Selective substitution of long-acyl groups into alcohols of kraft lignin over transesterification using ionic liquid

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Abstract

Kraft lignin is a valuable aromatic renewable resource that is discharged in large quantities during the kraft pulping process. In this study, kraft lignin derivatives with improved solubility and thermal properties were prepared by a facile chemical modification of the aliphatic hydroxy (R-OH) group in kraft lignin with various ester groups. Kraft lignin was subjected to homogeneous transesterification with vinyl esters as acyl donors using an ionic liquid as a green solvent and catalyst. The selective introduction of acyl groups into the R-OH group was confirmed by nuclear magnetic resonance (NMR) spectroscopy, and it was estimated that approximately 90% of the R-OH group was converted whereas more than 80% of the aromatic hydroxy (Ar-OH) group was retained. The R-OH-selective introduction of long-chain acyl groups of more than six carbons successfully provided superior solubility in common low-boiling solvents, such as chloroform and tetrahydrofuran, and sufficient heat-meltability to be molded into films by hot-pressing. All the kraft lignin derivatives showed high glass transition temperatures of over 100 °C, indicating their potential to be heat-resistant materials. The kraft lignin derivatives, in which only the R-OH group was acylated, retain their inherently rich Ar-OH groups and thus, can be applied as desirable precursors in a wide range of further chemical treatments for functional polymer materials.

Keywords: Lignin, Hydroxy groups, Transesterification, Ionic liquid

Introduction

Kraft lignin is an industrial lignin obtained from the byproduct (i.e., black liquor) of the kraft pulping process, which accounts for approximately 85% of the total lignin production in the world [1]. Currently, the annual production of kraft lignin is approximately 630,000 tons. However, it is mainly used in the form of combustion for heat recovery, resulting in low-value utilization. Although high-value utilization of kraft lignin is in demand, there has been no significant progress in industrialization. The major factors that prevent its effective utilization, such as polymeric materials, are: (1) low molecular weight due to considerable decomposition during alkaline cooking; (2) hard and brittle nature related to the high glass transition temperature (T_g), and (3) poor processability based on the insolubility in common solvents and lack of heat-meltability.

Despite the difficulties in material application, kraft lignin has an attractive character as an inherently multifunctional polymer having not only aliphatic hydroxy (R-OH) and carboxy (COOH) groups, but 5–10 times more abundant aromatic hydroxy (Ar-OH) groups than native lignin. Notably, the Ar-OH group is a valuable functional group, because it is more chemically reactive than the R-OH group and can easily serve as a reaction point for thermosetting and chemical cross-linking of kraft lignin. Furthermore, the Ar-OH group is known to have antioxidant ability [2, 3] and adsorption capability for metals [4, 5]. We hypothesized that

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if the poor processability of kraft lignin was improved by a certain modification method while retaining the rich Ar-OH group, the resultant kraft lignin derivative would be a valuable precursor for polymeric materials with the unique functions in addition to the inherent high thermal stability of aromatic polymers.

Esterification of the hydroxy (OH) groups in kraft lignin is one of the simplest and oldest chemical modification methods for improving its physicochemical properties [6–8]. Although acyl halides and anhydrides are typically used as highly activated acyl donors in the presence of catalysts, it has been reported that there is little chemoselectivity for R-OH and Ar-OH groups. We focused on the use of ionic liquids (ILs) to develop an efficient and sustainable functionalization process for kraft lignin.

ILs are molten organic salts with melting points below 100 °C [9] and can be a platform for biomass conversion in a wide range of applications [10, 11]. 1-Ethyl-3-methylimidazolium acetate (**EmimOAc**) is an excellent solvent for biopolymers such as cellulose [12] and lignin [13], and functions as an organocatalyst for the transesterification of R-OH and Ar-OH groups with relatively stable vinyl esters as acyl donors [14, 15]. Moreover, in situ ^{1}H nuclear magnetic resonance (NMR) spectroscopy of the transesterification between low-molecular-weight model compounds with R-OH and Ar-OH groups and isopropenyl acetate (IPAc) revealed that **EmimOAc** promotes not only acetylation of both OH groups but also selective deacetylation of the instantaneously formed aromatic acetyl (Ar-OAc) group [16, 17]. Consequently, it was demonstrated that only R-OH group in kraft lignin was acetylated in one-pot two-step reaction using **EmimOAc**, IPAc, and a tiny amount of water as a proton source for selective deacetylation of the Ar-OAc group [18].

The advantage of esterification is that it provides wide and desirable material properties by tuning the degrees of substitution and chemical structures of the introduced ester groups (e.g., alkyl chain lengths). The purpose of this study was to develop functional kraft lignin derivatives with excellent solubility, heat-meltability, and thermal stability, via simple and sustainable conversion process. First, the applicability of the R-OH-selective modification system using **EmimOAc** was verified using various types of vinyl esters with different alkyl chain lengths as acyl donors. Hereafter, the solubility in common solvents, thermal stability, and hot-press moldability of the obtained kraft lignin derivatives were investigated to clarify the correlation between the alkyl chain length of the ester groups, which was selectively introduced into the R-OH group

in kraft lignin, and the resultant physicochemical properties.

Materials and methods

Materials

EmimOAc was purchased from Nippon Nyukazai Co., Ltd. (Tokyo, Japan) and used without further purification. Anhydrous dimethyl sulfoxide (DMSO) was obtained from Sigma-Aldrich Co., LLC. (St. Louis, MO, USA). Vinyl esters were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and used as received. Kraft lignin ([R-OH]: 2.7 mmol g^{-1}, [Ar-OH]: 3.4 mmol g^{-1}) was procured from Sigma-Aldrich Co., LLC. (St. Louis, MO, USA) and dried under vacuum at 70 °C until a constant weight before use. Other chemicals were commercially available and used as received unless otherwise stated.
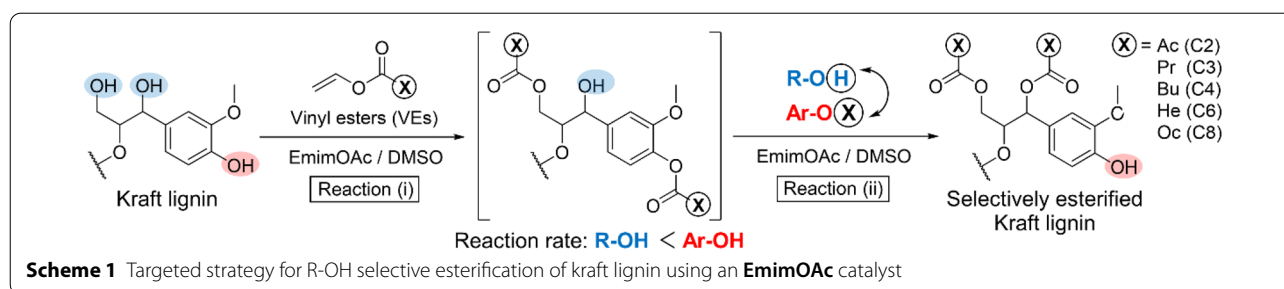
Selective R-OH modification in kraft lignin

Kraft lignin (0.60 g, 6 wt.%/**EmimOAc**]) in **EmimOAc** (10 g) was dried under vacuum at 80 °C for 2 h to remove moisture. After DMSO (15 mL) was added to the solution under a N$_2$ atmosphere, the resultant mixture was stirred at 80 °C for 2 h to completely dissolve the kraft lignin. As an acyl donor, 2 eq./[R-OH] of vinyl esters with different carbon numbers from 2 to 8 (Table 1) were added to the reactant solution using a micro-syringe. The resultant solution was further stirred for 2 h at 80 °C to perform the esterification of both R-OH and Ar-OH groups of kraft lignin and selective de-esterification of the generated aromatic ester (Ar-OR) groups (Scheme 1). The reacted solution was poured into 600 mL of distilled water to precipitate the light brown particles. After centrifugation (4 °C, 1 h, 18,000 rpm), the precipitated polymer was collected by

Table 1 Experimental conditions and yields of the kraft lignin derivatives

Entry	Kraft lignin (g)	Acyl donor			Yield (g)
		Reagent	Carbon number	mL[a]	
1	0.60	Vinyl acetate (VAc)	2	0.27	0.57
2	0.60	Vinyl propionate (VPr)	3	0.32	0.57
3	0.60	Vinyl butyrate (VBu)	4	0.37	0.61
4	0.60	Vinyl hexanoate (VHe)	6	0.46	0.66
5	0.60	Vinyl octanoate (VOc)	8	0.57	0.72

[a] Calculated as 2 eq./[R-OH] of kraft lignin

Scheme 1 Targeted strategy for R-OH selective esterification of kraft lignin using an **EmimOAc** catalyst

vacuum filtration and repeatedly washed with distilled water. After freeze-drying for 2 days, it was vacuum dried at 70 °C for over 24 h to yield the esterified kraft lignin.

Nuclear magnetic resonance (NMR) spectroscopy

The ^{1}H, ^{13}C, and ^{31}P NMR spectra in solution were recorded using a JNM-ECA 600 spectrometer (JEOL Ltd., Tokyo, Japan) in deuterated solvents. All NMR spectra were analyzed using a Delta NMR software (JEOL Ltd., Tokyo, Japan), and the chemical shifts (δ, ppm) were referenced to tetramethylsilane (TMS, $\delta = 0$ ppm) as an internal standard.

The contents of OH groups in kraft lignin and the ester derivatives were estimated by quantitative ^{31}P NMR analysis via phosphitylation of the samples, according to previous studies [19, 20]. First, the phosphitylation of kraft lignin and ester derivatives was conducted using the common phosphitylation reagent, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP), at room temperature (25 °C) for 15 min in the same manner as in our previous reports [16–18]. The used NMR spectrometer was the same JNM-ECA 600 spectrometer, and two kinds of internal standards of (1) *N*-hydroxy-5-norbornene-2,3-dicarboxylic acid imide and (2) cyclohexanol (10 g L^{-1}, each) were applied with a relaxation reagent of tris(2,4-pentanedionato)-chromium(III) (5 g L^{-1}) in chloroform-d_1/pyridine mixed solvent. The inverse-gated ^{1}H decoupling sequence was employed with a recycle delay of 25 s. The free induction decays of 128 were collected and averaged to obtain the ^{31}P NMR spectra.

Size exclusion chromatography (SEC)

The molecular weights distributions of kraft lignin and the ester derivatives were determined by SEC (UFLC system, Shimadzu Co., Kyoto, Japan) based on polystyrene standards. All SEC measurements were carried out at 40 °C using TSK gel α-M (Tosoh Co., Tokyo, Japan), and 0.01 mol L^{-1} LiBr in dimethylformamide (DMF, HPLC grade, Kanto Chemicals Co., Inc., Tokyo, Japan), which was used as the eluent at a flow rate of 1.0 mL min^{-1}.

Solubility test

The solubility of kraft lignin and the ester derivatives in common solvents was investigated by a brief test. All samples were vacuum dried at 70 °C for 24 h before testing. The dried sample (*ca.* 10 mg) was weighed into a 1-mL vial, and various solvents were added. Solubility was observed by visual confirmation after standing at room temperature for 24 h.

Thermogravimetric analysis (TGA)

TGA was performed using a TGA-50 (Shimadzu Co., Kyoto, Japan) equipped with a gas-flow controller (FC-60A, Shimadzu Co., Kyoto, Japan) and an analysis system (TA-60, Shimadzu Co., Kyoto, Japan). All samples were vacuum dried at 70 °C for 24 h prior to use, and the measurement temperature range was set from 50 to 500 °C at a heating rate of 10 °C min^{-1} in a N$_2$-flow rate of 50 mL min^{-1}. A sample of *ca.* 10 mg was pre-dried at 120 °C for 2 h. The thermal decomposition temperature (T_d) was taken as the onset of a 5% weight loss ($T_{d\text{-}5\%}$).

Dynamic mechanical analysis (DMA)

The glass transition temperature (T_g) was investigated using a DMA 8000 instrument (PerkinElmer Japan Co., Ltd., Yokohama, Japan) in a single cantilever mode. The powder samples (*ca.* 10 mg) were enclosed in a folded metal plate named "material pocket". The measurements were carried out under a N$_2$ atmosphere at a heating rate of 2 °C min^{-1} from 30 to 300 °C or to the temperature at which the T_g peak for each sample was clearly observed.

Hot-pressing test

The powder samples (*ca.* 0.3 g) were placed in a polytetrafluoroethylene (PTFE) mold (30 × 30 × 0.2 mm), covered between two PTFE sheets, and hot-pressed at a determined temperature under a constant pressure of 5 MPa using a MINI TEST PRESS 10 instrument (Toyo Seiki Seisaku-sho, Ltd., Tokyo, Japan). After hot-pressing, the molded film-like samples were naturally cooled and peeled off from the mold. The thermal processability of

each sample was determined based on whether the heat-molded sample was a self-standing film with appropriate flexibility.

Results and discussion

Strategy for development of one-step selective modification of R-OH group in kraft lignin

In our previous study, a one-pot two-step chemical modification method using **EmimOAc** was proposed for the acetylation of the R-OH group in kraft lignin with remaining the Ar-OH group intact. In this method, IPAc was firstly reacted with both R-OH and Ar-OH groups for 1 h at 80 °C. Hereafter, a small amount of water (2 eq./[Ar-OH]) was subsequently added as a proton source for the selective deacetylation of the generated Ar-OAc group and heated for more 1 h at 80 °C [18]. In this study, for developing a more facile method, our focus was on the fact that the reaction rate of acetylation of the Ar-OH group is much faster than that of the R-OH group under the presence of **EmimOAc** and a limited amount of IPAc [16]. Based on this fact, we assumed that the instantaneously and preferentially generated Ar-OAc group could be selectively deacetylated utilizing the unreacted R-OH group as a proton source, and consequently, only the R-OH group would be acetylated in a simpler one-step process without the further addition of any other proton sources (e.g., water) as depicted in Scheme 1. Furthermore, the applicability of the reaction system not only to IPAc, but also to various acyl donors is important with respect to the tunability of the material properties of the products. Therefore, a one-step chemical modification method for the esterification of only the R-OH group in kraft lignin was first verified using five types of vinyl esters with different alkyl chain lengths as acyl donors.

Appearance, isolated yield, and molecular weight distribution of products

The products obtained via the one-step chemical modification of kraft lignin using **EmimOAc** were collected as powder samples (Fig. 1). The original color of kraft lignin was brown, and the color changed to light brown after acetylation. With increasing alkyl chain lengths of the introduced ester groups, the color of the products further became darker.

Table 2 shows the isolated yields and molecular weight distributions determined by SEC measurements (Fig. 2) of the five types of kraft lignin ester derivatives. All the products were recovered in good isolated yields of 83–92%. Compared to the original kraft lignin, the weight average molecular weight (M_w) increased from 8.3 to 10×10^3 g mol^{-1} with an increase in the carbon number of the introduced ester groups. Thus, it was considered that no significant chemical degradation might have occurred during the reaction in the presence of **EmimOAc**. Furthermore, the polydispersity ($Đ$) of kraft lignin was originally 14, while those of the ester derivatives decreased to 9.3–8.9 due to a slight loss of

Table 2 Isolated yield, residual OH content, and molecular weight distribution of original kraft lignin and the ester derivatives

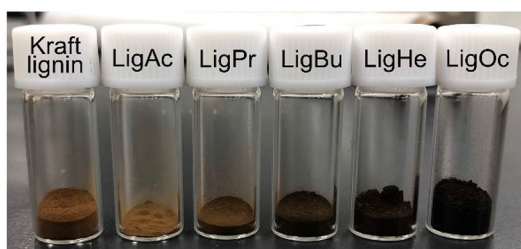| Sample	Isolated yield (%)	Molecular weight distribution	
		M_w (10^3 g mol^{-1})	$Đ^a$
Kraft lignin	–	8.7	14
LigAc	83	8.3	9.3
LigPr	86	9.5	9.2
LigBu	87	9.3	9.2
LigHe	89	10	9.1
LigOc	92	10	8.9

[a] Polydispersity, M_w/M_n

Fig. 1 Appearances of original kraft lignin and the ester derivatives
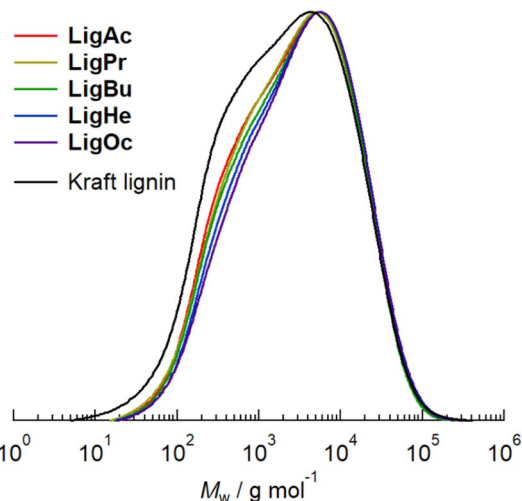

Fig. 2 Molecular distributions of original kraft lignin and the ester derivatives measured using SEC with polystyrene standards

the low-M_w parts through the reaction and subsequent purification process.

Chemical identification by NMR analyses

All the products were subjected to ^{1}H and ^{13}C-NMR analyses to verify the occurrence of esterification of the OH groups in kraft lignin. The ^{1}H NMR spectra (Fig. 3a) contained broad peaks at 6.2–7.5 ppm from the aromatic skeleton of lignin and strong peaks at approximately 3.7 ppm from methoxy (OMe) groups. In the spectrum of the original kraft lignin, no clear peak (except for solvent peaks) was observed at 0–3 ppm. On the other hand, for all kraft lignin ester derivatives, new peaks were observed in the same area due to the alkyl protons of the introduced ester groups. Therefore, it was confirmed that kraft lignin was esterified despite the type of vinyl esters.

According to a previous paper, it was reported that the peaks derived from methyl carbons (CH$_3$-) in R-OAc and Ar-OAc groups were observed at 1.7–2.1 ppm and 2.2–2.4 ppm, respectively [18]. However, the spectrum of **LigAc** prepared in this study showed only one peak at the former range, suggesting that the selective modification

of R-OH group in kraft lignin with Ac group succeeded. For other kraft lignin derivatives with longer acyl groups, almost all the peaks based on the alkyl protons were broadened, making it difficult to determine whether the R-OH and/or Ar-OH groups were esterified.

For additional chemical investigation of kraft lignin derivatives, ^{13}C-NMR analysis was performed (Fig. 3b). In the ^{13}C-NMR spectrum of the original kraft lignin, there were several peaks in the aromatic carbon region from 100 to 150 ppm and strong peaks at approximately 56 ppm corresponding to the OMe groups. Notably, kraft lignin derivatives showed new peaks due to carbonyl carbon (C=O) of acyl groups at approximately 170 ppm, and sharp peaks in the range from 10 to 30 ppm correspond to alkyl carbons of acyl groups. Therefore, consistent with the ^{1}H NMR results, the esterification of kraft lignin using vinyl esters with different alkyl chain lengths was proved.
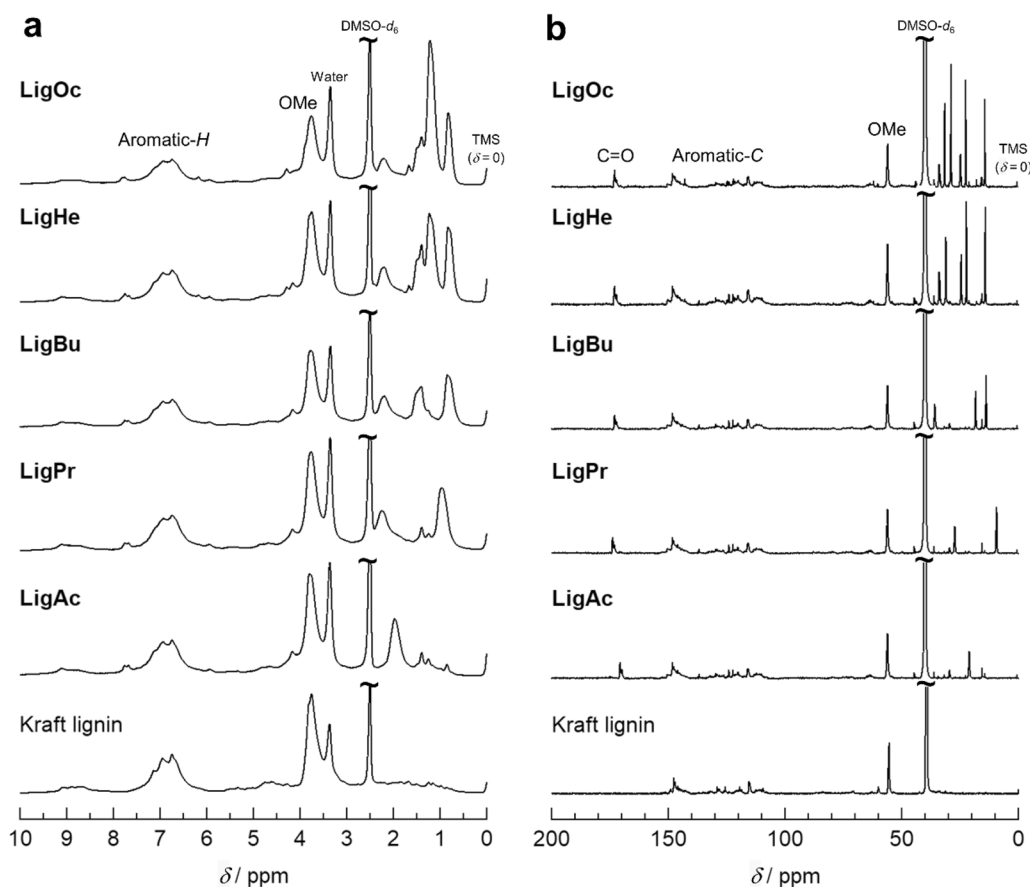

Fig. 3 **a** ^{1}H- and **b** ^{13}C-NMR spectra of original kraft lignin and ester derivatives

Verification of R-OH selectivity in transesterification of kraft lignin using EmimOAc

The above-described ^{1}H and ^{13}C-NMR analyses revealed the success of the esterification of kraft lignin using various vinyl esters, but it was difficult to verify the selectivity in the esterification of R-OH and Ar-OH groups, owing to the structural complexity of kraft lignin itself. Then, another analytical method was performed to quantify the remaining unreacted R-OH and Ar-OH groups in the kraft lignin ester derivatives by quantitative ^{31}P NMR analysis after phosphitylation of each sample. In this analytical method, the smaller amount of quantified OH groups for kraft lignin ester derivatives suggested that the corresponding OH groups were esterified to a higher degree by the reactions using **EmimOAc** and vinyl esters.

Figure 4 shows the quantitative ^{31}P NMR spectra of phosphitylated samples. As followed in previous reports [19, 20], the peaks of the phosphitylated R-OH and Ar-OH groups in lignin are observed in 145.4–150.0 ppm and 137.1–144.0 ppm, respectively. In fact, there were clear peaks in the spectrum of phosphitylated kraft lignin, suggesting that the original kraft lignin contains abundant R-OH and Ar-OH groups. Notably, kraft

lignin initially contains a small amount of COOH group, and this ^{31}P NMR analysis enables the identification of the phosphitylated COOH group observed in the range of 133.6–136.0 ppm. However, it was clarified by a previous report that the COOH group was not involved in the transesterification reactions in the presence of **EmimOAc** [16]. Furthermore, since little change in the COOH content was observed in this study, it was not included in the discussion here.

As listed in Table 3, although kraft lignin initially contained 2.4 mmol g^{-1} of R-OH group and 3.6 mmol g^{-1} of Ar-OH group, all the ester derivatives contained only 0.20–0.26 mmol g^{-1} of R-OH group, suggesting that almost all R-OH group was substituted with the corresponding ester groups. In contrast, the residual amount of Ar-OH group was 2.5–3.0 mmol g^{-1}: precisely, the OH content "per gram" slightly decreased, since the molecular weight of the ester derivatives increased with the increase in the carbon number of the introduced ester groups. Based on these results, it was confirmed that the R-OH group in kraft lignin was effectively substituted with various ester groups with the remaining the rich Ar-OH group through the one-step chemical modification process using **EmimOAc**.
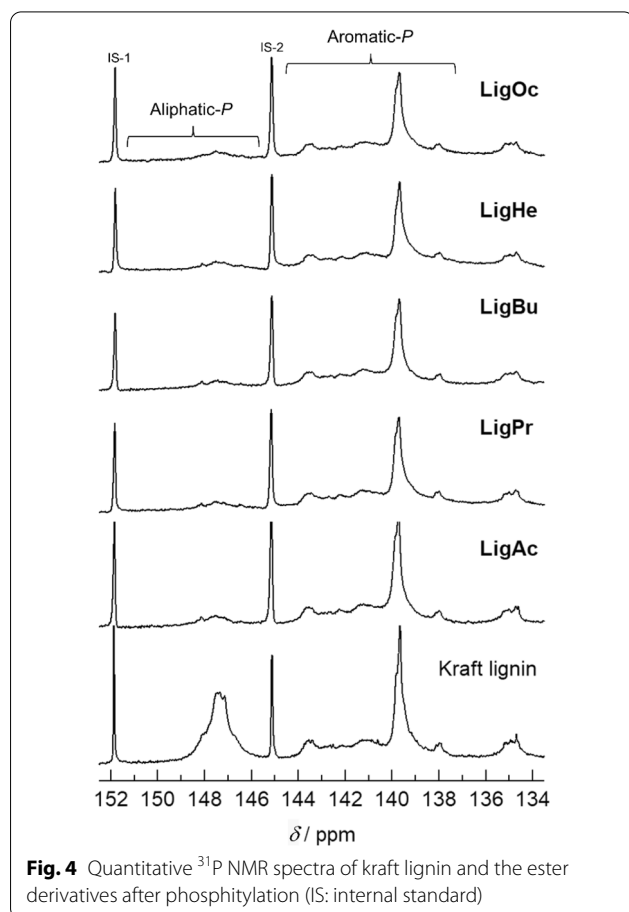
Improved solubility of kraft lignin derivatives by selectively introduced long-ester groups

The solubility of polymers in organic solvents with low boiling points is crucial because it enables various molding methods such as solvent casting [21], dry spinning [22], and preparation of nanoparticles in solvents [23]. Moreover, considering the effective utilization of kraft lignin as a polymeric material, it is desirable to increase the originally low molecular weight of kraft lignin [24], which can ensure a certain level of material strength. Therefore, it is essential to obtain "solubility in common solvents" for application to various chemical reactions in

Fig. 4 Quantitative ^{31}P NMR spectra of kraft lignin and the ester derivatives after phosphitylation (IS: internal standard)

Table 3 OH contents of original kraft lignin and the ester derivatives estimated by a quantitative ^{31}P NMR method

Sample	OH content (mmol g^{-1})		
	R-OH	**Ar-OH**	**Total OH**[a]
Kraft lignin	2.4	3.6	6.5
LigAc	0.26	3.0	3.6
LigPr	0.25	2.9	3.5
LigBu	0.20	2.8	3.3
LigHe	0.23	2.7	3.2
LigOc	0.20	2.5	3.0

[a] Sum up of R-OH, Ar-OH, and COOH groups

Table 4 Solubility of original kraft lignin and the ester derivatives in common solvents

Solvent	Kraft lignin	LigAc	LigPr	LigBu	LigHe	LigOc
Water	–	–	–	–	–	–
Methanol	–	–	–	–	–	–
DMSO	++	++	++	++	++	++
DMF	++	++	++	++	++	++
THF	–	–	–	–	++	++
Acetone	–	–	–	–	–	++
Chloroform	–	–	–	–	+	++
Hexane	–	–	–	–	–	–

++: soluble (≥ 2 g L^{-1}); +: partially soluble (< 2 g L^{-1}); –: insoluble

organic solvents, e.g., chemical cross-linking [25–27] and other polymerization reactions [28, 29].

Kraft lignin used in this study was soluble in DMSO and DMF, but insoluble in other single solvents listed in Table 4. Generally, the solubility of biopolymers in organic solvents improves by substituting the OH groups with ester groups. However, it was not clarified to what extent the solubility improves by increasing the alkyl chain lengths of the ester groups introduced onto only the R-OH group in lignin. Then, the solubility changes were briefly examined for five types of kraft lignin ester derivatives prepared in this study.

As summarized in Table 4, in the case of short-chain acyl groups, such as acetyl (Ac) and propionyl (Pr) groups, the solubility of the products did not change, plausibly due to the initially small content of the R-OH group in kraft lignin (i.e., 2.4 mmol g^{-1}). On the other hand, when long-chain acyl groups of hexanoyl (He) and octanoyl (Oc) were substituted with the R-OH group, the solubility in tetrahydrofuran (THF) and chloroform was found to improve. Therefore, it was demonstrated that even a low degree of esterification for only the R-OH group successfully enhanced the solubility, depending on the alkyl chain length of the introduced ester groups.

Evaluation of thermal properties of kraft lignin ester derivatives

Kraft lignin and the ester derivatives were subjected to thermal analyses by thermo-gravimetry (TG) and DMA measurements under a N$_2$ atmosphere. Figure 5a shows the TG curve and the thermal degradation temperature defined as a 5% weight loss temperature ($T_{d-5\%}$) for each sample. The $T_{d-5\%}$ of the original kraft lignin was 255 °C, and those of the ester derivatives ranged from 241 to 268 °C regardless of the alkyl chain length of the introduced ester groups. Therefore, it is suggested that the esterification of only the R-OH group in kraft lignin has little effect on the thermal stability.
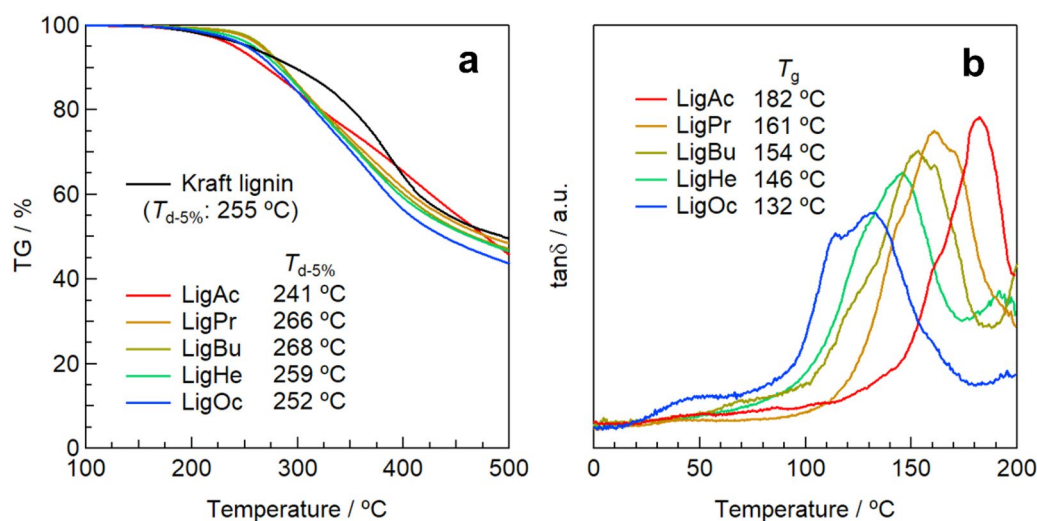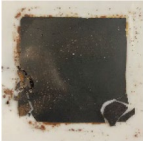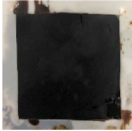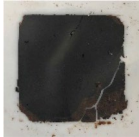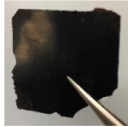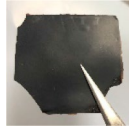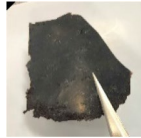

Fig. 5 a TG and **b** DMA: tan δ as a function of temperature for kraft lignin ester derivatives

Table 5 Evaluation of heat-moldability in hot-pressing and the resultant films of original kraft lignin and the ester derivatives

	Kraft lignin	LigAc	LigPr	LigBu	LigHe	LigOc
Press temp.[a]	200 °C	180 °C	160 °C	150 °C	145 °C	130 °C
Pictures of molded sample						
Availability[b]	−	+	+	++	++	++

[a] Determined by T_g and the samples were pressed twice for each 60 s

[b] Considered by the self-standing ability and flexibility of the hot-pressed films

Differential scanning calorimetry (DSC) is very popular for the determination of the glass transition temperature (T_g) of polymer materials. However, the glass transition of kraft lignin ester derivatives was not clearly observed in the DSC measurements, plausibly due to the heterogeneous structures. Then, the T_g values were determined as the peak top temperatures of tan δ measured by DMA for the powder-state samples. Figure 5b shows the tan δ plots as a function of temperature and the estimated T_g for kraft lignin ester derivatives. The highest T_g of 182 °C was observed in **LigAc** substituted with the shortest-chain acyl group, and T_g decreased with increasing the introduced acyl chain length. It should be noted that **LigOc** substituted with the longest-chain acyl group showed the lowest T_g value of 132 °C, but it was still over 100 °C, implying the potential of kraft lignin ester derivatives to be applied to highly heat-resistant materials.

Evaluation of thermoplasticity as hot-pressing moldability of kraft lignin derivatives

Thermoplasticity (or heat-meltability) is an important function of polymer materials that enables beneficial forming processes simply by heating, for example, melt spinning [30–32], hot-pressing [33], and injection-molding [34]. Furthermore, it also allows thermal-processing such as polymerization in the molten state in solvent-free systems [35], and melt kneading for blending multiple polymers [36, 37], contributing to the functionalization of polymers and the expansion of their applications. Then, the thermoplasticity was briefly examined by a hot-pressing test for kraft lignin ester derivatives.

Table 5 shows pictures of hot-pressed kraft lignin and the ester derivatives. Because kraft lignin does not exhibit thermoplasticity, it remained in a compacted powder form even after hot-pressing at 200 °C. In the case of **LigAc** and **LigPr**, it was observed that both powder samples were partially heat melted at the near temperature of T_g and molded as films. However, the resultant films were too brittle to be peeled off from the PTFE mold used during hot-pressing. On the other hand, kraft lignin derivatives with acyl groups longer than butyryl (Bu) showed good thermal moldability through hot-pressing, resulting in uniform and glossy films. These results suggest that kraft lignin successfully acquired sufficient thermoplasticity when the carbon number of the introduced ester groups was larger than 4, even though the esterification was limited to the R-OH group. Considered to be utilized as a single material, **LigBu**, **LigHe**, and **LigOc** still have some issues in terms of fragility due to their low molecular weights (M_w, *ca.* 10^4 g mol^{-1}, Table 5). However, the kraft lignin derivatives could be regarded as promising functional precursors that would be applicable to melt blending with other polymers or bulk polymerization such as thermosetting to overcome the disadvantage of molecular weights.

Conclusions

Through a facile and mild chemical modification method using **EmimOAc**, ester groups with different alkyl chain lengths were successfully introduced onto the R-OH groups in kraft lignin, leaving almost all the Ar-OH group intact. All the kraft lignin ester derivatives showed high T_g values above 100 °C, implying their potential as precursors for heat-resistant aromatic polymeric materials. Furthermore, it was found that the kraft lignin derivatives in which the R-OH group was selectively substituted with long acyl groups, such as He and Oc groups, showed improved solubility in THF and chloroform and sufficient thermoplasticity, which was evaluated as hot-press moldability at temperatures near T_g. Due to their low M_w of $8.3–10 \times 10^3$ g mol^{-1}, the kraft lignin ester derivatives might require additional chemical processing (e.g., polymerization and cross-linking) or blending with other polymers for practical use as materials. **LigHe** and **LigOc** have good solubility and heat-melting properties, and thus, they can be easily applied to these treatments in solution or melting states.

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