Preparation and structural characterization of lignin micro/nano-particles with ionic liquid treatment by self-assembly

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Abstract. In the present research, 1,3-dimethyl-imidazolium dimethyl phosphate ([Mmim][DMP]) ionic liquid was applied to dissolve alkali lignin from wheat grass to prepare for lignin micro/nano-particles. The alkali lignin can be dissolved completely at 80 °C in 30 min under microwave condition with [Mmim][DMP] (solid-liquid ratio of 1:10) which is easy to be recycled. The dissolved lignin can be precipitated by diluting the ionic liquid-lignin solution with water to get lignin micro/nano-particles with diameter ranged from 200 nm to 1.5 μ m. Structural analyses with Gel permeation chromatography (GPC), 2D heteronuclear single quantum coherence nuclear magnetic resonance (2D-NMR), Thermogravimetric Analysis (TGA), etc., indicate that a large number of dehydration reactions occurred during dissolution process to result in the generation of unsaturated bonds with higher degree of unsaturation (Ω) (from 197–334), lower polydispersity (from 1.49 to 1.12) and lower average molecular weight (from 8634 to 5406 Da). Compared with original alkali lignin, the regenerated alkali lignin as micro/nano-particles showed higher thermal stability. It was also found from the 2D NMR spectra that the cleavages of aryl-ether bonds dramatically happened during the dissolution process, [Mmim][DMP] ionic liquid is more likely to destroy lignin units linked by β -O-4' bonds to G-type lignin with less steric hindrance, resulting in the least amount of β -O-4' linkages. In addition, dehydration and demethylation of lignin occurred during the dissolution of ionic liquid.

Keywords: nanomaterials, ionic liquid, alkali lignin, dissolution, micro/nano-particles

1. Introduction

Lignin is one of the most abundant natural biopolymers on earth, which accounts for about 15–25 wt% of wood and is considered as a renewable source of aromatic and chemical feedstock [1, 2]. As a complex and heterogeneous biomacromolecule, with primary monomers of guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H) connected by various interunit linkage such as β -O-4, β - β , β -5, β -1, and 4-O-5, etc. [3, 4], lignin can be obtained as a byproduct from chemical pulping and biofuel production processes either in the form of valuable dispersing agent

lignosulfonate or as kraft lignin, which nowadays is mainly burned as fuel during the chemical recovery process of kraft pulping [5, 6].

Lignin conversion into simple aromatic products is a difficult task due to lignin's recalcitrant nature, its complex structure, variability of sources and extraction processes [7, 8]. It still takes a long way to realize the high value of lignin. Despite their usefulness, a comprehensive studies do have certain drawbacks namely high operating temperature and extended dissolution times are required for processing, (generally >12 h) etc. Therefore, it's necessary to develop

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low-temperature and rapid delignification with simplistic recovery of chemicals for advanced utilization of renewable and biodegradable lignin for a future bio-based economy. Recently ionic liquids (ILs) have been extensively used for the dissolution and delignification of biomass [9] with eco-friendly characteristics, being nonflammable and recyclable with low volatility and high thermal stability. More importantly, ionic liquids also have amphipathic properties which allows easy precipitation of dissolved lignin to form lignin micro/nano-particles by adding acid water (Acid deionized water).

In this paper, 1,3-dimethyl-imidazolium dimethyl phosphate ([Mmim][DMP]), which is known to have a good lignin solubility according to the researches by our team [10, 11], was employed to develop a rapid and complete alkali lignin dissolution method with low temperature and characterize the regenerated lignin micro/nano-particles by Fourier transform infrared spectroscopy (FT-IR), the elemental analysis, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), 2D heteronuclear single quantum coherence nuclear magnetic resonance (2D HSQC NMR) spectroscopy. Furthermore characterization of regenerated lignin micro/nano-particles morphology was observed by scanning electron microscopy (SEM) and polarized light microscopy (PLM).

2. Experimental

2.1. Materials

Ionic liquid [Mmim][DMP] ($\geq 99\%$) was made in the laboratory as previously described [12] with a yield of 97.5% and purity of 99.77%. Water content (measured by Karl-Fischer titration) in the ionic liquid was 0.5 wt%. Lignin (alkali lignin (Grass lignin) $\geq 99\%$ purity) purchased from Sigma-Aldrich Company (Beijing, China). All other reagents used in the experiments were analytical grade.

2.2. Solubility test for alkali lignin

A microwave extraction apparatus (XH-100B, XINGHU Microwave BEIJING, China) was chosen to improve the efficiency of lignin dissolution in ionic liquids [13, 14]. The dissolving conditions were as follows: microwave power, 500 W; temperature, 80 °C; reaction time, 30 min; and ratio of solid to liquid, 1:10. At the end of the preset reaction time, deionized water (5–10 °C) was added into the lignin-ionic liquid solution to terminate reaction of the regenerated

lignin. More lignin can be obtained by adjusting the pH of the added water to 2–3, using concentrated H₂SO₄ (96%). However, this strategy will pose a problem for further recycling of [Mmim][DMP]. Apart from visual observations the saturation point was also observed and confirmed using polarized light microscopy (PLM).

2.3. Characterizations

2.3.1. Morphology of regenerated lignin

Scanning electron microscopy (SEM; EV018, Carl Zeiss AG, Oberkochen, Germany) was used to observe the morphology of regenerated lignin in a vacuum. The samples were sputter-coated with gold to make the lignin conductive, avoiding degradation and buildup of charge on the specimen. The solid-liquid reaction system was observed by perpendicular polarizing microscopy (PLM; DM2700M, Leica Microsystems GmbH, Wetzlar, Germany). The size of LM/NPs were measured by Static and dynamic laser light Scatterometer (ALV/CGS-3, Germany).

2.3.2. Elemental analysis

Elemental analysis was performed to determine the carbon, hydrogen, oxygen, and nitrogen content in lignin samples using US/CHNS-932 (LECO Corp., USA).

2.3.3. Thermal characterization

Thermogravimetric analysis was performed to compare the stability of the original alkali lignin (OAL) and lignin micro/nano-particles (LM/NPs) by a TAQ500 instrument (TA Company, New Castle, USA) in a nitrogen atmosphere, and a heating rate of 15 °C/min from 25 to 700 °C.

2.3.4. Gel permeation chromatography (GPC)

The lignin was acetylated with acetic anhydride/pyridine (1:1 v/v) at 70 °C for 6 h, and the derivatized lignin was dissolved in tetrahydrofuran (THF) and analyzed by a GPC max instrument (ViscotekRImax, Viscotek, UK) equipped with a PLgel 5 μ m MIXED-C column (300 $\times$ 7.5 mm, VARIAN, Inc.) and PLgel 5 μ m guard column (50 $\times$ 7.5 mm, VARIAN, Inc.) using UV-Vis detection (VE3210, Viscotek). To determine the molecular weight of the effluent, polystyrenes with a mass range between 580 and 3250 000 Da were used to create a calibration curve.

2.3.5. Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra were recorded on a Nicolet 6700 spectrometer (Vector 33, Bruker, Karlsruhe, Germany) operating in the wavelength range of 4000–650 cm^{-1} . Each sample was coated by potassium bromide (KBr) and formed into a pellet for analysis.

2.3.6. NMR spectroscopy for dissolved lignin

2D heteronuclear single quantum coherence nuclear magnetic resonance (2D HSQC NMR) spectra were acquired on a Bruker Avance 600 MHz spectrometer fitted with a 5 mm gradient probe with inverse geometry (proton coils closest to the sample). 100 mg of lignin sample was dissolved in 0.5 mL of $\text{DMSO}-d_6$. A recent published 2D HSQC NMR quantitative method was applied to estimate the lignin-coupling bond in hardwood and softwood samples [15]. The method uses a cluster of signals as an internal standard that are representative of all C_9 units present in the sample. In this study, the quantitative method was applied with minor modification. For grass lignin (wheat grass lignin), the internal standard can thus be quantified by the total integration of the half syringyl signal ($\text{S}_{2,6}$) plus the G_2 signal as well as half of the integration of $\text{H}_{2,6}$ cross signal (Equation (1)):

$$\text{IC}_9 \text{ units} = 0.5\text{IS}_{2,6} + \text{IG}_2 + 0.5\text{IH}_{2,6}(\text{IC}_9) \quad (1)$$

where $\text{IS}_{2,6}$ is the integration of $\text{S}_{2,6}$, and include S and S'; IG_2 is the integral value of G_2 . $\text{IH}_{2,6}$ is the integral value of $\text{H}_{2,6}$. IC_9 represents the integral value of the aromatic ring. According to the internal standard (IC_9), the amount of IX [%] could be obtained by Equation (2):

$$\text{IX} [\%] = \frac{\text{IX}}{\text{IC}_9} \cdot 100\% \quad (2)$$

where IX is the integral value of α -position of A ($\beta\text{-O-4}$), B ($\beta\text{-}\beta$), and C ($\beta\text{-5}$); the integration should be conducted in the same contour level.

3. Results and discussion

3.1. SEM and PLM observation

The morphology of alkali lignin before and after treated by [Mmim][DMP] ionic liquid were confirmed by SEM and PLM images in Figure 1. and Figure 2. Interestingly, that nanoscale lignin particles formed through the self-assembly of dissolved lignin after dilution by water. From the image of PLM, the

Figure 1. SEM images of a) original alkali lignin, b), c) regenerated lignin micro/nano-particles.

fluorescent particles are lignin particles. The solid particles were composed of mainly small particles and a number of large particles with the size ranging from 200 nm to 1.5 μm , which agreed well with the particle size measured by the dynamic light scattering (DLS). And from the DLS, the large size particles may be due to the agglomeration of lignin

Figure 2. PLM images of (a) all dissolving picture of alkali lignin, (b) lignin micro/nano-particles regenerated with water in [Mmim][DMP].

Figure 3. The size distribution of lignin micro/nano-particles.

Figure 4. Lignin solubility in pure and recycled [Mmim][DMP] ionic liquid.

particles after centrifugation, drying and dispersed in the water (Figure 3).

Interests in using lignin micro/nano-particles for developing biodegradable materials are growing for many potential applications [16–18]. Many studies on lignin micro/nano-particles production used alkali lignin that was dissolved in organic solvents, such as ethylene glycol [18], acetone, tetrahydrofuran (THF) etc. Organic solvents bring an environmental concern and increases cost for solvent recovery. In contrast, [Mmim][DMP] ionic liquid can be recycled 3–5 times, the recovered mass of [Mmim][DMP] ionic liquid after recycling was found to be more than 95% (Figure 4.), which indicated a potentially well recyclable solvent.

3.2. Elemental analysis

Table 1 shows the elemental composition, C_9 formula and degree of unsaturation of OAL and LM/NPs. The elemental carbon content of OAL (26.5%) was determined to be obviously lower than that of LM/NPs (49.1%), whereas the oxygen content of LM/NPs (43.1%) was lower than that of OAL (66.1%). This may be due to the large amount of dehydration and demethoxylation reactions that occurred during dissolution process, which is consistent with other literature reports [19]. The relatively high nitrogen content (2.1%) of LM/NPs was particularly notable,

Table1. Elemental composition, calculated C_9 formula, and degree of unsaturation of original alkali lignin (OAL) and lignin micro/nano-particles (LM/NPs).

Lignin	C [%]	H [%]	O [%]	N [%]	S [%]	C_9 formula	Degree of unsaturation
OAL	26.5	3.5	66.1	0.6	3.3	$C_{900}H_{1426}O_{1683}N_{17}S_{42}$	197
LM/NPs	49.1	5.3	43.1	2.1	0.4	$C_{900}H_{1165}O_{592}N_{32}S_3$	334

most of the nitrogen in the LM/NPs probably came from the solvent. Interestingly, the content of sulfur element is basically gone off after treatment by ionic liquid, from 3.3 to 0.4%. The literature [20] reports that compared with macromolecule lignin, the sulfur content of small molecular weight lignin is higher. The components of the small molecular weight have some loss in the process of treatment by ionic liquid, which can reasonably explain the lower sulfur content in the LM/NPs. It is noteworthy that the unsaturation of the alkali lignin rises from 197 to 334, indicating the formation of unsaturated bonds during dissolution process which inferred a positive possibility for modifications.

3.3. Molecular weight distribution

The values of the weight-average (M_w), number-average (M_n) molecular weight, and the polydispersity index (M_w/M_n) of OAL and LM/NPs, as revealed by GPC analysis, are shown in Table 2. The M_w of LM/NPs was determined to be 5406 Da, which was only 3/5 of the M_w of OAL (8634 Da). This lower M_w value for LM/NPs is good evidence for lignin fragmentation by the ionic liquid. In contrast, the difference between the M_n values of both LM/NPs and OAL is relatively small. The polydispersity index (M_w/M_n) of OAL and LM/NPs was calculated to be 1.49 and 1.12, respectively. This result indicates that

Table 2. Average molecular weight and polydispersity index (M_w/M_n) of original alkali lignin (OAL) and lignin micro/nano-particles (LM/NPs).

Lignin	M_w [Daltons]	M_n [Daltons]	M_w/M_n
OAL	8634	5779	1.49
LM/NPs	5406	4793	1.12

Figure 5. Thermogravimetric analysis of original alkali lignin (OAL) and lignin micro/nano-particles (LM/NPs).

compared to OAL, LM/NPs was formed with a relatively uniform lignin fragment size and a lower number of condensed linkages.

3.4. Thermal behavior

Thermogravimetric (TGA) of OAL and LM/NPs are described in Figure 5. As to the OAL, may be due to the influence of the moisture, the weight loss of lignin before 100 °C is larger. But the processing temperature for thermoplastic polymers rises above 200 °C. The weight loss of thermal degradation of lignin samples is mainly distributed in the range of 200–450 °C, in which the lignin side chain bonds are cleaved and the benzene ring structure is degraded [21]. During dissolution process, the lignin degraded to a certain degree, the molecular weight decreased. Some condensation reactions occurred in the molecular or intramolecular, such as the formation of β -5' bonds, etc. Finally, the degradation rate of lignin at 200–450 °C was accelerated. The results of the TGA curves, indicates that the lignin obtained after dissolution and regeneration process with [Mmim][DMP] is thermally more stable than that of the original alkali lignin. In addition, lignin thermal decomposition of its carbon residue is proportional to the size of the molecular weight, which was consistent with the results obtained from molecular weight distribution.

3.5. FT-IR spectra

In the present study, FT-IR spectra of OAL and LM/NPs are illustrated in Figure 6. The absorption at 3385 cm^{-1} is due to the O–H stretching and that at 2925 and 2852 cm^{-1} to the C–H stretching. In the fingerprint region, between 1800 and 900 cm^{-1} , many sharp and discrete absorption bands due to various functional groups present in LM/NPs and OAL were

Figure 6. FTIR spectra for (A) original alkali lignin (OAL), (B) lignin micro/nano-particles (LM/NPs).

Table 3. Band assignments for FTIR spectra.

Band [cm ⁻¹]	Assignment
3385	O–H vibrations
1596	Aromatic skeletal vibration breathing with C=C stretching
1510	Aromatic skeletal vibration
1460	CH asymmetric deformation
1422	Aromatic skeletal vibrations
1326	Syringyl ring breathing with CO stretching
1209	Guaicyl ring breathing with CO stretching
1115	–CH in plane deformation in syringyl ring
1030	–CH in plane deformation in guaiacyl and CO deformation in primary alcohols

observed (Table 3). The bands for aromatic skeleton vibrations, assigned at 1596, 1510, 1460, and 1422 cm⁻¹, show the typical signal pattern expected for a lignin moiety. The band at 1209 cm⁻¹ is assigned to guaiacyl ring breathing with CO stretching, the band at 1326 cm⁻¹ is associated with syringyl (*s*) units and the band at 1115 cm⁻¹ is CH in plane deformation in syringyl ring. In addition, the occurrence of the intensive peak at 1030 cm⁻¹ is due to the aromatic C–H in-plane deformation were visible in both lignin spectra. On the whole, as can be seen from the spectra, some changes have occurred in the LM/NPs structural units. There is an increased proportion of G-type structure of LM/NPs, which was consistent

with the results obtained from 2D-HSQC NMR spectra. This also indicates that the breakage of chemical bonds in the lignin macromolecules resulted in changes in the number of G and S lignin molecules.

3.6. 2D-HSQC NMR spectra

To further investigate structural changes of lignin during ionic liquid dissolution process, the OAL and LM/NPs were comparatively characterized by the 2D-HSQC NMR technique. The side chain (δ_C/δ_H 90–50/6.0–2.0 ppm) and the aromatic regions (δ_C/δ_H 135–95/8–6) of the HSQC spectra are shown in Figures 7 and 8. The main cross-signals assigned according to the literatures [22–24] are listed in Table 4.

Figure 7. The side chain region of the HSQC spectrum of a) original alkali lignin, b) lignin micro/nano-particles

Figure 8. The aromatic region of the HSQC spectrum of a) original alkali lignin, b) lignin micro/nano-particles.

In the side-chain region of the lignin, cross-peaks of different interunit linkages were identified, such as β -aryl-ether (β -O-4', A), resinol (β - β' , B), and phenylcoumaran(β -5', C), and it can also be evidently observed that, the cross-signals of methoxy groups ($-\text{OCH}_3$, $\delta_{\text{C}}/\delta_{\text{H}}$ 55.2/3.76 ppm) and β -O-4', A sub-

structures (A) were the most prominent, A_{α} and A_{γ} positions of which were presented at $\delta_{\text{C}}/\delta_{\text{H}}$ 72.0/4.88 and 59.9/3.2–3.5 ppm. C_{β} positions of β -O-4' in G and S type lignins were also detected at $\delta_{\text{C}}/\delta_{\text{H}}$ 83.7/4.31 and 86.3/4.01 ppm, respectively. In these lignin samples, a clear signal at $\delta_{\text{C}}/\delta_{\text{H}}$ 63.9/3.91 ppm

Table 4. Assignments of ^{13}C - ^1H correlation signals in the HSQC NMR spectrum of original alkali lignin (OAL) and lignin micro/nano-particles (LM/NPs).

Labels	$\delta_{\text{C}}/\delta_{\text{H}}$ [ppm]	Assignment
B_{β}	53.7/3.07	C_{β} - H_{β} in β - β' (resinol) substructures (B)
C_{β}	53.9/3.45	C_{β} - H_{β} in phenylcoumaran substructures (C)
MeO	55.2/3.76	C-H in methoxyls
A_{γ}	59.9/3.2–3.5	C_{γ} - H_{γ} in β -O-4' substructures (A)
C_{γ}	63.5/3.65	C_{γ} - H_{γ} in phenylcoumaran substructures (C)
A'_{γ}/A''_{γ}	63.9/3.91	C_{γ} - H_{γ} in <i>g</i> -acylated/ <i>g</i> - <i>p</i> -coumaroylated β -O-4' substructures (A'/A'')
B_{γ}	70.9/3.77, 4.15	C_{γ} - H_{γ} in β - β' resinol substructures (B)
A_{α}	72.0/4.88	C_{α} - H_{α} in β -O-4' substructures linked to an S units (A)
$A_{\beta(\text{G})}$	83.7/4.31	C_{β} - H_{β} in β -O-4' substructures linked to G and H units (A)
B_{α}	85.7/4.63	C_{α} - H_{α} in β -O-4' (resinol) substructures (B)
$A_{\beta(\text{s})}$	86.3/4.01	C_{β} - H_{β} in β -O-4' substructures linked to S units (A)
C_{α}	86.9/5.5	C_{α} - H_{α} in phenylcoumaran substructures (C)
$S_{2,6}$	104.2/6.62	$\text{C}_{2,6}$ - $\text{H}_{2,6}$ in S units (S)
$S'_{2,6}$	106.7/7.24	$\text{C}_{2,6}$ - $\text{H}_{2,6}$ in C_{α} -oxidized S units (S')
G_2	111.4/6.95	C_2 - H_2 in G units (G)
G'_2	109.0/7.15	C_2 - H_2 in C_{α} -oxidized G units (G')
G_5	115.1/6.7	C_5 - H_5 in G units (G)
G_6	119.3/6.78	C_6 - H_6 in G units (G)
$\text{H}_{2,6}$	123.79/7.57	$\text{C}_{2,6}$ - $\text{H}_{2,6}$ in H units (H)

Figure 9. Main substructures observed in grass lignin: (A) β -O-4' linkages; (A') β -O-4' linkages with acetylated at γ -carbon; (A'') γ -*p*-coumaroylated β -O-4' linkages; (B) resinol formed by β - β' , α -O- γ' , and γ -O- α' linkages; (C) phenylcoumaran structures formed by β -5' and α -O-4' linkages; (G) guaiacyl units; (G') oxidized guaiacyl units with a C_α ketone; (S) syringyl units; (S') oxidized syringyl units with a C_α ketone; (H) *p*-hydroxyphenyl units.

assigned to C_γ/H_γ correlations in γ -oxidized lignin units (A'/A'') was also identified. Signals for resinol substructures (β - β' , B) were observed in all the HSQC spectra, with their C_α/H_α , C_β/H_β , and double C_γ/H_γ correlations at δ_C/δ_H 85.7/4.63, 53.7/3.07 and 70.9/3.77, 4.15 ppm, respectively. Phenylcoumaran substructures (β -5'/ α -O-4', C) were distinguished in the signals for their C_α/H_α and C_β/H_β , correlations being presented at δ_C/δ_H 86.9/5.5 and 53.9/3.45 ppm, and that of C_γ/H_γ correlation overlapping with xylan C_5/H_5 cross-signals around δ_C/δ_H 63.5/3.65 ppm. The NMR spectrum of lignin dissolved with ionic liquid treatment indicates that the LM/NPs has clear structure changes in comparison to the OAL, and the intensity of these signals in OAL is stronger than in LM/NPs (Figure 9).

In the aromatic region (δ_C/δ_H 95–130/6.0–8.0 ppm), the main cross-signals from the aromatic rings of guaiacyl (G), syringyl (S) and *p*-hydroxyphenyl (H) were clearly observed in the spectra. The S units showed a prominent signal for the $C_{2,6}$ - $H_{2,6}$ correlation at δ_C/δ_H 104.2/6.62 ppm, and the signal corresponding to $C_{2,6}$ - $H_{2,6}$ correlations in C α -oxidized S units (S') was identified at δ_C/δ_H 106.7/7.24 ppm. In addition, the G units showed different correlations of C_2 - H_2 (δ_C/δ_H 111.4/6.95 ppm), C_5/H_5 (δ_C/δ_H

115.1/6.7), and C_6/H_6 (δ_C/δ_H 119.3/6.78 ppm). In addition, a clear signal for the $C_{2,6}$ - $H_{2,6}$ correlation at δ_C/δ_H 123.79/7.57 ppm originating from *p*-hydroxyphenyl (H) lignin units was detected in OAL. Therefore, the lignin was mainly composed of guaiacyl and syringyl units with minor amounts of *p*-hydroxyphenyl unit. This conforms to the structure of the grass lignin. The contours of S, G and H units substantially shrank, probably caused by lignin condensation at the 2-, 5-, and 6-positions because any new aromatic linkages at these positions would lack hydrogens and would be consequently invisible in the HSQC correlation spectra. The results indicate that the [Mmim][DMP] ionic liquid treatment effectively depolymerized the lignin and also led to lignin condensation.

In order to compare the quantitative structural features of the OAL and LM/NPs, the number of specific structures per aromatic ring and the G/S ratios was obtained by integrating the contour signals [25], and the results are listed in Table 5. In general, the arylglycerol-*b*-aryl ether linkage (β -O-4) is considered to be a typical linkage type in lignin macromolecules. The frequency of the β -O-4 linkage accounts for 40–65% of the various coupling patterns and greatly affects the chemical and physical properties

Table 5. Amount of inter-unit Linkages (% of C₉ units) in original alkali lignin (OAL) and lignin micro/nano-particles (LM/NPs) by integration of ¹³C–¹H correlation signals in the HSQC spectra.

Linkage relative abundance [%]	OAL	LM/NPs
β–O–4' aryl ethers (A)	46.10	42.80
Resinols (β–β', B)	9.41	6.14
Phenylcoumarans (β–5', C)	6.34	5.52
G/S ratio	2.11	3.05

of the lignin [8]. In this study the lignin shared a common characteristic of a relatively higher proportion of β–O–4' ether linkages and a lower proportion of carbon-carbon linkages (i.e., β–β', β–5'). The number of these linkages is reduced by ionic liquid treatment, of which β–O–4' is the most significant. The G/S ratio of OAL (2.11) was obviously lower than that of LM/NPs (3.05), indicating that the G-type lignin was more easily extracted than the S-type lignin, during treatment with ionic liquid.

3.7. Formation mechanism of lignin micro/nano-particles

Previous studies have proposed that alkali lignin trends to form molecular aggregates [26, 27], and the π–π interaction of the aromatic rings has been reported to be responsible for lignin association phenomena in organic solvents. The possible formation mechanism of lignin micro/nano-particles in ionic liquids can be obtained through the above research is presented in Figure 10. In the case of alkali lignin, the hydrogen bonding between hydroxyl groups and the intermolecular and intramolecular aggregation caused by π–π interaction are more intense, and therefore they coexist in the form of single molecules and aggregates in solution. And the shape of the single molecule is more distorted. The hydrophobic chains of the complexes continue to aggregate to form a stable micro/nano-particle core when deionized water is added to the solution. And the ionic liquid

Figure 10. Preparation of lignin micro/nano-particles a) dissolve b) intermix c) aggregation d) solidification, centrifugation.

molecules now acting as a surfactant with a weaker hydrophobicity are still dispersed in solution. With the further increase of deionized water, micro/ nano-particles composed of a hydrophilic shell and a hydrophobic core are formed. This unique self-assembly method does not require the use of a surfactant, environmentally friendly, the process is simple, and its particle size can be controlled by adjusting the stirring speed and the dripping speed. Our group will continue to report on follow-up research.

4. Conclusions

1. Alkali lignin (solid-liquid ratio of 1:10) can be dissolved completely at 80 °C in 30 min under microwave condition with [Mmim][DMP] which is easy to be recycled, lignin micro/nano-particles (LM/NPs) with diameter ranged from 200 nm to 1.5 μm can be easily obtained by diluting ionic liquid-lignin solution with water. The micro/nano-particles possess hydrophilic shells and hydrophobic cores which show very good stability in acidic conditions.
2. Characterization of the LM/NPs showed much lower polydispersity and unsaturation, the average molecular weight was reduced 8634 to 5406 Da with better thermal stability. Furthermore, the cleavage of the β–O–4' linkage, degradation of β–β' and β–5' linkages as well as demethoxylation reactions occurred in this dissolution process. The higher G/S ratio of LM/NPs (3.05) indicates G-type lignin was more extractable than S-type lignin during the dissolution process which also indirectly proves the occurrence of demethoxylation.

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