts in organic chemistry, these catalysts have gradually integrated with polymer chemistry. For example, organocatalysts were revealed to be efficient for a range of polymer synthesis including ring opening polymerizations of cyclic esters,[38-45] epoxides,[46-48] and cyclic siloxane,[49] the group transfer polymerization of vinyl monomers,[50-55] step-growth polymerizations, [38, 56-57] as well as post-polymerization modification reactions,[58] to mention a few.[59-60] When considering that organocatalysts are free from organometallics and thus involve green natures, an integration of organocatalysts into bio-renewable resources should provide new directions in biomass related science and polymer chemistry. For example, organocatalysts have been utilized for ring-opening polymerization of bio-based cyclic esters,[61] vinyl polymerization of bio-renewable monomers,[62-63] and polymer analogous reactions of cellulose[64-68] Organocatalytic transesterifications of cellulose using the ionic liquid 1-butyl-3-methylimidazolium chloride (BmimCl) as a media and 1,5,7-triazabicyclo [4,4,0] dec-5-ene (TBD) as a catalyst were accomplished to produce cellulose derivatives with a limited DS values up to 0.69.[64] The dissolution process of 3-20 wt% microcrystalline cellulose was treated with EmimOAc (Figure 2.2) and a mixture of EmimOAc with DMSO at different temperatures.[69] The vapor of EmimOAc was dominated by the *N*-heterocyclic carbine-acetic acid complex which was highly reactive organocatalyst,[70] and EmimOAc can be recycled and reused.[71]

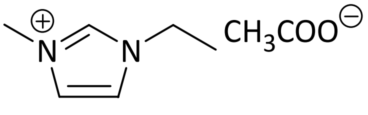
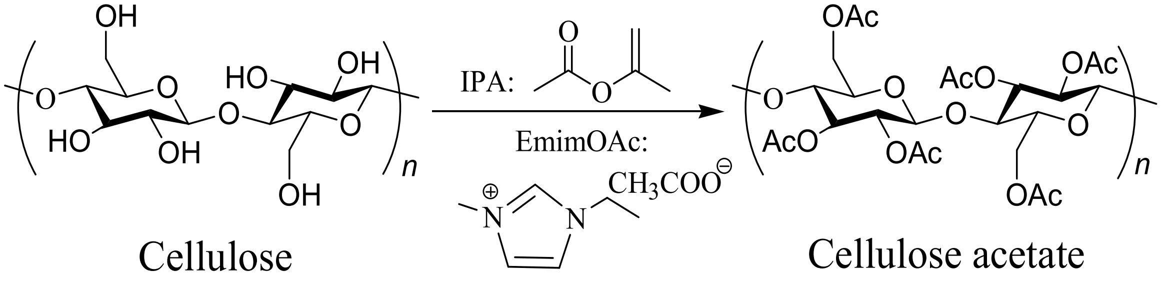

EmimOAc

Figure 2.2 Structure of EmimOAc

Since polysaccharides including cellulose are known to be one of the most important chemical feedstock, the utilization of cellulose as a starting material has been a long-lasting challenge in biomass related chemistries.[72] Due to their strong inter- and intra-hydrogen bonding, cellulose is hardly soluble in any reaction medium ranging from aqueous to organic ones. In this context, Im-ILs have been spotlighted in the field of biomass-related technologies since Im-ILs are known to dissolve cellulose under mild condition without harming the cellulose chemical structures.[27, 73] Along with the privileged cellulose dissolving property of the Im-ILs, Im-ILs have found their way in organocatalysts based on their molecular structures.[74] Recently, we have reported that the Im-ILs could provide dual functionalities of organocatalysts and reaction solvent for cellulose modification reactions.[66-67] In detail, cellulose was subject to transesterification reactions in Im-

ILs with stable esters such as isopropenyl acetate where Im-ILs behaved as not only a reaction medium but also an organocatalyst for the transesterification (Scheme 2.3). Thus, our synthetic protocol has realized not only active but also instinctively green cellulose modification reactions, potentially leading to materials science based on cellulose.

Scheme 2.3 Schematic representation of the transesterification reaction of cellulose in EmimOAc[67]



Despite the inherent green nature of the cellulose modification protocol, practical aspect of the reaction system has been a remaining consideration. In fact, the cellulose modification reactions were conducted on mg scale, thus limiting its application to other chemical sciences. In addition, reusability of Im-ILs should be verified because Im-ILs are rather expensive as compared to common organic solvents. It must be worth noting here that Im-ILs are at the same time known to be chemically stable and hardly volatile even under high vacuum conditions. This leads to a potential advantage of the Im-ILs in recyclability because high vacuum distillation of the reaction system should realize easy recovery of the Im-ILs. However, above-mentioned issues have not been addressed in detail in our latest works. Along with the intrinsic green advantage of cellulose, enriching practical applicability of the cellulose modification protocol is rationally expected to provide practical and operationally easy synthetic strategy to not only polymer chemists but also materials scientists who wish to handle cellulose derivatives.

Herein, we now wish to provide an insight into practical applicability of our synthetic protocol (Scheme 2.4 and Scheme 2.5). This chapter represents: 1) recyclability of Im-ILs for cellulose modification reactions, 2) scaling up the cellulose modification reactions with different cellulose sources such as avicel, pulps and rayon, 3) developing a homogeneous transesterification system composed ionic liquid EmimOAc as both catalyst and solvent, or EmimOAc as a catalyst with co-solvent DMSO (EmimOAc/DMSO) and IPA or VBu or VPiv or VBn without using additional catalysts and corrosive chemicals to efficiently synthesize cellulose derivatives with high DS values (Scheme 2.6 and Scheme 2.7); 4) the ^{1}H NMR and FT-IR spectroscopy techniques were applied to elucidate the structural cellulose derivatives; 5) the thermal properties of these cellulose derivatives were also characterized by TGA; and moreover, 6) the solubility behavior of cellulose derivatives in commercial organic solvents was also investigated.

2.2 Materials

1-Ethyl-3-methylimidazorium acetate (EmimOAc; 95 %), dichloromethane, methanol, chloroform, deuterated NMR solvents (DMSO-d_6, $CDCl_3$-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; The apparent molecular weight of the avicel was determined by size exclusion chromatography (SEC) measurements in THF with polystyrene calibrations of carbanilated cellulose sample (reacted with phenyl isocyanate). The carbanilation reaction was carried out essentially according to a previously reported method.[75] The apparent number average degree of polymerization of original cellulose was calculated to be 105; pulp A, B, C and rayon were kindly offered by DAICEL Chemical Industries Ltd, Japan. All other chemicals such as dimethyl sulfoxide (DMSO, anhydrous >99.9%), benzoyl chloride were commercially available and used without further purification unless otherwise stated.

2.3 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 in solution of products (10mg) dissolved in 800μl of deuterated solvents (such as DMSO-d_6, $CDCl_3$-d, or Acetone-d), the chemical shifts (δ) were given in ppm as either the solvent peak or TMS as the internal standard. The Degree of substitution (DS) values of the CA, CBu, CPiv and CAPiv were determined by ^1H NMR measurements of the cellulose derivatives and that were obtained by the reaction of cellulose derivatives with an excess amount of benzoyl chloride. The typical procedure is as follows: A solution of the cellulose derivatives (100 mg, 347 μmol), 4 ml $CHCl_3$, benzoyl chloride (440 mg, 3.1 mmol) and triethylamine (318 mg, 3.1 mmol) was stirred for 24 hours at room temperature. The reaction mixture was then poured into a large amount of MeOH to precipitate the products. The obtained products were collected by filtration and dried under vacuum conditions. In order to avoid potential overlapping of the aromatic protons and solvent peak, NMR measurements were conducted in DMSO-d_6. The DS values were calculated using the following equation:

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

The DS of CBn was calculated from ^{1}H NMR spectrum by the equation:

$$DS = \frac{7Iphenyl}{5IAUG}$$

Where: I_{phenyl}, the peak integral of phenyl protons, I_{AUG}, peak integral of protons of anhydroglucose unit.[76]

Size exclusion chromatography measurements for polysaccharides were performed at 40°C using Prominence gel permeation chromatography system (DGU-20A degassing unit, LC-20AD pump, SIL-20A HT auto sampler, CTO-20A column oven, and RID-20A refractive index detector) with two shodex KF-806L columns. The number average molecular weight ($M_{\mathrm{n,SEC}}$) and polydispersity ($M_{\mathrm{w}}/M_{\mathrm{n}}$) were determined by the RI based on polystyrene standards (PStQuick A and PStQuick C).

2.4 Syntheses of cellulose derivatives

2.4.1 Transesterification reaction of cellulose in EmimOAc/DMSO mixed solvents

A typical reaction based on the transesterification reaction of cellulose was carried out as follows. A solution of cellulose (120 mg, [monomeric unit]$_0$ = 0.74 mmol) in EmimOAc (4.00 g, 23.5 mmol) was dried for 16 hours under vacuum conditions at 80˚C. After drying process was finished, DMSO (4.00 mL) and IPA (4.00 mL, 36.8 mmol) were added under an argon atmosphere. After the reaction mixture was stirred for 30 minutes, the reaction mixture was diluted with CH_2Cl_2 and poured into a large amount of methanol. The obtained polymer was purified by reprecipitation (CH_2Cl_2/methanol) to yield a pale yellowish powder. Yield: 192 mg.

2.4.2 Scaling up and expanding the cellulose sources for the organocatalytic transesterifications in EmimOAc/DMSO mixed solvent systems

In an 1000ml schlenk flask equipped with a magnetic stirrer, 2.4g of cellulose materials (Avicel-Run 6, rayon-Run 7 or pulp C-Run 8, pulp B-Run 9, pulp A-Run 10) and 6.0g of EmimOAc as a solvent and an organocatalyst were added. The mixture was dried and heated at 80°C using oil bath for 3h under vacuum conditions. After drying step was completed, 80 mL of DMSO was added as a co-solvent to completely dissolve the mixture under an argon atmosphere. Then, 12 mL of IPA (the initial [IPA]/[OH] was adjusted to be 2.5/1) was added to the mixture and stirred for 18h at 80°C. At the end of the reaction, the homogeneous mixture was poured slowly into 800 mL MeOH, the precipitates were collected by filtration in duplicate. The obtained products were dried under vacuum for overnight at 50°C. Yield: 3.45 g.

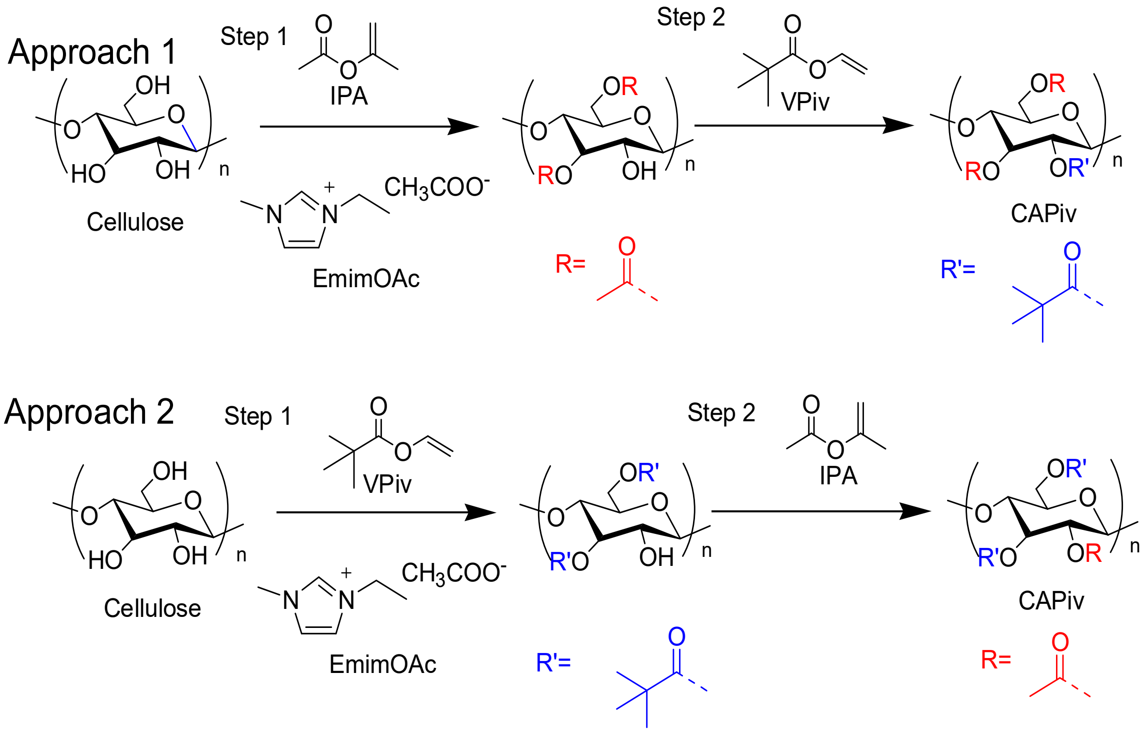
2.4.3 Synthesis of cellulose derivatives using EmimOAc or EmimOAc/DMSO with various esterification reagents

Synthesis of CA with small scale: In a schlenk flask equipped with a magnetic stirrer, 120mg (3 wt%) of cellulose (filter paper-Run 11) and 4g of EmimOAc as an organocatalyst and solvent were added. The mixture was heated at 80ºC using oil bath for 3h under vacuum conditions to get complete cellulose dissolution. Then, 4mL of IPA was added to the mixture under an argon atmosphere and stirred for different reaction time from 18h at 80ºC. At the end of the reaction, the mixture was poured slowly into methanol and filtered in duplicate. The obtained product was dried in a vacuum oven for 24h at 50ºC. Yield: 148 mg.

Synthesis of cellulose benzoate (CBn-Run 12) and cellulose pivalate (CPiv-Run 13) with large scale: In an 1000ml schlenk flask equipped with a magnetic stirrer, 2.4g of cellulose rayon and 6.0g of EmimOAc were added. The mixture was dried and heated at 80ºC using oil bath for 3h under vacuum conditions. Then, 80 ml of DMSO as a co-solvent was added to completely dissolve the mixture under an argon atmosphere, then 98 mL of VBn (or 104mL of VPiv) was added to the mixture and stirred for 1h at 80ºC. At the end of the reaction, the mixture was precipitated in 800mL MeOH and filtered in triplicate. The obtained product was dried under vacuum for overnight at 50ºC. Yield: 3.48 g (CBn); 3.12 g (CPiv).

Synthesis of cellulose acetate pivalate (CAPiv-Run 14, 16-17): The reaction procedure was shown in scheme 2.4. Cellulose (240 mg; AGU, 1.48 mmol) and 1-ethyl-3-methylimidazorium acetate (EmimOAc; 8.0 g; 47.0 mmol) were added to a schlenk flask in the argon atmosphere. The mixture was dried at 80°C under reduced pressure for 3h. Then, the amount of esterification reagents (IPA and VPiv) as shown in Table 2.3 was added under Ar condition. At the end of the reaction, the mixture was precipitated in a mixture of MeOH: H_2O and filtered in triplicate. The obtained products were dried under vacuum for overnight at 50ºC. Yield: 230 mg.

Scheme 2.4 The schematic representation of transesterification reactions of cellulose in EmimOAc with by changing the amount of IPA and VPiv



Synthesis of cellulose butyrate (CBu-Run 15): In a schlenk flask equipped with a magnetic stirrer and a condenser, 240mg of cellulose and EmimOAc as an organocatalyst (0.25 mole equivalent) was added. The mixture was heated at 80°C using oil bath for 3h in vacuum conditions. Then, 2mL of DMSO as a co-solvent was added to dissolve the mixture under an argon atmosphere. Thereafter, VBu with the amount is 16 mole equivalent to molar amount of hydroxyl group in an AGU was added to the mixture and stirred for overnight. At the end of the reaction, the mixture was evaporated and poured slowly in methanol and filtered in duplicate. The obtained product was dried in a vacuum oven for 24h at 50°C. Yield: 344 mg.

2.5 Results and discussion

2.5.1 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. Due to high viscosity and cost associated with the use of Im-ILs, the cellulose modification reaction was optimized in our latest work.[66] In this context, the optimized reaction was employed for our study. 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 transesterification reaction was conducted for 18h under Ar atmosphere at 80ºC. As already reported, the cellulose transesterification reaction led to cellulose acetate featuring high degree of substitution (DS) value of 2.95. After the cellulose acetate was isolated by a simple reprecipitation into MeOH, the resultant MeOH layer was subject to evaporation and subsequently high vacuum distillation (Scheme 2.5). This gave the employed EmimOAc in 99.2 wt % recovery ratio (Run 1, Table 2.1). As shown in the ^{1}H NMR spectrum of the recovered EmimOAc depicted in Figure 2.3, 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 2.1), cellulose acetate 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 2.1). 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 three times.

Scheme 2.5 Recyclable reaction of cellulose in EmimOAc/DMSO mixed solvent system

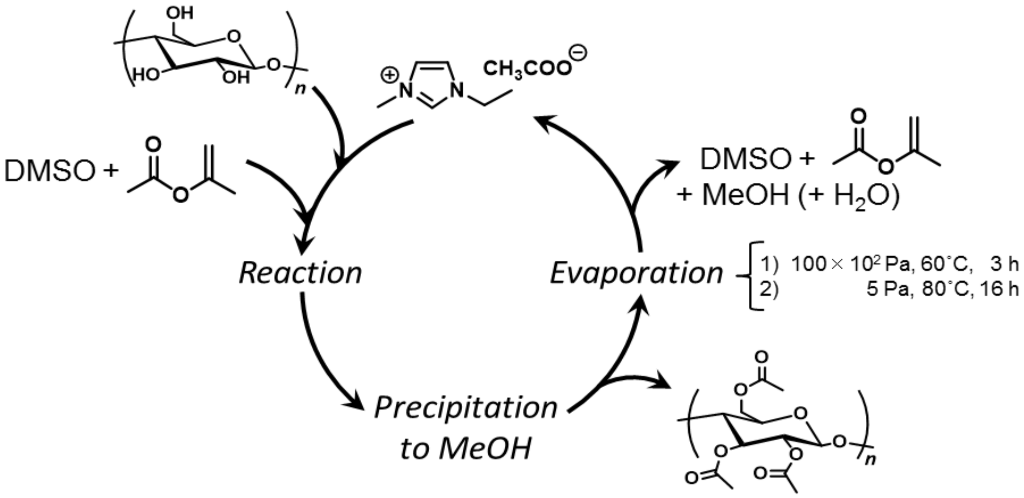


Table 2.1. Recycling EmimOAc in the cellulose modification reactions in EmimOAc/DMSO mixed solvent systems [a]

Run	EmimOAc	DS values[b]	Recovery rate of EmimOAc [wt %][c]	$M_{\mathrm{n,SEC}}$ [d]	M_w/M_n [d]
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

[a] The reaction conditions for the transesterification reactions of cellulose with IPA are as follows; EmimOAc as a solvent and an organocatalyst; the reaction was conducted for 18 hours; 4 mL of DMSO was used as a co-solvent; 120 mg of cellulose was used as a starting compound; initial [IPA]/[OH] was adjusted to be 16.5/1; Ar atmosphere. [b] Determined by ^{1}H NMR measurements in DMSO-d_6. [c] The recovery ratio was determined after vacuum drying of the resultant EmimOAc. [d] Determined from SEC measurement in $CHCl_3$ using polystyrene standards.

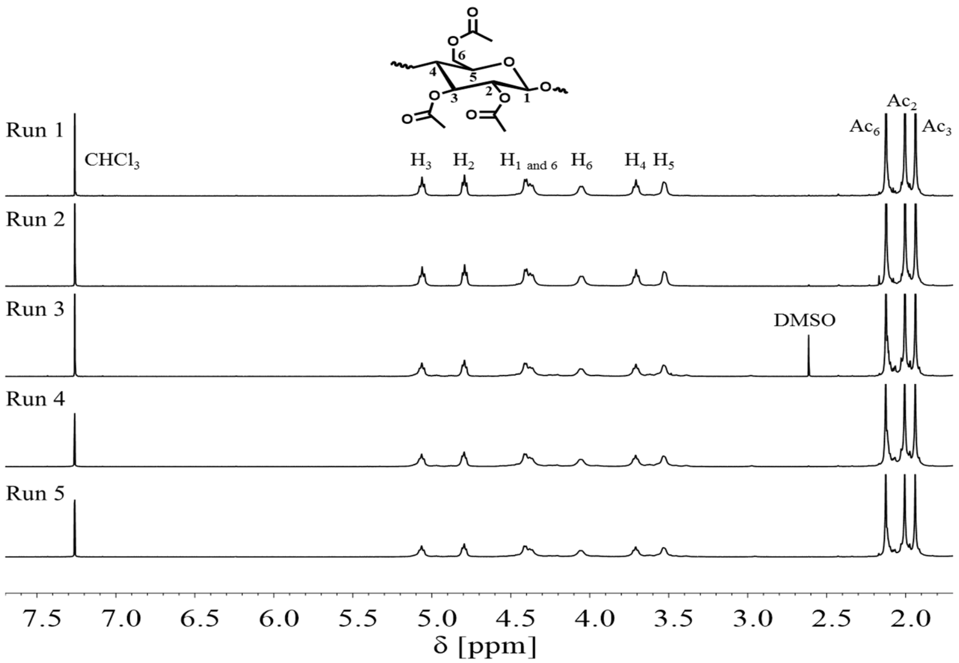


Figure 2.3. ^{1}H NMR spectra in $CDCl_3$ of the obtained CAs (Table 2.1, Runs 1-5).

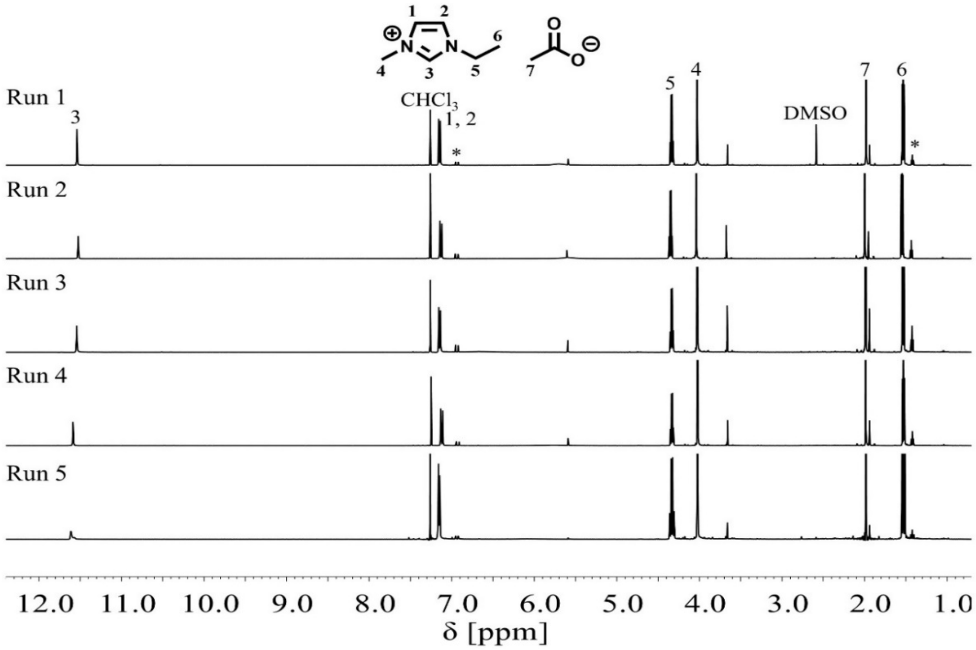


Figure 2.4 ^{1}H NMR spectra in CDCl$_3$ of the recovered EmimOAc after the cellulose modification reactions (Table 2.1, Runs 1-5).

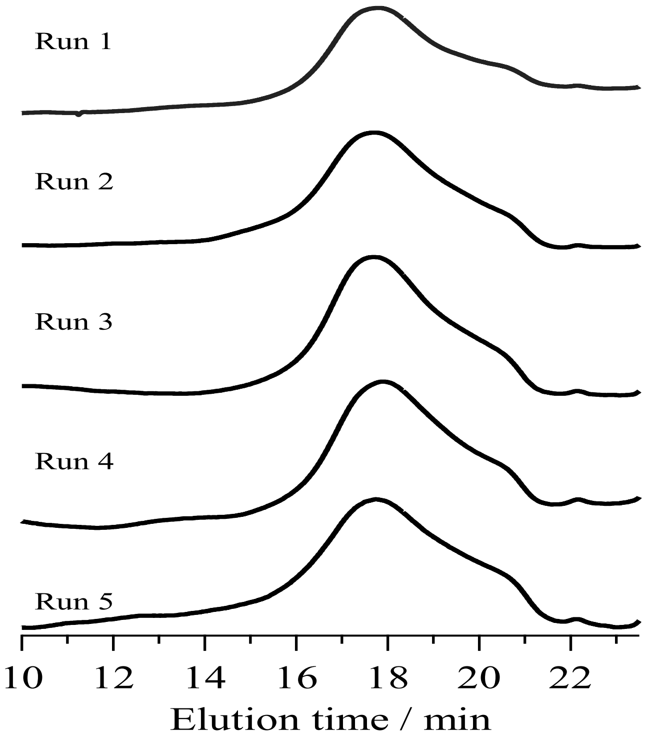


Figure 2.5 SEC traces of the obtained CA (solvent, CHCl$_3$; flow rate, 1.0 mL min^{-1}).

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

As precisely discussed in the previous section, the facile recyclability and reusability of the employed EmimOAc were validated. Next, we turned our attention to a practical aspect of the cellulose modification protocol. 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. Apart from synthetic polymers, the source of naturally occurring polymers shows a decisive impact on their materials natures despite their identical monomeric structures. In the case of cellulose, the cellulose source could lead to a clear discrepancy in its molecular weights. In this context, we verified a tolerance of our synthetic protocol toward above-mentioned points. First, scaling-up of our previously reported protocol with standard cellulose of avicel was targeted as shown in Run 5 (Table 2.1). The reaction scale of the cellulose modification reaction 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 by simply scaling up the original reaction conditions, demonstrating that the reported synthetic protocol is indeed reliable and robust. Next, a range of cellulose source was utilized for the cellulose modification reactions. In addition to avicel, pulps and rayon were examined as the cellulose source (Runs 6 ~ 10, Table 2.2) where pulp 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 cellulose acetates with high DS values (~ 2.9).

Table 2.2 A large scale cellulose modification reactions by using a range of cellulose sources[a]

Run	Cellulose (source)	DS values [b]	$M_{\mathrm{n,SEC}}$ [c]	M_w/M_n [c]
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

[a] The reaction conditions for the transesterification reactions of cellulose with IPA are as follows; 6g of EmimOAc as a solvent and an organocatalyst; the reaction was conducted for 18 hours; 80 mL of DMSO was used as a co-solvent; 2.4 g of cellulose was used as a starting compound; initial [IPA]/[OH] was adjusted to be 2.5/1; argon atmosphere. [b] Determined by ^{1}H NMR measurements in DMSO-d_6. [c] Determined from SEC measurement in $CHCl_3$ using polystyrene standards. [d] insoluble in $CHCl_3$ under the SEC measurement condition.

2.5.3 Physicochemical characterizations of cellulose derivatives synthesized by using EmimOAc or EmimOAc/DMSO with various ester donating reagents

FT-IR analysis: The transesterification reaction of cellulose could lead to the substitution of OH groups in cellulose with carbonyl groups, which can be confirmed by FT-IR spectra with scanning range from 500 to 4000 cm^{-1} depicted in Figure 2.6. In the IR spectrum of unmodified cellulose (A), there are several discernible peaks between 930 cm^{-1} and 1200 cm^{-1}, which were attributed to the characteristic absorption of cellulose backbone. The peaks at 1080 and 1021 cm^{-1} were ascribed to C-O bond stretching of C-O-C group in the anhydrous glucose ring, and the characteristic peak at 1155 and 930 cm^{-1} was due to the stretching of the C-OH bond in anhydroglucose units (AGU) and the whole glucose ring stretching vibrations, respectively.[77, 78] In addition, an extremely broad band at 3390 cm^{-1} was originated from the vibration of the hydroxyl groups (O-H) of cellulose.

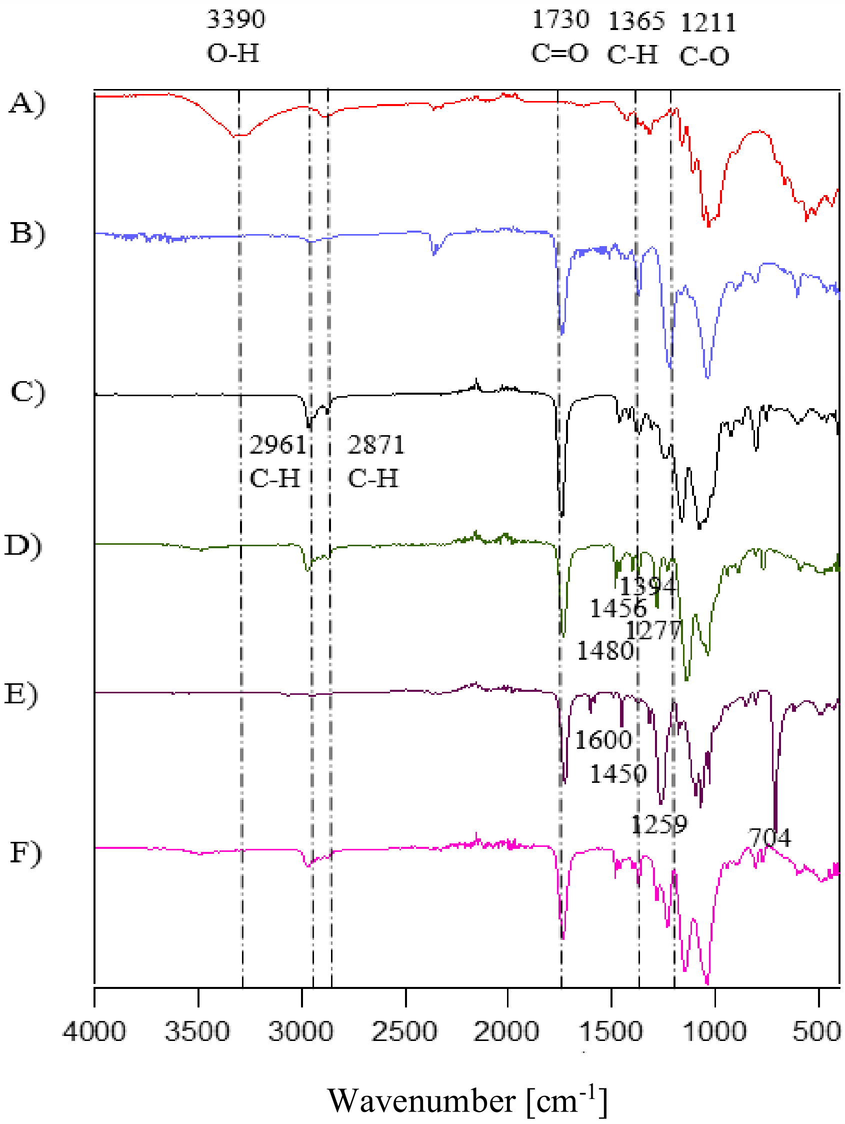


Figure 2.6 FT-IR spectra of cellulose (A), CA–Run 11 (B) and CBu-Run 15 (C), CPiv-Run 13 (D), CBn-Run 12 (E), and CAPiv-Run 14 (F).

IR measurements of all the obtained cellulose derivatives indicated that the clear band at 1730 cm^{-1} due to the ester stretching developed after reaction. FT-IR spectrum of CA-Run 11 (B) showed some new absorption peaks besides the characteristic absorption peaks of cellulose. The peak at 1730 cm^{-1} was attributed to carbonyl C=O vibrations, and the absorption bands at 1365 and 1211 cm^{-1} were associated with CH_3 symmetry deformation vibration and C-O stretching vibration, respectively,[67] these peaks were also observed in the spectrum of CBu-Run 15 (C), the peaks between 2871 and 2961 cm^{-1} due to C-H stretching.[79] FT-IR spectra of CPiv-Run 13 (D) and CAPiv-Run 14 (F) showed some new absorption peaks at 1730 cm^{-1} for C=O, the peaks at 2961 and 2871 cm^{-1} for C-H stretching, the peaks at 1480, 1456, 1394 cm^{-1}for $v(C(CH_3)_3$, the peak at 1277cm^{-1} for (C-O-C).[80] FT-IR spectrum of CBn-Run 12 (E) provided some important peaks at 1730 cm^{-1} for C=O stretching in ester, 1259 cm^{-1} for stretching of (O) C-O, 1600 and 1450 cm^{-1} for aromatic C=C stretching and 704 cm^{-1} for the out-of-plane C-H bending of the monosubstituted benzene.[81]

^{1}H NMR analysis: Representative ^{1}H NMR spectra of CA (Run 6-11), CBn CPiv, CAPiv and CBu (Runs 12-15) are shown in Figure 2.7 and Figure 2.8.

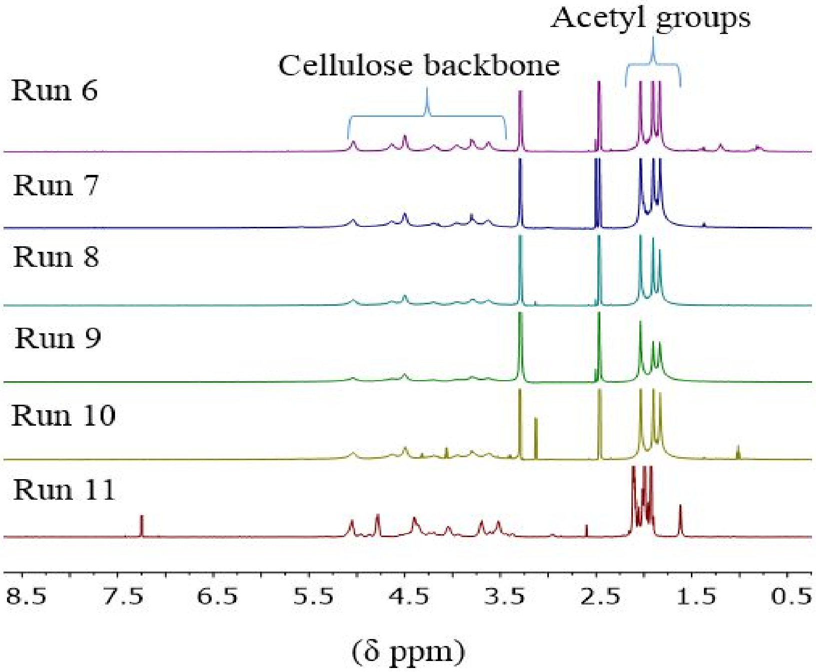


Figure 2.7 ^{1}H NMR spectra of CA synthesized from different cellulose materials recorded in DMSO-d_6 (Runs 6-10) and $CDCl_3$ (Run 11).

The peaks arising from the ring-protons of the sugar backbone were seen in the region ranging between 3.0 and 5.3 ppm. The signals of protons of acetyl groups (CH_3) appeared in the spectra between 1.6 and 2.3 ppm,[67] from 1.1 to 1.23 ppm (CH_3-pivalate).[81] The signals of protons in CBu (Run 15) spectrum appeared at 0.92 ppm (-CH_2-CH_2-C$\underline{H_3}$), 1.6 ppm (-CH_2-C$\underline{H_2}$-CH_3), and 2.3 ppm (-C$\underline{H_2}$-CH_2-CH_3), which confirm the butyration of cellulose.

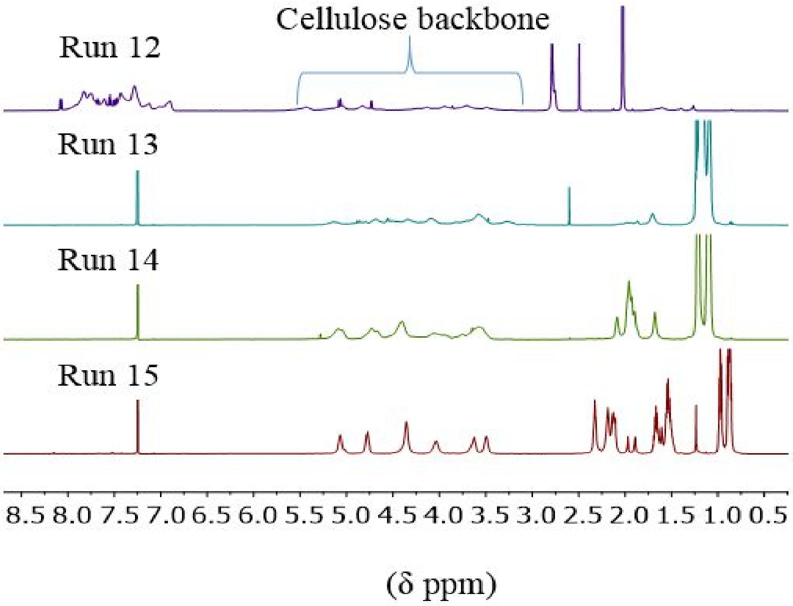


Figure 2.8 ^{1}H NMR spectra of CBn-Run 12 recorded in acetone-*d_6*, CPiv-Run 13, CAPiv-Run 14, and CBu-Run 15 recorded in $CDCl_3$.

The signals observed in spectrum of CBn (Run 12) from 6.8 to 8.2 ppm due to phenyl protons,[82] The solvent peaks from DMSO, $CDCl_3$ and the peak of residual water are located at 2.5 ppm, 7.25 ppm and 3.33 ppm, respectively. Based on these data, the cellulose derivatives were confirmed the successful syntheses of CA, CBu, CPiv, CBn and CAPiv which were formed during the transesterification process using the EmimOAc or EmimOAc/DMSO mixed solvent.

Degree of substitution (DS): The DS values of these cellulose derivatives were determined to provide a detailed structural insight into the synthesized cellulose derivatives. The DS values were calculated based on ^{1}H NMR measurements of the cellulose derivatives that were obtained by the benzoylation reactions of the obtained cellulose derivatives with benzoyl chloride in $CHCl_3$ with Net_3 as a proton scavenger.[67] The DS values of cellulose derivatives synthesized in EmimOAc and EmimOAc/DMSO under various conditions are presented in Table 2.3.

Table 2.3 Synthesis of cellulose derivatives with various DS value at 80°C under different conditions

Run	Starting material (amount / mg)	EmimOAc / g	Ester reagents (amount / ml)	DMSO /ml	Time / h	DS
11	Filter paper (120)	4	IPA (4)	-	18	2.93
12	Rayon (2400)	6	VBn (98)	80	1	2.78
13	Rayon (2400)	6	VPiv (104)	80	1	2.55
14	Avicel (240)	8	VPiv (0.44) IPA (9.23)	-	16 +3	1.27 +1.39
15	Avicel (240)	0.189	VBu (7.3)	2	18	2.93
16	Avicel (240)	8	VPiv (0.73) IPA (9.23)	-	16 +3	1.26 +1.42
17	Avicel (240)	8	IPA (0.33) VPiv (11.0)	-	16 +3	1.01 +1.45

The DS values of CA (Run 6-11: avicel, rayon, pulp C, B, A, and filter paper) synthesized for 18h at 80°C were calculated by 2.96, 2.94, 2.91, 2.96, 2.88, and 2.93, respectively. CBn-Run 12, CPiv-Run 13 were synthesized from rayon for 1h also presented high DS of 2.78 and 2.55, respectively. The DS value of CBu-Run 15 was calculated by 2.93. Regioselective CAPiv-Run 14, 16-17 (from Avicel) were carried out showing the DS_{acetyl} of 1.27, 1.26, 1.01 and the $DS_{pivaloyl}$ of 1.39, 1.42 and 1.45, respectively. The results showed that the high efficient TER of cellulose from different cellulose materials in a homogeneous system composed EmimOAc and EmimOAc/co-solvent DMSO without any additional catalysts and corrosive chemicals were successfully proceeded.

2.6 Conclusions

As successfully demonstrated, the Im-IL catalyzed transesterification was revealed to show not only robustness on gram-scale synthesis but also sufficient green nature with high recyclability. The TER of a series of cellulose materials using homogeneous system composed EmimOAc or EmimOAc/DMSO with IPA/VBu/VPiv/VBn as donating ester reagents without using additional catalysts and corrosive chemicals were successfully accomplished affording cellulose derivatives. The structural characterization of the obtained products were confirmed by FT-IR and ^{1}H NMR analyses indicated that CA, CBu, CPiv, CBn and CAPiv with high DS values were successfully synthesized in short reaction time. The $M_{n,SEC}$ and M_w/M_n were determined by the SEC measurements, which indicated the Im-IL-catalyzed TER was the mild reaction without any cellulose decompositions. The chemical modification of various cellulose sources in EmimOAc or EmimOAc/DMSO mixed solvent is a sustainable and effective method for synthesizing cellulose derivatives in industry. The obtained results should shed light on the synthetic utility of Im-ILs in polymer sciences from the view point of not only a green solvent but also a recyclable organocatalyst.

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Chapter 3 Synthesis and characterization of xylan, dextrin, pullulan derivatives and kinetic evolution of the TER of polysaccharides in EmimOAc

In this chapter, the Im-IL catalyzed transesterification was applied to other kinds of polysaccharides such as xylan, dextrin, and pullulan. In order to show the applicability of the Im-IL catalyzed transesterifications, the EmimOAc-catalyzed cellulose modification, which mentioned in previous chapter, was expanded to gram-scale reaction. The TER of xylan, dextrin and pullulan was investigated using the homogeneous system composed EmimOAc or EmimOAc/DMSO with IPA or VBu as esterification reagents without using additional catalysts and corrosive chemicals. FT-IR and ^{1}H NMR measurements were used confirming the successful synthesis of high DS values of xylan, dextrin, and pullulan derivatives bearing acetyl and butyryl groups. In addition, SEC measurements indicated that the obtained products had no decomposed compound during the EmimOAc-catalyszed TER. The amount of IPA, reaction time and temperature are important factors, which significantly affected on the efficiency of TER of polysaccharides in EmimOAc. The thermal stability (based on the TGA measurement), and the solubility behavior of these polysaccharide derivatives in commercial organic solvents were significantly improved after transesterification.

3.1 Introduction

Recently, the environmental pollution, climate change and energy security are global issues because of the increasing rate of petroleum usage and the depletion of its reserves. The necessary to look for an alternative and renewable materials has been required to replace the petroleum-based resources, which were mainly used to produce fuels, chemical and materials. Plant biomass has been considered as a potential renewable resources because it supplies a huge amount of polysaccharides. Plant polysaccharides, a group of biopolymers such as cellulose and starch which have been isolated and used as substrates for chemical modification to produce plastics, films and nanofibers.[1-3]

Hemicelluloses are a class of heteropolysaccharides which were extracted from plant cell wall by water and/or aqueous alkali.[4] After cellulose, hemicelluloses are the second most abundant polysaccharide family which comprise about 25-35% of the plant's materials, forest and agricultural wastes.[5-8] Hemicelluloses are divided into four general classes due to the differences of structural polysaccharide types such as xylans, mannans, glucans and xyloglucan.[9] Hemicellulose chains are formed by the majority of β-(1→4) D-xylopyranoside monomer units which are maned xylans (Figure 3.1). Xylans can be found in hardwood species, grasses and agro-industrial by-products such as cereal straws, sugarcane bagasse, corn stover and wood sawdust.[10] Xylan comprises 10-15% in softwoods, 10-35% in hardwoods up to 40% of agricultural residues in annual plants dry weight.[11] Chemical modifications of xylan, especially esterification is one of the most important procedure to introduce the functional groups with various valuable properties into structure of xylan. The obtained xylan esters with lower hydrophilicity can be applied as bioactive polymers,[12] biodegradable plastics,[13] and coating materials in paint industry.[14] Using alkaline catalyst in polar solvents

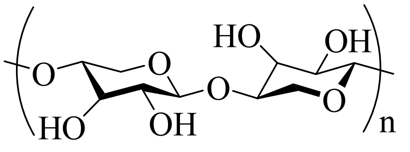


Figure 3.1 Structure of xylan

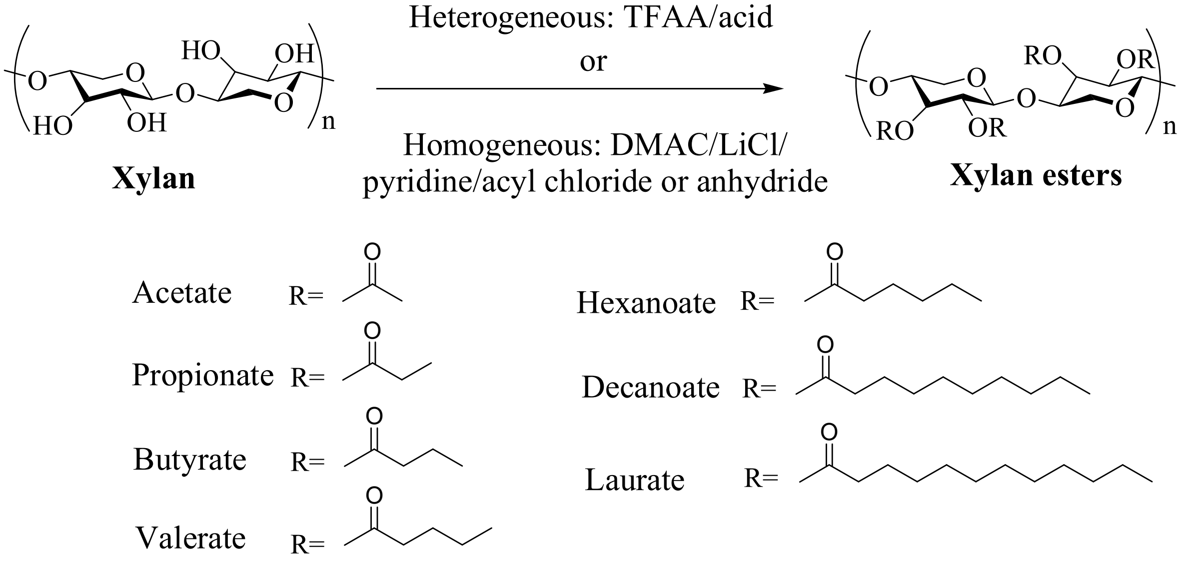
is a standard method for producing hemicellulose esters with high DS values from corn cob under optimized conditions.[15-17] The esterification of arabinoxylan from wheat straw or rye straw in homogeneous system of DMA/LiCl as a solvent in the presence of DMAP as a catalyst and acetic anhydride or HCl as esterifying reagents had already been explored and developed.[18-22] The esterification of anhydrous gel of wheat straw hemicellulose was improved by using DMF/LiCl in the presence of *N*-bromosuccinimide (NBS) as a catalyst under conditions of microwave heating for 5min at 78℃ resulting the DS up to 1.34.[23] Xylan acetates with different DS values were successfully synthesized in homogeneous conditions of DMF/LiCl/acetic anhydride/DMAP and listed in Table 3.1.[24]

Table 3.1 Degree of substitution (DS) of and yield of xylan acetate synthesized under various conditions in DMF/LiCl

Entry	Ac_2O (equiv/X.U)	Temp (°C)	Time (h)	DS	Conversion (%)	Mass yield (%)
1	1	85	2	0.9	90	87
2	3	85	2	2.0	67	75
3	1.5	85	2	1.4	93	81
4	1.5	35	2	1.2	80	84
5	1.5	65	2	1.4	93	83
6	1.5	85	1	1.4	93	84
7	1.5	85	4	1.5	100	77

Synthesis of xylan acetates were conducted by homogeneous system in DMAC/LiCl/pyridine at 50°C resulting complete acetylation within 6 h.[25] Xylan esters with different alkyl chain lengths (C2-C12) were also synthesized by heterogeneous and homogeneous reactions and depicted in Scheme 3.1.[26]

Scheme 3.1 Schematic representation of xylan esters in heterogeneous or homogeneous systems



Dextrin is low-molecular weight polysaccharide synthesized by acid or/and enzymatic partial hydrolysis of starch or glycogen. The structure of dextrin is consisted of α-(1→4) linked D-glucose structure of amylose and the α-(1→4) and lower polymerization of α-(1→4,6) linked D-glucose branched structure of amylopectin (Figure 3.2).[27,28] The degree of hydrolysis is indicated in terms of dextrose equivalent (DE). The same DE dextrin can display different properties such as hygroscopicity, fermentability, viscosity, sweetness, stability, solubility, and bioavailability because of distinct structural features,[29] the source of the native starch and the hydrolysis conditions. Dextrin is known a natural and processed carbohydrate-based raw polymeric material, generally regarded as safe (GRAS),[30] renewable, biodegradable, and non-toxic.[31, 32] It is applied widely in industry such as adhesives, foods, textiles and cosmetics,[33] drug delivery solution[34, 35] and wound dressing agent.[36] Dextrin-based

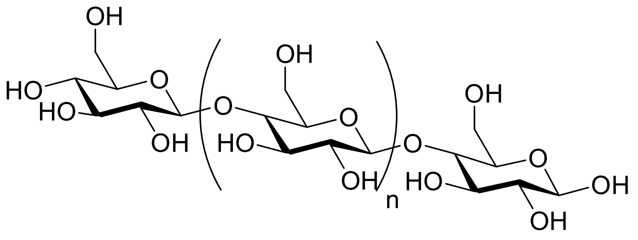


Figure 3.2 Structure of dextrin[28]

hydrogels were created by radical polymerization.[37-40] Oxidized dextrin hydrogel cross-linked using adipic acid dihydrazide was described.[41] Stearic acid dextrin ester was synthesized by using lipase as a catalyst.[42] The characterization of cationic dextrin obtained by ultrahigh pressure-assisted cationization reaction between dextrin and 2,3-epoxypropyltrimethylammonium chloride was discussed.[43]

Pullulan is introduced firstly in 1938 by Bauer obtaining from fermented starch broth by strain of fungus *Aureobasidium pullulans*.[44] Pullulan is a linear polysaccharide, its structure consists of α-(1→4) glycosidic bond within maltotriose repeating units, which is connected by α-(1→6) linkages (Figure 3.3).[45]

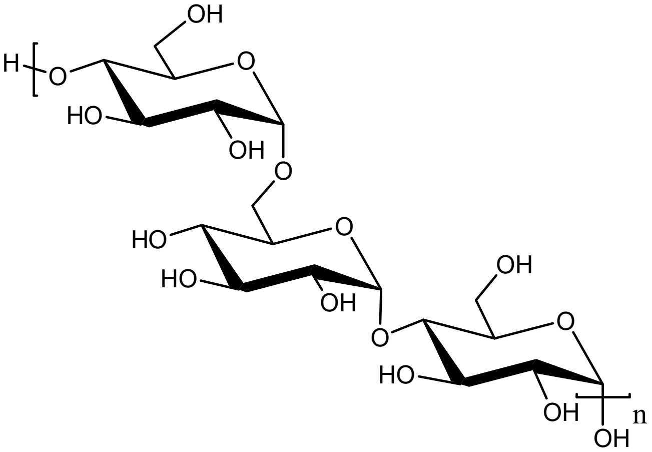
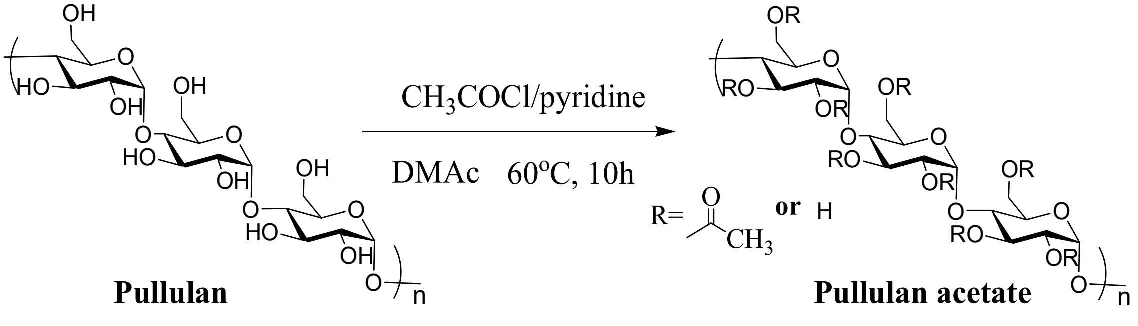


Figure 3.3. Structure of pullulan

Pullulan is high molecular weight from 4.5×10^4 to 6×10^5 Da depending cultivation conditions such as culture strain, pH and substrates used.[46] Because of its unique structure, pullulan has valuable properties such as water-soluble, non-ionic, blood compatible, biodegradable, non-toxic, non-immunogenic, non-mutagenic and non-carcinogenic,[47] adhesive ability, fiber forming capacity, and thin biodegradable films, which are transparent and impermeable to oxygen.[45] Pullulan has been used in various fields especially in food manufacturing and pharmaceutical industry. The applications of pullulan have been reviewed comprehensively.[47-49]

Pullulan modification methods have been developed and reported. The synthesis and characterizations of palmitoyl[50] and cholesteryl[51] modified pullulan derivatives, and the synthesis of adenine, thymine, and pyrene modified pullulan derivatives.[52] Chloroalkylation,[53] nitroalkylation,[54] alkyl etherification,[55] and modification with isocyanates[56] and mesyl chloride[57] have also been carried out and reported. The modification of pullulan acetate for adhesives,[58] and the plasticization of pullulan with acetic anhydride have been reported.[59] The morphology and self-association behavior of pullulan acetate has been investigated to control drug release.[60] Pullulan acetate was prepared by the reaction of pullulan with acetyl chloride in the presence of pyridine without reducing molecular weight, and thermal, mechanical and biodegradable properties were described and depicted in Scheme 3.3.[61] Recently, ionic liquids, new class of solvents has emerged. These solvents are often fluid at or close to room temperature.[62] ILs have many fascinating properties such as very low vapor pressure.[63] Therefore, ILs can be used to replace the employment of volatile organic compounds (VOCs), a significant source of environmental pollution.[64] ILs have been enormous concerns as media for green synthesis. ILs were used as a solvent for acetylation of hemicellulose with the catalyst of iodine resulting DS values of products from 0.49 to 1.53.[65] However, the employment of ILs for synthesis of dextrin and pullulan derivatives has not been reported.

Scheme 3.2 Schematic representation of pullulan acetate in DMAc/pyridine/CH_3COCl



This chapter presents the synthesis of xylan, dextrin, and pullulan derivatives by the EmimOAc or EmimOAc/DMSO catalyzed TER with the donation of IPA and VBu. The reaction-scale of the TER of these polysaccharides in a mixed solvent of EmimOAc and DMSO was expanded by 20 times of initial starting compounds (Scheme 3.3). In addition, the modification of the polysaccharides was explored by the kinetic evolution changing the amount of IPA, reaction time, and reaction temperature. Moreover, the thermal properties of the obtained derivatives were also characterized by TGA. Finally, the solubility behavior of these polysaccharide esters in commercial organic solvents was also investigated.

3.2 Materials

1-Ethyl-3-methylimidazorium acetate (EmimOAc; 95 %), dichloromethane, methanol, chloroform, deuterated NMR solvents (DMSO-*d*$_6$, $CDCl_3$-*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) were purchased from Tokyo Chemical Industry Co., Ltd, Japan and used as received. As the polysaccharide sources, xylan and pullulan were purchased from Tokyo Chemical Industry Co., Ltd, Japan, dextrin was purchased from Nacalai, Kyoto, Japan. All other chemicals such as dimethyl sulfoxide (DMSO, anhydrous >99.9%), benzoyl chloride were commercially available and used without further purification unless otherwise stated.

3.3. Characterization methods

The FT-IR spectra were observed by a Thermo Fisher Scientific Nicolet iS10 equipped with an ATR unit. All the ^{1}H NMR spectra were recorded by JEOL 400 and 600 MHz FT-NMR spectrometers in solution of products (10mg) dissolved in 800μL of deuterated solvents (such as DMSO-*d*$_6$, $CDCl_3$-*d*) the chemical shifts (δ) were given in ppm as either the solvent peak or TMS as the internal standard. The Degree of substitution (DS) values of the XA, XBu, DA, DBu, PuA and PuBu were determined by ^{1}H NMR measurements of the xylan, dextrin and pullulan derivatives and that were obtained by the reaction of these derivatives with an excess amount of benzoyl chloride. The typical procedure is as follows: A solution of the these derivatives (100 mg, 347 μmol), 4 mL $CHCl_3$, benzoyl chloride (440 mg, 3.1 mmol) and triethylamine (318 mg, 3.1 mmol) was stirred for 24h at room temperature. The reaction mixture was then poured into a large amount of MeOH to precipitate the products. The obtained products were collected by filtration and dried under vacuum conditions. In order to avoid potential overlapping of the aromatic protons and solvent peak, NMR measurements were conducted in DMSO-*d*$_6$. The DS values of XA and XBu were calculated using the following equation (1) the DS values PuA, PuBu, of DA and DBu were determined by the followed equation (2):

(1) $$DS = \frac{peak\ area\ (CH3)/3}{peak\ area\ (CH3)/3 + peak\ area\ (7.0\sim 8.5ppm)/5}\ x\ 2$$

(2) $$DS = \frac{peak\ area\ (CH3)/3}{peak\ area\ (CH3)/3 + peak\ area\ (7.0\sim 8.5ppm)/5}\ x\ 3$$

For the kinetic evolution of DS values for XA and PuA synthesized by TER in EmimOAc, the DS values of XA was calculated by the equation (3)[24] and the DS values of PuA was determined using the equation (4)[66]

(3) $$DS = \frac{6Imethyl}{3Icarbohdrate}$$

Where: I_{methyl}: area of methyl protons of esters chains at 1.9-2ppm

$I_{carbohydrate}$: sum of areas of six protons in anhydroxylose unit

(4) $$DS = \frac{peak\ area\ (CH3)/3}{peak\ area\ (ring\ H)/7}$$

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 (DGU-20A degassing unit, LC-20AD pump, SIL-20A HT auto sampler, CTO-20A column oven, and RID-20A refractive index detector) with two shodex KF-806L columns. 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.

3.4 Synthesis of xylan, dextrin and pullulan derivatives

Synthesis of xylan acetate (XA-Run 27-35, Table 3.2): In a schlenk flask equipped with a magnetic stirrer, 120mg of xylan and 4g of EmimOAc as a catalyst and solvent were added. The mixture was heated at 80°C using oil bath for 3h under vacuum condition to dissolve xylan completely. Then, 4mL of IPA was added to the mixture under an argon atmosphere and stirred from 5min to 16h at 80°C. At the end of the reaction, the mixture was diluted with CH_2Cl_2 and poured slowly into a large amount of methanol and filtered in duplicate to get purified polymer. The obtained product was dried in a vacuum oven for 24h at 50°C. Yield: 85.9mg

Synthesis of xylan vinyl butyrate (XB-Run 36, Table 3.2): In a schlenk flask equipped with a magnetic stirrer and a condenser, 240mg of xylan and EmimOAc as a catalyst (0.25 mole equivalent) was added. The mixture was heated at 80°C using oil bath for 3h in vacuum condition. Then, 2mL DMSO was added as a solvent to dissolve the mixture under an argon atmosphere. Thereafter, VBu with the amount is 16 mole equivalent to molar amount of hydroxyl group in an anhydroxylose unit (XU) was added to the mixture and stirred for 18h. At the end of the reaction, the mixture was evaporated and poured slowly in methanol and filtered in duplicate. The obtained product was dried in a vacuum oven for 24h at 50°C. Yield: 264mg

Synthesis of dextrin acetate (DA- Run 38-55, Table 3.3): In a 25mL schlenk flask equipped with a magnetic stirrer, 120mg of dextrin (3wt%) and 4g of EmimOAc as a catalyst and solvent were added and heated to 80°C using oil bath for 3h under vacuum condition to get complete dextrin dissolution. Then, various concentrations of IPA to the OH groups ratios were added to this solution under an argon atmosphere and stirred from 5min to 18 hours at a range of temperature between 40 and 80°C. At the end of the reaction, the mixture was dropped into a mixture of MeOH: H_2O and filtered in duplicate. The obtained products were dried in a vacuum oven for 24h at 50°C. Yield: 114.2mg

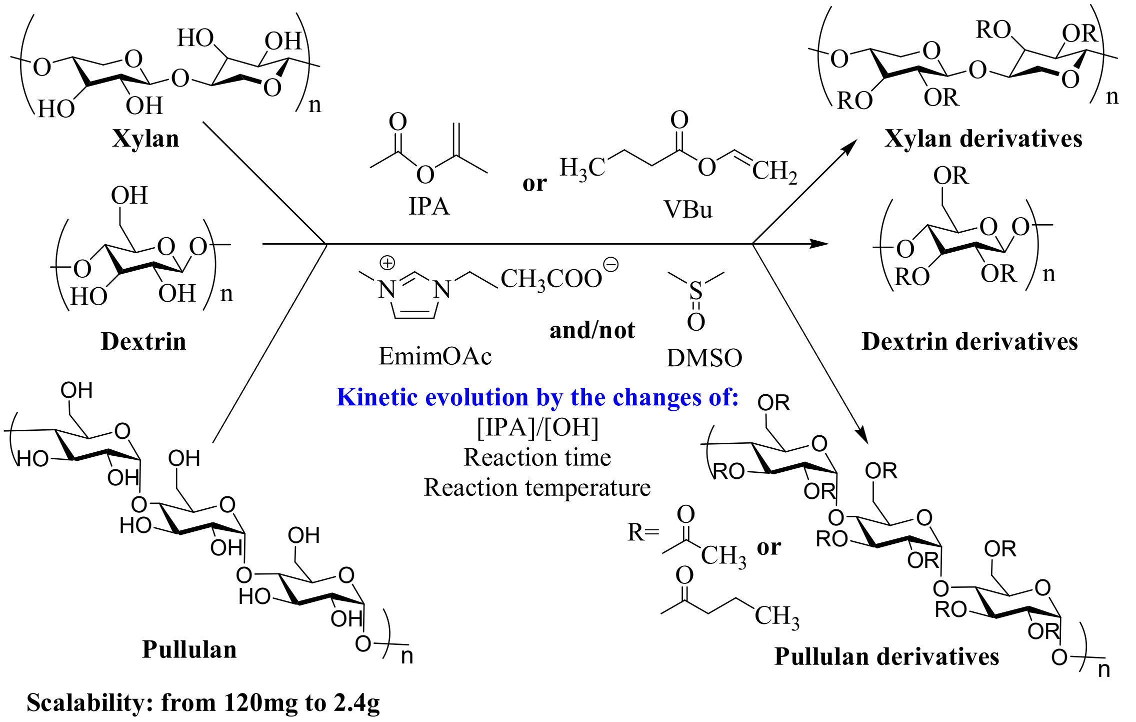
Synthesis of dextrin butyrate (DBu- Run 56, Table 3.3): In a schlenk flask equipped with a magnetic stirrer, 240mg of dextrin and EmimOAc as a catalyst (0.25 mole equivalent) was added. The mixture was heated at 80ºC using oil bath for 3h in vacuum condition. Then, 2mL DMSO was added as a solvent to dissolve the mixture under an argon atmosphere. Thereafter, VBu with the amount is 16 mole equivalent to molar amount of hydroxyl group in an AGU was added to the mixture and stirred for 18h. At the end of the reaction, the mixture was evaporated and poured slowly in into a mixture of MeOH: H_2O and filtered in duplicate. The obtained product was dried in a vacuum oven for 24h at 50ºC. Yield: 235.9mg

Synthesis of pullulan acetate (PuA-Run 58-63, Table 3.4): In a schlenk flask equipped with a magnetic stirrer, 240mg of pullulan and 8g of EmimOAc as a catalyst and solvent were added. The mixture was dried at 80ºC using oil bath for 3h under vacuum condition, 4mL DMSO was added as a solvent under an argon atmosphere to get complete pullulan dissolution. Then, 8ml of IPA was added to per mixture under an argon atmosphere and stirred from 5min to 16h at 80ºC. At the end of the reaction, the mixture was poured slowly into methanol and filtered in duplicate. The obtained product was dried in a vacuum oven for 24h at 50ºC. Yield: 223.9mg

Synthesis of pullulan butyrate (PuBu- Run 64, Table 3.4): In a schlenk flask equipped with a magnetic stirrer and a condenser, 240mg of pullulan and EmimOAc as a catalyst (0.25 mole equivalent) was added. The mixture was heated at 80ºC using oil bath for 3h in vacuum condition. Then, 2ml DMSO was added as a solvent to dissolve the mixture under an argon atmosphere. Thereafter, vinyl butyrate with the amount is 16 mole equivalent to molar amount of hydroxyl group in an AGU was added to the mixture and stirred for overnight. At the end of the reaction, the mixture was evaporated and poured slowly in methanol and filtered in duplicate. The obtained product was dried in a vacuum oven for 24h at 50ºC. Yield: 400mg

Synthesis of xylan, dextrin and pullulan acetates (expanded gram-scale, Run 37- Table 3.2, Run 57-Table 3.3, Run 65-Table 3.4): In an 1000ml schlenk flask equipped with a magnetic stirrer, 2.4g of xylan or dextrin or pullulan and 6.0g of EmimOAc as a solvent and an organocatalyst were added. The mixture was dried under elevated temperature at 80°C using oil bath for 3 h under vacuum conditions. After drying step was completed, 80 mL of DMSO was added as a co-solvent to completely dissolve the mixture under an argon atmosphere. Then, 12 mL of IPA (the initial [IPA]/[OH] was adjusted to be 2.5/1) was added to the mixture and stirred for 18h at 80°C. At the end of the reaction, the homogeneous mixture was poured slowly into 800 mL MeOH (in case of Run 37 and Run 57) or into 800 mL a mixed of MeOH: H_2O (in case of Run 65), the precipitates were collected by filtration in duplicate. The obtained products were dried under vacuum for overnight at 50°C. Yield: XA (3.2g), DA (2.08g), and PuA (3.2g)

Scheme 3.3 Schematic representation of synthesis of xylan, detrin and pullulan derivatives using EmimOAc as both solvent and organocatalyst or a mixed solvent of EmimOAc/DMSO



3.5 Characterizations of xylan, dextrin and pullulan derivatives

Xylan, dextrin and pullulan derivatives were successfully synthesized by the transesterification reaction of xylan, dextrin and pullulan with IPA or VBu using EmimOAc as both solvent and organocatalyst or a mixed solvent of EmimOAc and DMSO. The structures of the obtained polymers were demonstrated. The kinetic evolution of DS values for polysaccharide acetates synthesized in EmimOAc, characterizations and solubility behavior were also discussed.

The structural determinations of these derivatives were clearly elucidated by the employment of FT-IR measurement depicted in Figure 3.4 and ^{1}H NMR spectroscopy presented from Figure 3.5 to Figure 3.8.

FT-IR analysis: The transesterification reaction of xylan, dextrin and pullulan could result in the substitution of hydroxyl groups in the structures of these polysaccharides with carbonyl groups, which can be elucidated by FT-IR spectra with scanning region between 500 and 4000 cm^{-1} depicted in Figure 3.4. This Figure shows the FT-IR spectra of native polysaccharides and their derivatives. The FT-IR spectra of xylan, dextrin and pullulan indicate that the peak at 3295 cm^{-1} is due to O-H stretching vibrations, a small peak at 2879 cm^{-1} is assigned to the stretching vibrations of C-H, stretching vibrations of C-O-C appeared at 1139 and 983 cm^{-1}.[39] In all the FT-IR spectra of polysaccharide acetates (XA, DA, PuA) and polysaccharide butyrates (XBu, DBu and PuBu), some new additional peaks were observed comparing with those of native polysaccharides. The strong and sharp peak at 1735 cm^{-1} due to ester stretching vibration of C=O absorption increased after reaction, C-H peak at 1363 cm^{-1}, and the peak of C-O-C stretching vibrations appeared at 1210 cm^{-1}. The appearance of methyl and methylene asymmetric stretching vibrations were observed at around 2962 and 2871 cm^{-1}.[24, 61, 66]

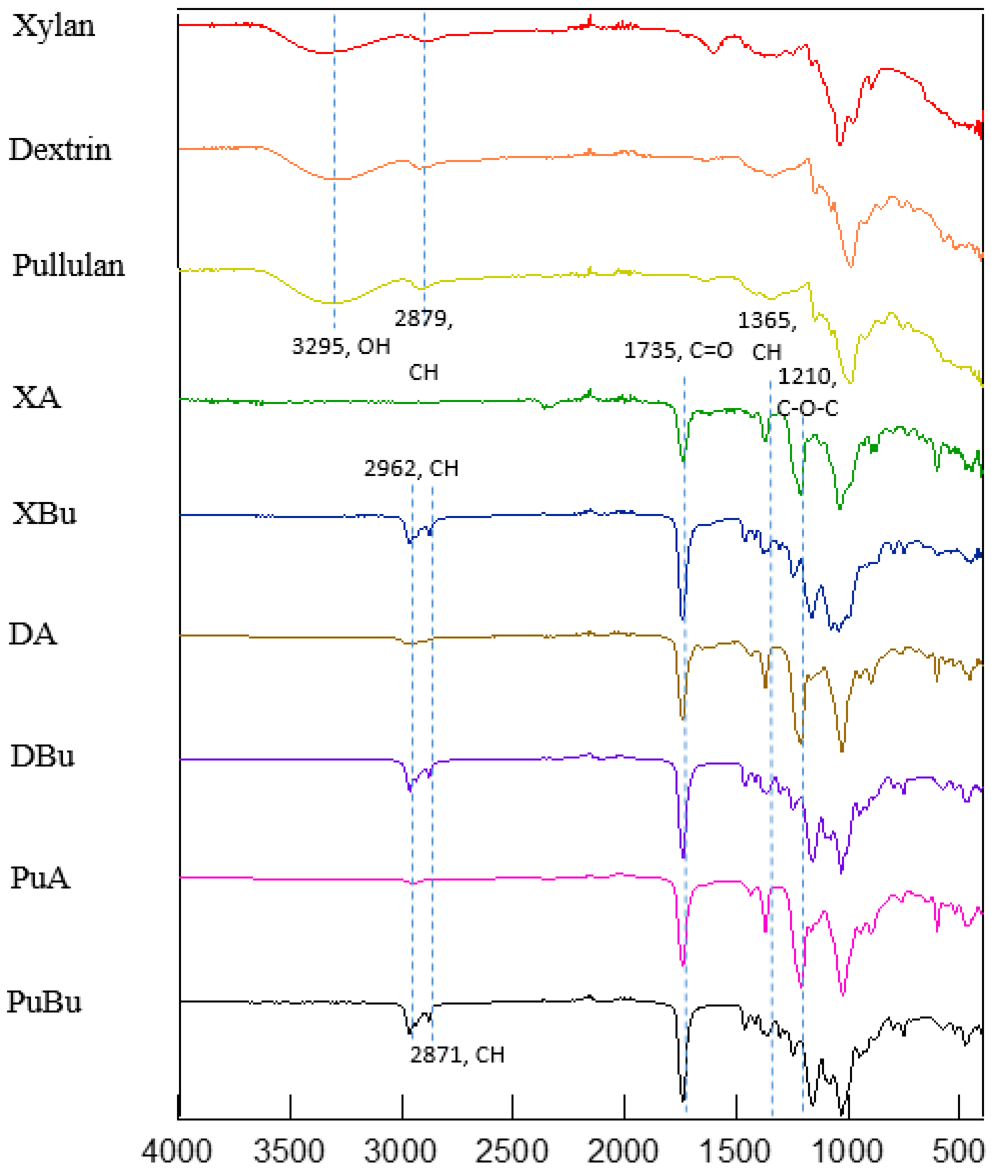


Figure 3.4 FT-IR spectra of xylan, XA, XBu, dextrin, DA, DBu, pullulan, PuA and PuBu.

^{1}H NMR analysis: The ^{1}H NMR spectra of xylan, XA and XBu are depicted in Figure 3.5. From the ^{1}H NMR spectrum of xylan, the signals between 3.3 and 5.3 ppm correspond to the protons of xylan backbone. In the ^{1}H NMR spectrum of XA, the signals within the range of 3.3-5.0 ppm are assigned to the ring protons XA, and the strong signal at 2.0 ppm due to the methyl protons ($-CH_3$), the observed signals between 0.9 and 2.5 ppm due to the butyryl group. The results confirm the successful transesterification of xylan bearing acetyl and butyryl groups, respectively.[24, 25]

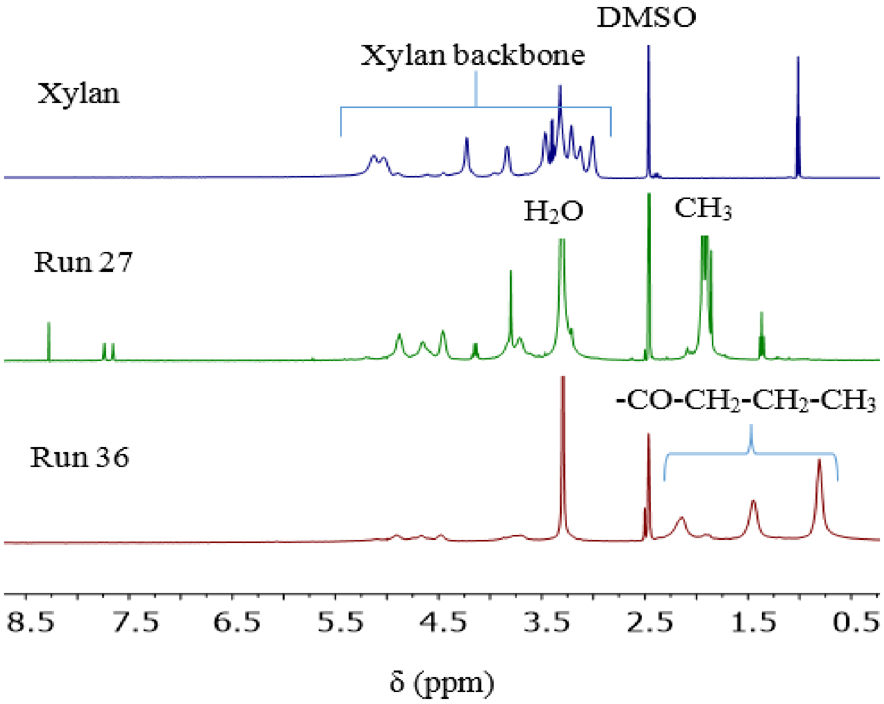


Figure 3.5 ^1H NMR spectra of xylan, XA and XBu recorded in DMSO-d_6.

Figure 3.6 presents the ^1H NMR spectra of dextrin recorded in D_2O, DA and DBu recorded in DMSO-d_6. From the ^1H NMR spectrum of dextrin, the signals in the region from 3.3 to 5.3 ppm assigned to the protons of dextrin backbone. The ^1H NMR spectrum of DA observed the signals within the range of 3.3-5.0 ppm corresponding to the ring protons of DA, and the methyl protons (-CH_3) appeared at 2.0 ppm, the signals between 0.9 and 2.5 ppm assigned to the protons of butyryl group. In addition the peaks due to H_2O and DMSO were observed at 3.3 ppm and 2.5 ppm. The results elucidate the successful synthesis of dextrin acetate and dextrin butyrate.

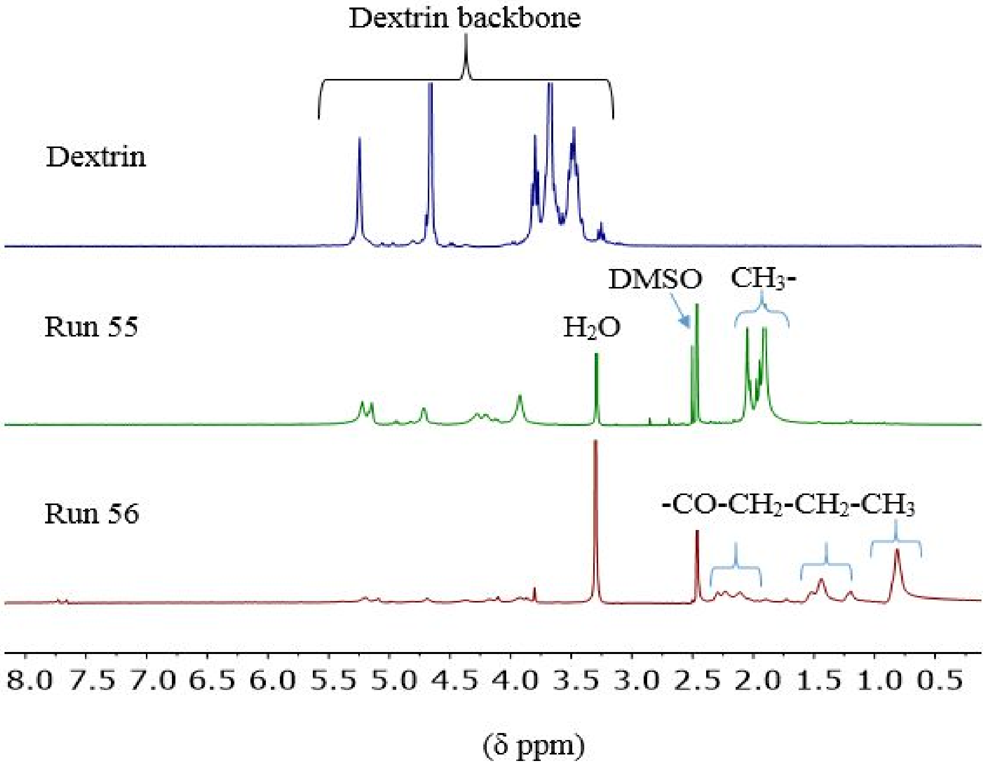


Figure 3.6 ^{1}H NMR spectra of dextrin recorded in D_2O, DA and DBu recorded in DMSO-d_6.

Figure 3.7 shows ^{1}H NMR spectra of pullulan recorded in DMSO-d_6, PuA and PuBu recorded in $CDCl_3$. The peaks arising from the ring-protons of the pullulan backbone were observed in the range from 4.5 to 5.6 ppm in the ^{1}H NMR spectrum of pullulan. These peaks decreased, and the peaks due to the acetyl groups appeared around 1.8-2.2 ppm in the ^{1}H NMR spectrum of the PuA. The peaks appeared between 0.9 and 2.5 ppm in the ^{1}H NMR spectrum of the PuBu assigned to butyryl groups. These results indicate that the successful synthesis of pullulan derivatives bearing acetyl and butyryl groups.[61, 66]

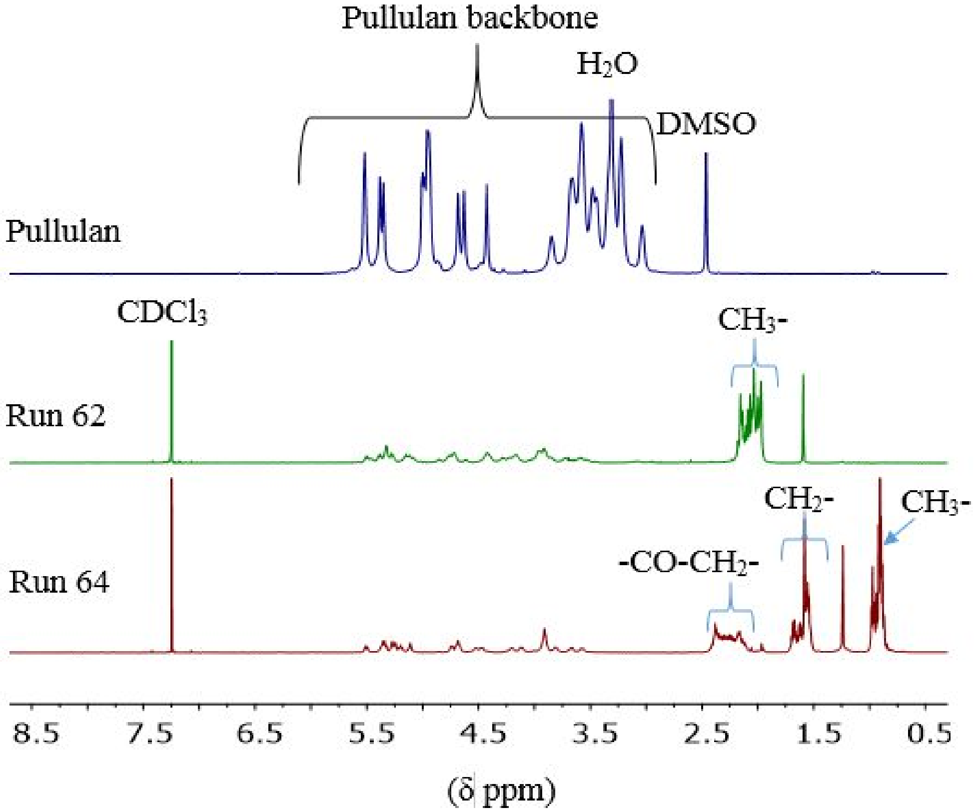


Figure 3.7 ^{1}H NMR spectra of pullulan recorded in DMSO-d_6, PuA-Run 62 and PuBu-Run 64 recorded in $CDCl_3$.

The applicability of the large scale TER of polysaccharides using a mixed solvent of EmimOAc and DMSO was demonstrated by the ^{1}H NMR spectra of the obtained products in DMSO-d_6 presenting in Figure 3.8. The similar signals were observed in the ^{1}H NMR spectra, the signals appeared in the region between 3.3 ppm and 5.5 ppm due to the protons of polysaccharide backbones, the methyl proton signals at 1.8-2.2 ppm assigned to the acetyl groups.

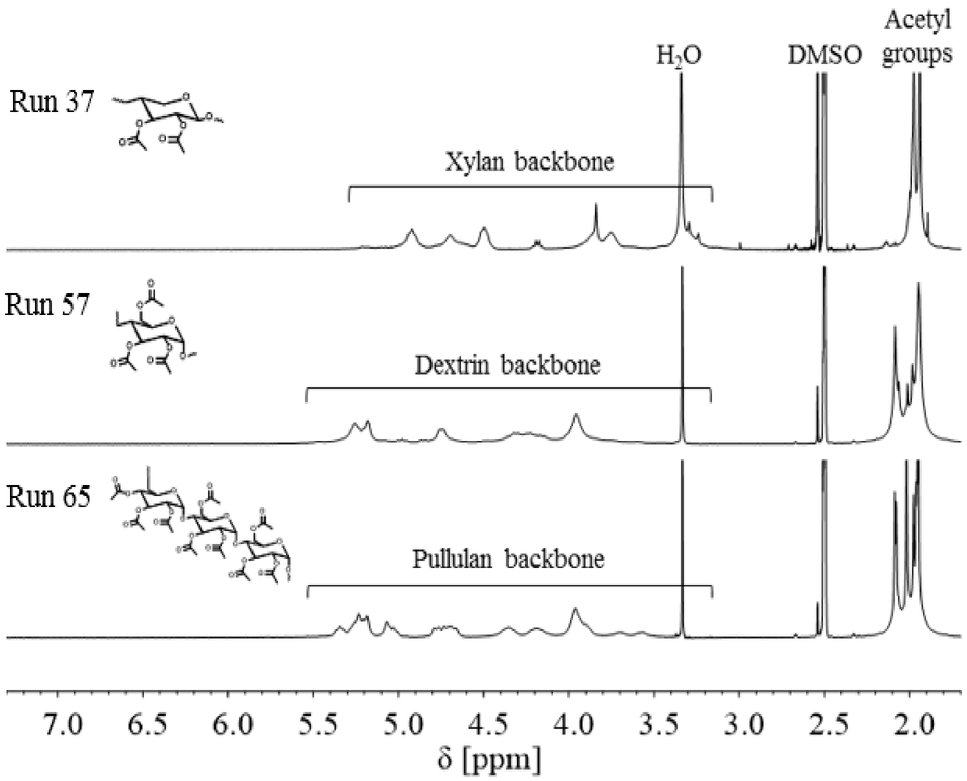


Figure 3.8 ^{1}H NMR spectra in DMSO-d_6 of the polysaccharide acetates obtained from a large scale reaction.

The kinetic evolution of the TER of polysaccharides: In order to provide a detailed structural insight into the obtained polysaccharide derivatives, the DS values were determined for the obtained polysaccharide derivatives. The DS values of XA was calculated by the equation according to Perez, et al., 2011.[24] The DS values were calculated based on ^{1}H NMR measurements of the CA (from filter paper) and dextrin derivatives that were obtained by the per-benzoylation reaction of the obtained CA and dextrin derivatives with benzoyl chloride in $CHCl_3$ with Net_3 as a proton scavenger. The DS of PuA was determined as the equation according to Iwata, et al., 2015.[66] The obtained polysaccharide derivatives with different DS values were successfully synthesized under various conditions listed in Table 3.2, Table 3.3 and Table 3.4.

Table 3.2 Synthesis of CA (from filter paper) and xylan derivatives with different DS values under various reaction conditions

Run	Starting material/mg	ILs/g	Ester reagents/mL	DMSO/mL	Time	DS
18	Filter paper (120)	4	IPA (4)	-	5min	2.55
19	Filter paper (120)	4	IPA (4)	-	15min	2.84
20	Filter paper (120)	4	IPA (4)	-	30min	2.85
21	Filter paper (120)	4	IPA (4)	-	45min	2.87
22	Filter paper (120)	4	IPA (4)	-	1h	2.88
23	Filter paper (120)	4	IPA (4)	-	1.5	2.91
24	Filter paper (120)	4	IPA (4)	-	2	2.93
25	Filter paper (120)	4	IPA (4)	-	2.5	2.95
26	Filter paper (120)	4	IPA (4)	-	3	2.97
27	Xylan (120)	4	IPA (4)	-	5min	1.39
28	Xylan (120)	4	IPA (4)	-	10min	1.43
29	Xylan (120)	4	IPA (4)	-	15min	1.50
30	Xylan (120)	4	IPA (4)	-	30min	1.67
31	Xylan (120)	4	IPA (4)	-	45min	1.77
32	Xylan (120)	4	IPA (4)	-	1h	1.88
33	Xylan (120)	4	IPA (4)	-	2h	1.89
34	Xylan (120)	4	IPA (4)	-	3h	1.93
35	Xylan (120)	4	IPA (4)	-	16h	1.96
36	Xylan (240)	0.077	VBu (3.84)	4	18h	1.91
37	Xylan (2400)	6	IPA(12)	80	18	1.88

Table 3.3 Synthesis of dextrin derivatives with different DS values under various reaction conditions

Run	Starting material/mg	Emim-OAc	Ester reagents/mL	Time	DMSO /mL	Temp [ºC]	DS
38	Dextrin (120)	4g	IPA (4)	24h	-	40	2.64
39	Dextrin (120)	4g	IPA (4)	4h	-	50	2.75
40	Dextrin (120)	4g	IPA (4)	1h	-	60	2.84
41	Dextrin (120)	4g	IPA (4)	1h	-	70	2.89
42	Dextrin (120)	4g	IPA (4)	5min	-	80	2.66
43	Dextrin (120)	4g	IPA (4)	10min	-	80	2.78
44	Dextrin (120)	4g	IPA (4)	15min	-	80	2.83
45	Dextrin (120)	4g	IPA (4)	30min	-	80	2.86
46	Dextrin (120)	4g	IPA (4)	45min	-	80	2.91
47	Dextrin (120)	4g	IPA (0.25)	1h	-	80	2.38
48	Dextrin (120)	4g	IPA (0.5)	1h	-	80	2.53
49	Dextrin (120)	4g	IPA (1)	1h	-	80	2.75
50	Dextrin (120)	4g	IPA (1.5)	1h	-	80	2.85
51	Dextrin (120)	4g	IPA (2)	1h	-	80	2.87
52	Dextrin (120)	4g	IPA (2.5)	1h	-	80	2.89
53	Dextrin (120)	4g	IPA (3)	1h	-	80	2.9
54	Dextrin (120)	4g	IPA (3.5)	1h	-	80	2.91
55	Dextrin (120)	4g	IPA (4)	1h	-	80	2.93
56	Dextrin (240)	189mg	VBu (7.3)	18h	2	80	2.74
57*	Dextrin (2400)	6g	IPA (12)	18h	80	80	2.94

* M_{nSEC}= 11,400, $M_{\mathrm{w}}/M_{\mathrm{n}}$=1.97, determined from SEC measurement in $CHCl_3$ using polystyrene standards.

Table 3.4 Synthesis of pullulan derivatives with different DS values under various reaction conditions

Run	Starting material/mg	EmimOAc /g	Ester reagents/mL	Time	DMSO /mL	DS
58	Pullulan (240)	8	IPA (8)	5 min	4	2.55
59	Pullulan (240)	8	IPA(8)	15 min	4	2.61
60	Pullulan (240)	8	IPA (8)	30 min	4	2.68
61	Pullulan (240)	8	IPA (8)	45 min	4	2.9
62	Pullulan (240)	8	IPA (8)	1h	4	2.94
63	Pullulan (120)	4	IPA (4)	16h	-	3.00
64	Pullulan (240)	0.125	VBu (5.6)	18h	2	2.93
65*	Pullulan (2400)	6	IPA (12)	18h	80	2.99

* M_{nSEC}= 129,900, M_w/M_n=8.76, determined from SEC measurement in $CHCl_3$ using polystyrene standards.

The obtained results showing that the transesterification reaction of polysaccharides in EmimOAc or in EmimOAc/DMSO without any additional catalysts and corrosive chemicals were successfully proceeded with a high efficiency. The detailed kinetic evolution of TER of polysaccharides in EmimOAc was investigated. The kinetic evolution of the DS values or conversion rate of polysaccharide acetate was shown in Figure 3.9 and Figure 3.10. 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. As indicated in Figure 3.11 and Table 3.3, Run 47-55, 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 40ºC (Run 38) and 50ºC (Run 39) for 1h, but after 24 hours at 40ºC the reaction occurred to result in the obtained product with DS 2.64, while at 50ºC within 4h the achieved product has a DS of 2.75. The reaction efficiently carried out at 60ºC (Run 40) to obtain the DS of 2.84, the DS values continuously peaked by 2.89 and 2.93 at 70ºC (Run 41) and 80ºC (Run 55), respectively.

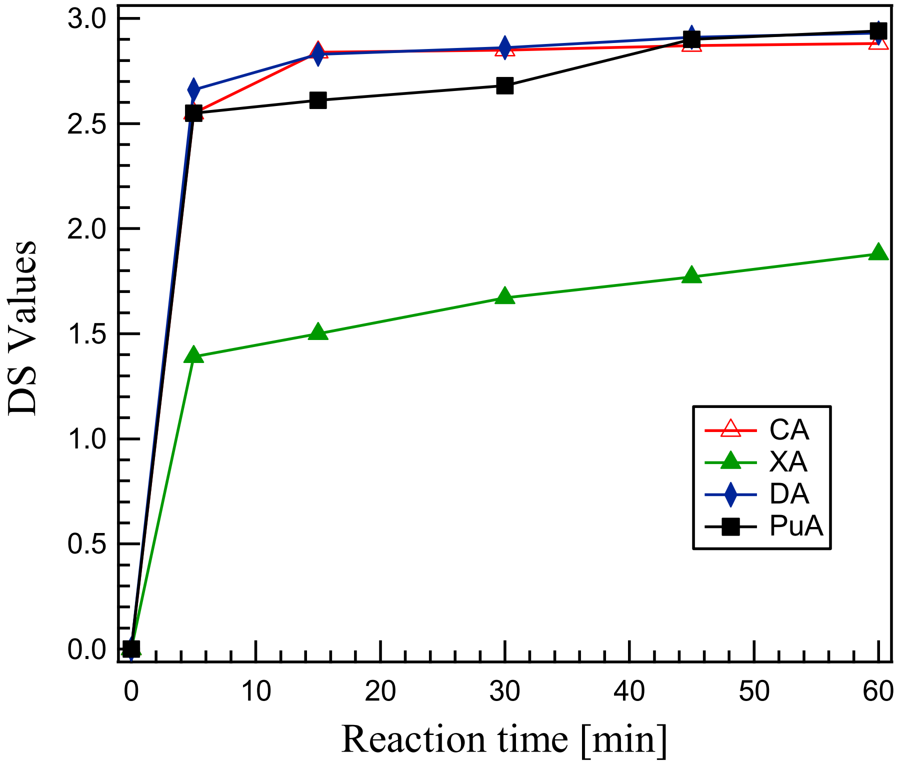


Figure 3.9 The effect of reaction time on the DS values of polysaccharide acetates.

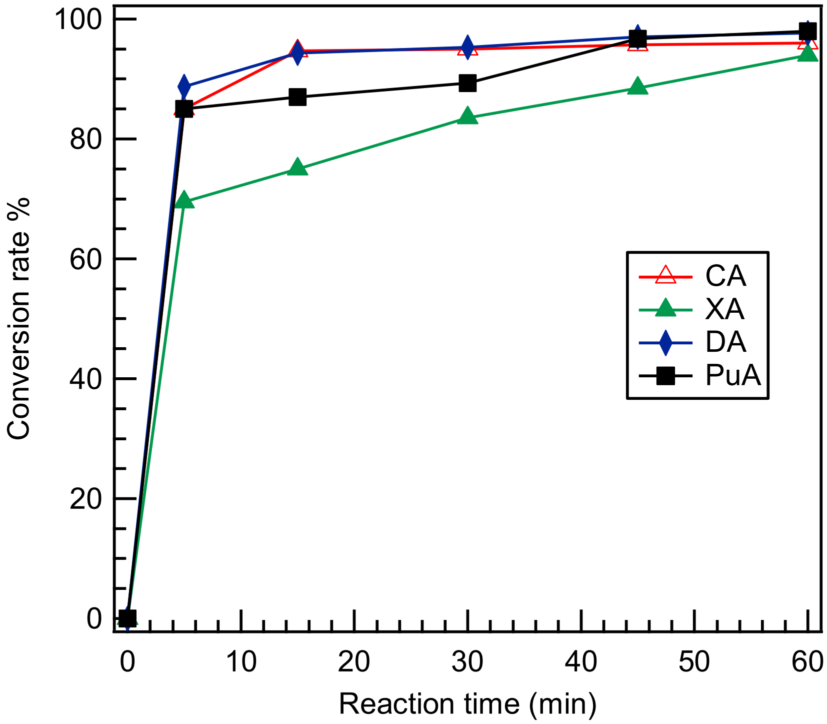


Figure 3.10 The effect of reaction time on the conversion rate of polysaccharide acetates.

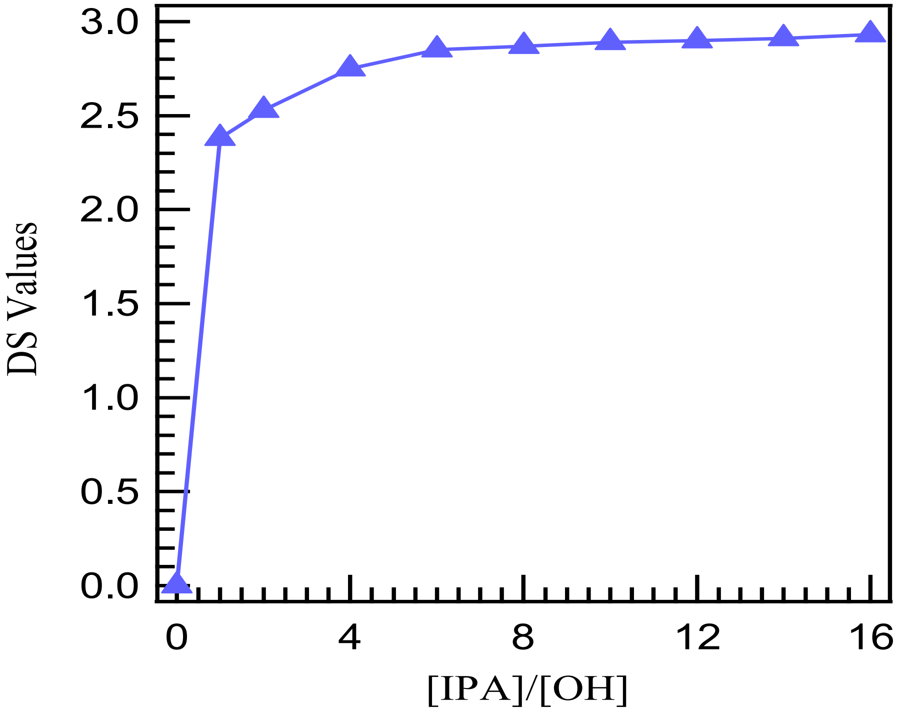


Figure 3.11 The effect of the IPA concentration to the OH group ratios on the DS values of DA.

Thermal property: The thermal stability of native polysaccharides and their derivatives were determined by TGA measurement and depicted in Figure 3.12 and detailed decomposition temperature at 5% and 50% weight loss listed in Table 3.5. 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 due to the disappearance of the hydroxyl groups.

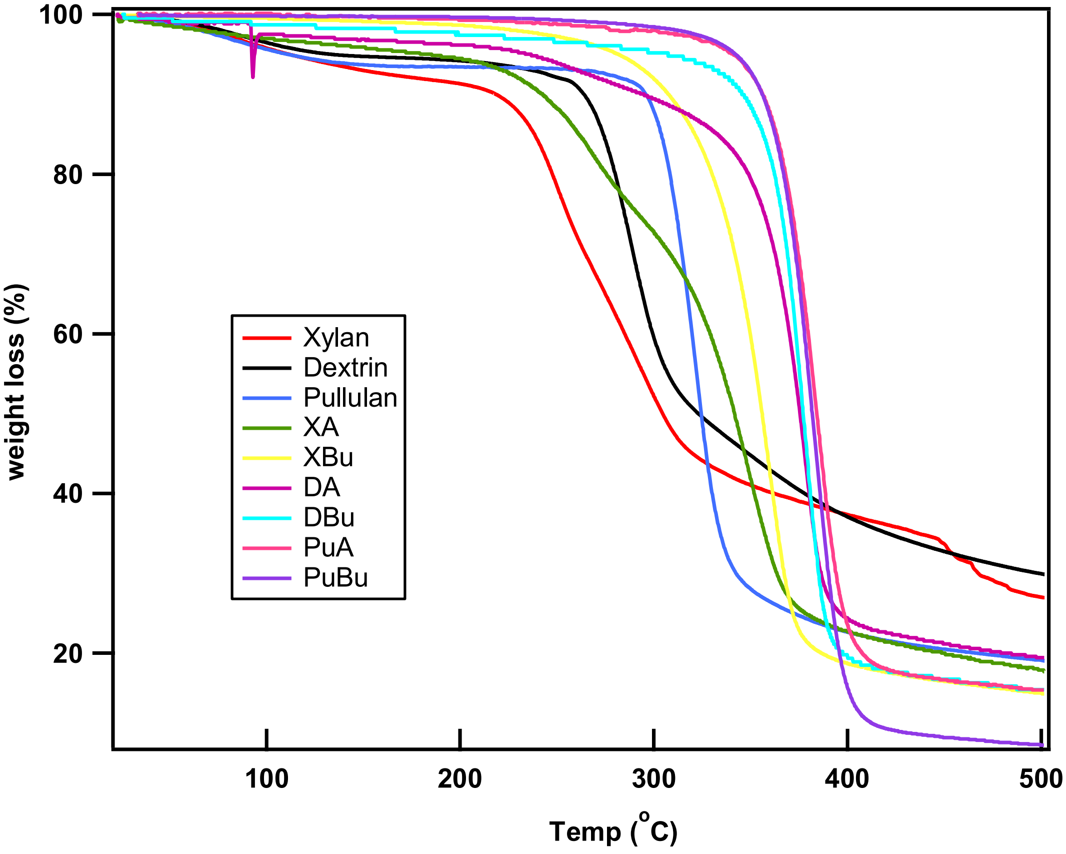


Figure 3.12 TGA spectra of native xylan, XA,and XBu, native dextrin, DA and DBu, native pullulan, PuA and PuBu.

Table 3.5 Solubility behavior and thermal property of polysaccharide derivatives in common organic solvents

Samples	Solubility				Thermal property	
	$CHCl_3$	DMSO	C_3H_6O	CH_2Cl_2	$T_{d5\%}$	$T_{d50\%}$
Cellulose	-	-	-	-	275	332
Run 6	+	+	+	+	338	379
Run 7	+	+	Δ	+	269	368
Run 8	+	+	Δ	+	234	372
Run 9	+	+	-	+	336	372
Run 10	+	+	-	+	338	374
Run 11	+	+	-	+	337	372
Run 12	+	+	+	+	328	373
Run 13	+	+	+	+	327	381
Run 14	+	+	+	+	326	377
Run 15	+	+	+	+	342	384
Run 32	-	+	-	-	183	342
Run 36	+	+	Δ	+	281	356
Run 55	+	+	+	+	237	375
Run 56	+	+	+	+	307	377
Run 62	Δ	+	Δ	Δ	341	384
Run 64	+	+	+	+	342	382

(+ soluble, - insoluble, Δ partly soluble)

Solubility: The important reason that limits the use of polysaccharides for industrial application is its poor solubility in organic solvents. Esterification of polysaccharides is an efficient approach to address this problem. An alteration in the chemical structure of the polysaccharides consequently leads to a change in their solubility behavior. In this study, the solubility behavior of polysaccharide derivatives in organic solvents such as DMSO, chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2) and acetone was investigated. Table 3.5 illustrates a significant improvement of the solubility of all polysaccharide derivatives in a series of organic solvents. All the obtained cellulose derivatives dissolve in $CHCl_3$, DMSO and CH_2Cl_2 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 $CHCl_3$, acetone and CH_2Cl_2.

3.6 Conclusions

The first investigation of xylan, dextrin and pullulan transesterification was successfully conducted using EmimOAc as both solvent and organocatalyst and DMSO as a co-solvent with IPA and VBu as esterification reagents without complicated reaction techniques. The ^{1}H NMR spectra demonstrated that successful synthesis of high DS values of xylan, dextrin, and pullulan derivatives bearing acetyl and butyryl groups. In addition, the scalability of the TER of xylan, pullulan, and dextrin was expanded by 20 times into gram-scale resulting xylan acetate, dextrin acetate, and pullulan acetate with the DS values of 1.88, 2.94 and 2.99, respectively. The $M_{\mathrm{n,SEC}}$ and $M_{\mathrm{w}}/M_{\mathrm{n}}$ were determined by the SEC measurements, which indicated the Im-IL-catalyzed TER was the mild reaction without any polysaccharide decompositions. Furthermore, the kinetic evolution of transesterification reactions of polysaccharides was also accomplished indicating that the ratios of IPA concentration to hydroxyl groups, reaction time and reaction temperature are very important factors, which significantly affected on the efficiency of TER of polysaccharides in EmimOAc. The thermal stability (based on the TGA measurement), and the solubility behavior of these polysaccharide derivatives in commercial organic solvents were significantly improved after transesterification.

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Chapter 4: Application of the TER using 1-ethyl-3-methylimidazolium acetate to directly acetylate lignocellulose from raw lignocellulosic biomass

In this chapter, the author tried to apply the TER system consisted of EmimOAc, DMSO and esterification reagent (IPA) to directly acetylated polysaccharide (cellulose and hemicellulose) within lignocellulosic raw biomass such as rice husk and coconut fiber. The EmimOAc was recovered and reused after reactions. The structure of the obtained polymers was confirmed by FT-IR and ^{1}H NMR spectroscopy. The thermal property and solubility were also investigated. From above mentioned results indicated that the presented IL-catalyzed TER is the one of the best method for esterification of cellulose including raw biomass.

4.1 Introduction

Recently, human activities based on fossil resources such as coal, gas and oil to generate energy and produce chemical products.[1] The over exploration of fossil resources results in the emission of greenhouse gas and climate change. However, fossil resources are limited reserves and non-renewable, they will be depleted and not enough to offer for human needs in the near future while the global population has being increased. Therefore, environmental protections and energy security are main global interests.[2] Biomass, a non-fossil renewable resource of biological origin has been considered to convert into bioenergy and bio-based chemicals and materials to replace the use of fossil resources. Lignocellulosic biomass refers to inedible and the most abundant plant material in the planet. The component of lignocellulose consists mainly of carbohydrate polymers (such as 45% of cellulose and 25% of hemicellulose), 25% of aromatic polymer lignin and other compounds such as pectins, protein, waxes and lipids (5%). It has been investigated as a promising potential resource to obtain chemicals, energy and various materials because of its renewable and biodegradable characteristics.[3-5] Rice husk and coconut fiber are sources of lignocellulose from agricultural waste. Rice husk (or hull) is the outermost layer of the paddy grain. Around 20% of paddy weight is husk that is separated from the rice grains during the milling process.

The estimated world rice production in 2014 was about 741.3 million tons reported by the Food and Agricultural Organization (FAO),[6] which means approximately 1.482×10^8 tons of rice husk biomass will be generated globally in this year. Studies have reported that the components of rice husk including silica (15−28 wt %), cellulose (35−40 wt %), hemicellulose (15−20 wt %), and lignin (20−25 wt %)[7, 8] depending on the variety, origin, climate, and geographic location.[9, 10] Rice husk is tough and bulky biomass and low nutritional value, which lead the limited application of rice husk.[11] Currently, open field burning and land filling are the two most common rice husk disposal methods. However, they lead to energy waste, greenhouse gas emission, air pollution, and huge landfill space occupancy because of their low bulk density.[12, 13] To solve these problems, scientists have been exploring to develop more economical methods to utilize rice husk.[10, 14−17] Rice husk is used to make bio-fertilizer for agriculture by composting,[18] materials for construction (such as bricks, insulation fillers, etc.),[19] electricity (by controlled burning),[20] higher values silicon based materials.[11, 9, 21] Coconut fiber (coir fiber) is isolated from coconut husk. Coconut fiber (coir) is a renewable and abundant resource, which has important properties such as non-toxic, biodegradable, low density and CO_2-neutral material. The composition of coir fiber consist of high lignin content (41-45wt%), cellulose (36-43wt%), hemicellulose (10-20wt%) and others.[22] Coir fiber has been used in the fabrication of helmet and bulletproof jackets because of their remarkable mechanical properties.[23] Coir fiber reinforced polymer composite has been developed.[22] Chemical modification of coconut fiber such as mercerization, dewaxing, bleaching, acrylation, acetylation, cyanoethylation, silane treatment, benzoylation, peroxide treatment, isocyanate treatment, latex coating, and steam-explosion have studied to improve the interfacial properties.[23] Thus, the author focused on the modification of these raw biomass, such as rice husk and coconuts fiber, for direct conversion to the cellulose derivatives using ionic liquid (IL)-mediated transesterification as cost-effective method.[24-29]

In this chapter, the IL-mediated TER system, which was mentioned in the previous chapters, was applied to directly acetylation of lignocellulosic raw biomass as mixture of the cellulose and the hemicellulose. Furthermore, EmimOAc was recovered and reused after reactions. The structural analysis of the obtained polymers was confirmed by FT-IR and ^{1}H NMR measurements. The thermal properties and solubility were also investigated.

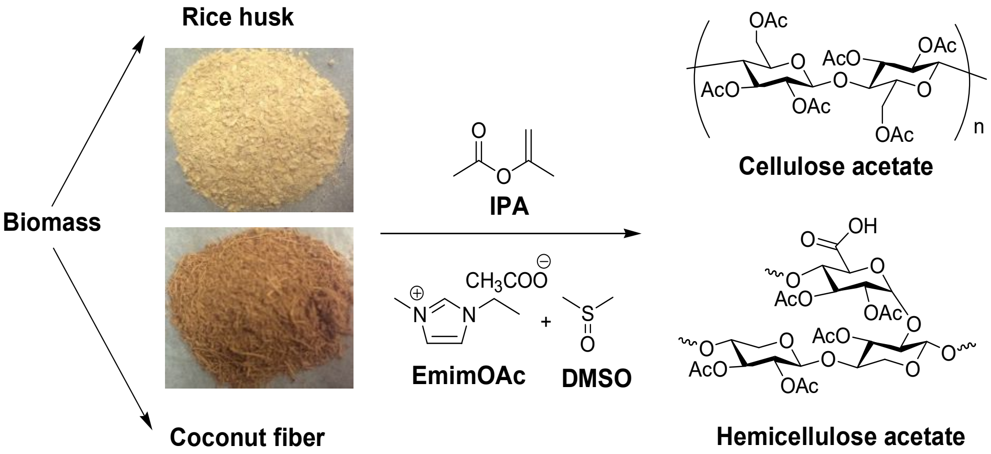
4.2 Materials

The ionic liquid 1-ethyl-3-methyl-imidazolium acetate (EmimOAc) (95%) was purchased from Tokyo Chemical Industry Co., Ltd, Japan and used without further purification. The esterification reagent (isopropenyl acetate 99%), and co-solvent DMSO were available from the Sigma-Aldrich Chemicals Co. The biomasses (RH and CF) were washed three time with deionized water to remove dirt and then dried at 105°C overnight in a vacuum oven. The dried biomass was crushed into powder (75-125μm) to increase the surface area by using a blender.

4.3 Experimental section

Transesterification reaction of raw biomass: A mixture of 600mg (6 wt%) of biomass powder (rice husk or coconuts fiber) and 10 g of EmimOAc was stirred by a magnetic stirrer and dried at 80°C in an oil bath for 3 h under vacuum condition; then 15 ml DMSO was added under argon atmosphere to dissolve completely biomass at 110°C for overnight; then after drying, 20 ml IPA was added into the solution and reacted with biomass for 18 h at 80°C; at the end of reaction, the solution was precipitated in MeOH and filtrated to collect acetylated polysaccharides (rice husk, Run 66; coconuts fiber, Run 68). The EmimOAc was recovered after reaction by evaporation and reused for the next experiment as the ionic liquid, afforded acetylated polysaccharides derived from rice husk (Run 67) and coconuts fiber (Run69) (Scheme 4.1).

Scheme 4.1 The schematic representation of direct transesterification reactions of lignocellulosic biomass in EmimOAc and DMSO



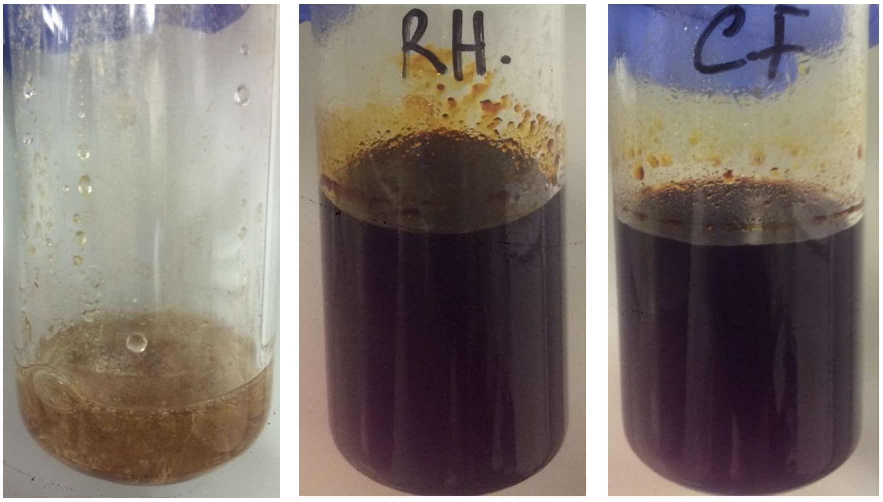
4.4 Characterization methods

The FT-IR spectra were observed by a Thermo Fisher Scientific Nicolet iS10 equipped with an ATR unit. All the ^{1}H NMR spectra were recorded by JEOL 400 and 600 MHz FT-NMR spectrometers in solution of products (10mg) dissolved in 800μL of deuterated solvents (such as DMSO-d_6, $CDCl_3$-*d*) the chemical shifts (δ) were given in ppm as either the solvent peak or TMS as the internal standard. Thermogravimetric analysis (TGA) was performed on a DTG-60AH instrument (Shimadzu) with a heating rate of 10ºC/min under nitrogen atmosphere. The decomposition temperature (T_d) was determined as the onset temperature of decline in the TGA chart. In the solubility check, ten milligram of the obtained products were dissolved in various organic solvents. The solubility behavior was observed.

4.5 Results and discussion

4.5.1 Confirmation of the obtained acetylated polysaccharides

The most important step of the modification of raw biomass is deconstruction of the biomass structure. In this experiment, a mixture of EmimOAc, biomass, and DMSO was heated at elevated temperature (110ºC) for overnight. The state of the mixture was shown in Figure 4.1. This step leaded to break down the bonds between lignin and carbohydrates obtaining cellulose and hemicellulose. Then after, cellulose and hemicellulose reacted with isopropenyl acetate affording polysaccharide acetate (PA) which containing cellulose acetate (CA) and hemicellulose acetate (HA). The structure of these polymers was confirmed by FT-IR and ^{1}H NMR measurements.



A) B) C)

Figure 4.1 Direct transesterification reaction of polysaccharides from lignocellulosic biomass using EmimOAc/DMSO with IPA (A: EmimOAc+biomass before reaction, B: the obtained product from RH, C: the obtained product from CF)

FTIR analysis; The FT-IR spectra of RH, CF and the obtained products (Run 66, 68 using pure EmimOAc and Run 67, 69 using recycled EmimOAc) are observed and depicted in Figure 4.2. It could be clearly observed that the intensity of the broad peak around 3340 cm^{-1} in both RH and CF, which is assigned to OH stretching, was significantly decreased after transesterification, suggesting the substitution of OH groups along polysaccharide chains by acetyl groups. IR measurements of the obtained products using fresh EmimOAc (Run 66, 68) and using recycled EmimOAc (Run 67, 69) indicated the same spectra. The sharp peaks present at 1733 and 1211 cm^{-1} assigned to the C=O and C-O stretching absorption of saturated carboxylic esters,[30] and C-H absorption at 1365 cm^{-1}. The peak at 1031 cm^{-1} belongs to the asymmetric stretching of C-O-C from the pyranose ring.[31] The characteristic bands of polysaccharide acetate appear in all products indicating the successful synthesis of polysaccharide acetates from RH and CF.

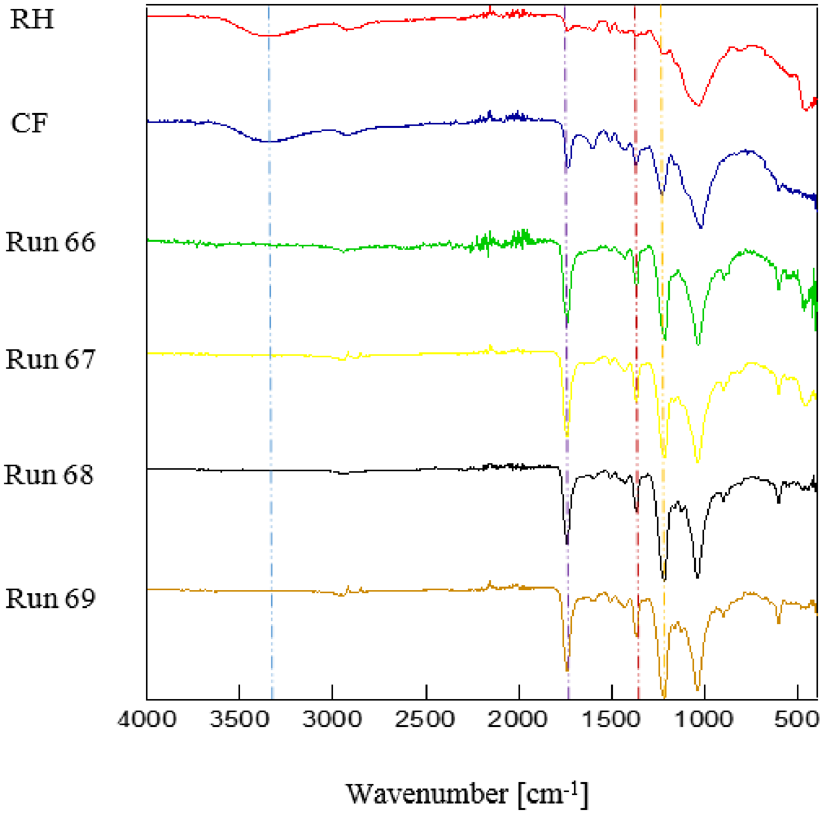


Figure 4.2 FT-IR spectra of RH, CF, and PAs isolated from RH (Run 66 using fresh EmimOAc, Run 67 using recycled EmimOAc) and from CF (Run 68 using fresh EmimOAc, Run 69 using recycled EmimOAc).

^{1}H NMR analysis; Figure 4.3 shows the ^{1}H NMR spectra of the obtained polymers dissolved in $CDCl_3$ recorded at 25◦C. The peaks in the region of 2.8-5.2 ppm are corresponded to the seven ring protons of AGU, and the signals of the acetyl groups (CH_3) appeared at 1.6-2.3ppm. The peaks around 2.5, 3.3 and 7.2 ppm is related to the protons of DMSO, H_2O and $CDCl_3$, respectively. Based on ^{1}H NMR spectra, the obtained polymers were confirmed as PAs including CA and HA by using fresh EmimOAc/DMSO system. When the recycled EmimOAc was employed (Run 67 and 69), although the reaction was proceeded, some incorrected peaks was observed.

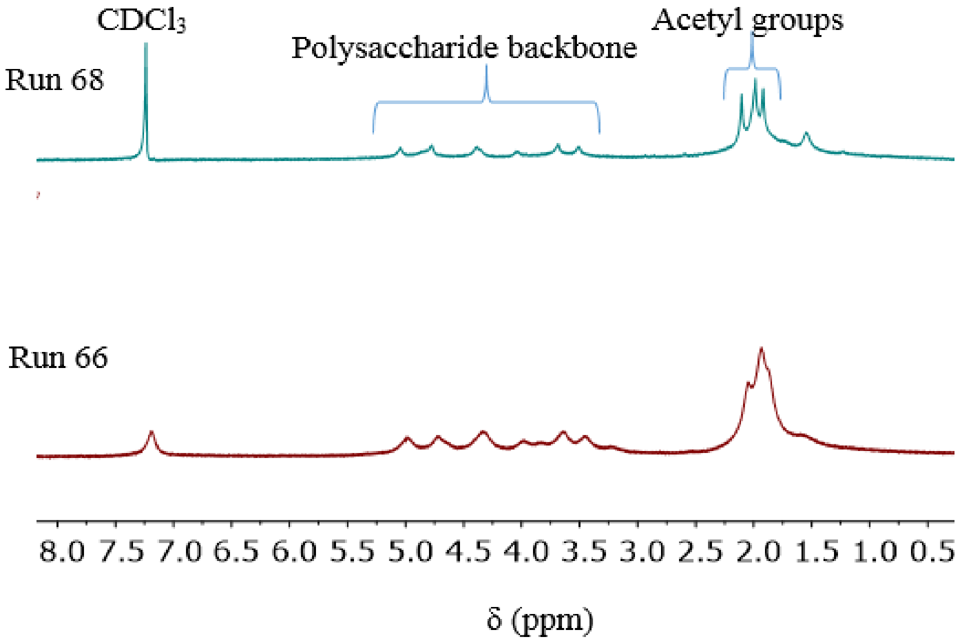


Figure 4.3 ^{1}H NMR spectra of PAs obtained from RH (Run 66) and CF (Run 68) using fresh EmimOAc recorded in $CDCl_3$.

4.5.2 Recover and reuse the EmimOAc

In recent years, EmimOAc was increasingly investigated as solvent and acetylation media solving high amount of lignocellulosic biomass. In this work, evaporation method was used to remove the impurities such as DMSO, IPA, MeOH and H_2O from the precipitated solution for purification of EmimOAc. After the polysaccharide acetates were isolated by a simple reprecipitation into MeOH, the resultant MeOH layer was subject to evaporation and subsequently high vacuum distillation. The evaporation conditions were conducted as followed 1) 100×10^2 Pa, at 60°C for 3h, 2) 5 Pa, at 80°C for 16h. The ^1H NMR spectra of recycled EmimOAc in $CDCl_3$ were presented in Figure 4.4 compared to ^1H NMR spectrum of fresh EmimOAc. As shown in the ^1H NMR spectra of the recycled EmimOAc, beside the peaks due to the peaks of fresh EmimOAc, a slight amount of impurity was observed. The recovered EmimOAc was then reused for the next lignocellulose modification reaction without any cautions.

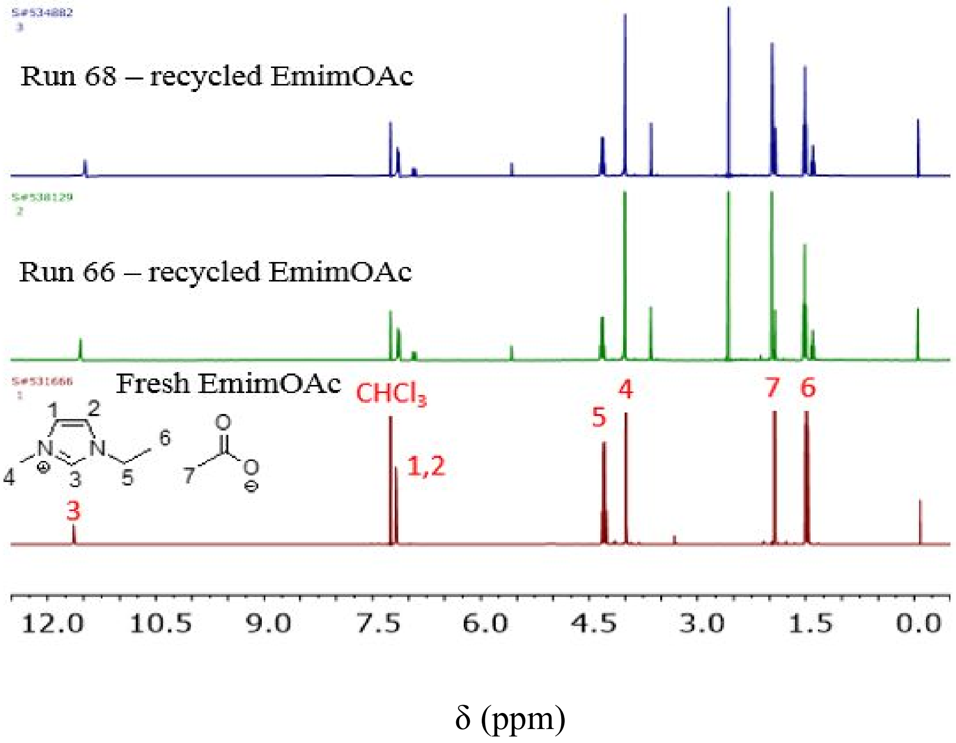


Figure 4.4 ^1H NMR spectra of recycled EmimOAc collected from TER of RH (Run 66), CF (Run 68), and pure EmimOAc recorded in $CDCl_3$.

As the results shown in Table 4.1, PAs were obtained with high yields (746mg – Run 66, 713mg – Run 67, 693mg – Run 68 and 560mg – Run 69) and good recyclability of the EmimOAc (Run 67, 98.6% and Run 69, 97.8%). This procedure was successfully reused for the next time without any difficulties and a decrease in catalytic activities. 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 lignocellulose modification reaction.

4.5.3 Thermal property of the obtained PAs

The TGA thermal curves of RH, CF and the obtained PAs from RH (Run 66) and CF (Run 68) using fresh EmimOAc are observed in Figure 4.5 and Table 4.1.

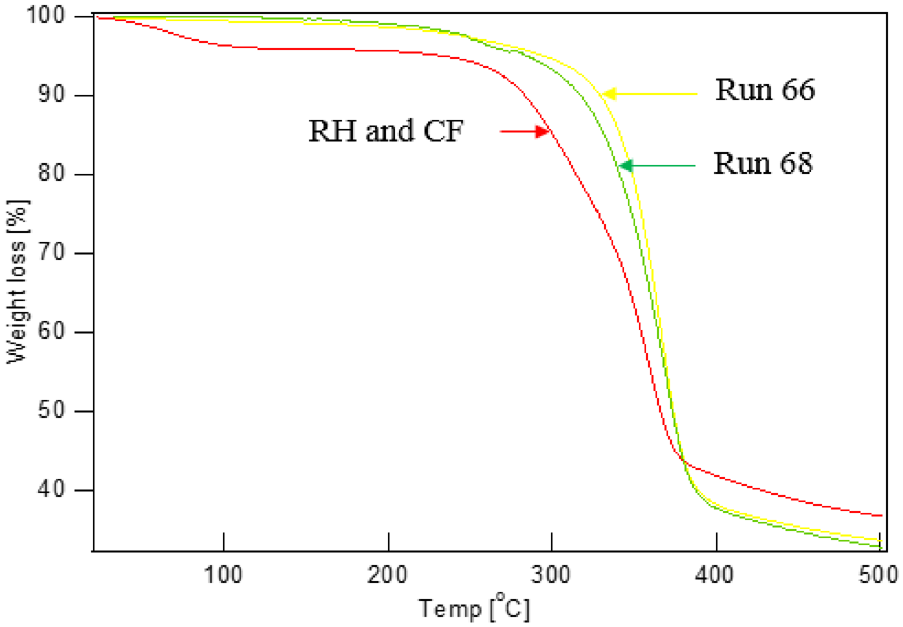


Figure 4.5 TGA thermograms of RH and CF (red, overlap), PAs from RH (Run 66) and CF (Run 68).

The TGA curves of RH and CF were overlap and 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).

4.5.4 The solubility of the PAs

The solubility of obtained PAs in $CHCl_3$, CH_2Cl_2, DMSO and acetone was investigated and shown in Table 4.1. The results illustrate that all PAs revealed good solubility in CH_2Cl_2, 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.

Table 4.1 The yield, solubility and thermal property of the PAs obtained directly from RH and CF using fresh EmimOAc (Run 66, 68) and recycled EmimOAc (Run 67, 69)

Run	Yield /mg	EmimOAc recycled / wt %	Solubility				$T_{d50\%}$ / °C
			$CHCl_3$	CH_2Cl_2	DMSO	Acetone	
66	746	-	O	O	Δ	X	374
67	713	98.6	O	O	O	Δ	371
68	693	-	O	O	Δ	X	373
69	560	97.8	Δ	O	O	X	374

O-soluble, X-insoluble, Δ- partly soluble

4.6 Conclusions

The homogeneous system of the EmimOAc/DMSO-mediated transesterification reaction of rice husk and coconut fiber, as a raw biomass, could produce acetylated biomass which containing cellulose acetate and hemicellulose acetate with the high yields and high degree of substitution. The obtained products were confirmed successful synthesis of polysaccharide acetates, including cellulose acetate and hemi-cellulose acetate, by FT-IR and ^{1}H NMR spectroscopy. The thermal property of the obtained products was also investigated using TGA measurement which shows the increased decomposition temperature compared with raw biomass. The solubility of the synthesized acetylated polysaccharide in dichloromethane, DMSO, chloroform, and acetone was investigated. Furthermore, the EmimOAc could be highly recovered from the filtrates after the precipitation step and reused effectively in consecutive biomass acetylation batches.

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Chapter 5: Conclusions and future work

5.1 Conclusions

In this dissertation, 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. The homogeneous system consisted of mixed solvent of EmimOAc and DMSO catalyzed transesterification was revealed to show not only robustness on gram-scale synthesis but also sufficient green nature with high recyclability. 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. The thermal properties and solubility of polysaccharide derivatives were observed showing a remarkable improvement after reaction.

The detailed conclusions of this research were summarized as follows:

In chapter 2, the recyclability and scalability of the Im-ILs were evaluated for the catalytic transesterifications of cellulose. For the organocatalytic transesterifications with EmimOAc as a solvent and an organocatalyst, 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 %). Beside that, in order to show the applicability of the EmimOAc catalyzed transesterifications, the above-mentioned EmimOAc-catalyzed polymer modification was expanded to gram-scale reaction with various cellulose sources such as avicel, pulps and rayon, affording cellulose esters with practically perfect conversions of the starting hydroxyl groups. Moreover, 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 ^{1}H NMR analyses indicated that CA, CBu, CPiv, CBn and CAPiv with high DS values were successfully and rapidly synthesized. The $M_{n,SEC}$ and M_w/M_n were determined by the SEC measurements, which indicated the Im-IL-catalyzed TER was the mild reaction without any cellulose decompositions. The chemical modification of various cellulose resources in EmimOAc or in a mixed solvent of EmimOAc and DMSO is a sustainable and effective method for synthesis of cellulose derivatives in industry. The obtained results should shed light on the synthetic utility of Im-ILs in polymer sciences from the view point of not only a green solvent but also a recyclable organocatalyst.

In chapter 3, the first investigation of xylan, dextrin and pullulan transesterification by using EmimOAc as both solvent and organocatalyst or EmimOAc as an organocatalyst and DMSO as a co-solvent with IPA and VBu as esterification reagents without using additional catalysts and corrosive chemicals was successfully conducted. The FT-IR and ^{1}H NMR measurements were used to confirm the structures of the achieved polymers. The observed spectra demonstrated that successful synthesis of high DS values xylan, dextrin, and pullulan derivatives bearing acetyl and butyryl groups. In addition, the scalability of the TER of xylan, pullulan, and dextrin was expanded by 20-times-scale (gram-scale) resulting xylan acetate, dextrin acetate, and pullulan acetate with the DS values of 1.88, 2.94 and 2.99, respectively. In addition, SEC measurements indicated that the obtained products had no decomposed compound during the EmimOAc-catalyszed TER. Furthermore, the kinetic evolution of TER of polysaccharides was also accomplished indicating that the ratios of IPA concentration to hydroxyl groups, reaction time and reaction temperature are very important factors, which significantly affected on the efficiency of TER of polysaccharides in EmimOAc. Finally, the thermal stability and the solubility behavior of polysaccharide derivatives in commercial organic solvents were significantly improved after transesterification reactions.

In chapter 4, the homogeneous system consisted of EmimOAc, co-solvent DMSO and IPA could be used to directly obtain high yield polysaccharide derivatives from lignocellulosic biomass such as RH and CF which are abundant agricultural waste in Vietnam. The structure of the obtained products were confirmed by FT-IR and ^{1}H NMR spectroscopy. The results indicate that successful synthesis of polysaccharide acetates including CA and HA. The TGA measurement was employed to analyze the thermal property of the acetylated polysaccharides showing the increased decomposition temperature compared with those of raw lignocellulosic biomass. In addition, the synthesized polysaccharide acetates show a different soluble ability in various common organic solvents such as dichloromethane, DMSO, chloroform, and acetone. Finally, the EmimOAc could be highly recovered from the filtrates after the precipitation step and reused effectively in consecutive lignocellulosic biomass acetylation batches.

5.2 Proposed future work

The research has been developed and achieved some remarkable results in synthesis of various polysaccharide derivatives in not only milligram-scale but also gram-scale using ionic liquid catalyzed TER. The obtained polysaccharide derivatives showed a great thermal property and excellent solubility in a range of common organic solvents. However, to apply these polysaccharide derivatives for making carbon fiber reinforced plastics (CFRP) in case of cellulose and xylan derivatives, producing membrane for food parking or using for drug delivery in case of pullulan and dextrin derivatives, further characterizations such as differential scanning calorimetry (DSC), tensile modulus, scanning electron microscopy (SEM), interfacial shear strength between fiber and resin (microdroplet test) and biodegradability of these polysaccharide esters need to be investigated. In addition, to make this methodology more sustainable and economical, reducing the amount of ionic liquid, finding effective recovery method and the reaction conditions are necessary to optimize. Finally, based on what I have learned and conducted during the doctoral course in field of ionic liquid application for synthesis of polymers or biomass conversion into biomaterial and biofuel, in near future, I will apply these eco-friendly technologies for utilization of the agricultural residues in my country to produce useful materials. The application and research about ionic liquids are new theme and limited in my country. I will face to many difficulties in real study because of poor facilities and advanced experiences. Therefore, I am positively believe that with the help and corporation of the ionic liquids experts from Kanazawa University, I will get great achievements in study and develop the ionic liquids researcher network.