

PAPER • OPEN ACCESS

Purification of Monomers Leads to High-Quality Lignin Macromonomers

To cite this article: S.A.R. Syed Azhar and Dong June Ahn 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **548** 012021

View the [article online](#) for updates and enhancements.

Purification of Monomers Leads to High-Quality Lignin Macromonomers

S.A.R. Syed Azhar^{1,2} and Dong June Ahn^{1,3*}

¹. Department of Chemical and Biological Engineering, College of Engineering, Korea University, Seoul 02841, Republic of Korea.

². Universiti Kuala Lumpur, Malaysian Institute of Chemical & Biological Technology, Lot 1988, Vendor City Industrial Area, 78000 Alor Gajah, Malacca, Malaysia

³. KU-KIST Graduated School of Converging Science & Technology, Korea University, Seoul 02841, Republic of Korea.

E-mail: ahn@korea.ac.kr

Abstract. Purification is critical in any chemical process. The removal of impurities will produce the product in better quality and high standard. In this study, a new type of monomer was prepared by condensation polymerization of alkali lignin (AL) and methacryloyl chloride (MAC). The effect of AL/MAC ratio and the purification of MAC were investigated. The physical and chemical properties of the product obtained which is lignin methacrylate (LMA) were characterized by Fourier Transformed Infrared spectroscopy (FT-IR) and Nuclear Magnetic Resonance (¹H-NMR). The result reveals that the purification was successfully removed the hydroxyl groups from the stabilizer in MAC and it is found that all the hydroxyl groups are coming from AL. The single interaction between AL and MAC has successfully enhanced the product obtain which does show no hydroxyl groups. The ¹H-NMR data also showed that the purification of MAC influences the outcome. The noise and impurities were eliminated after the purification of MAC, and more pure products were obtained. This new monomer (LMA) synthesis that can be further utilized for various applications.

1. Introduction

Paper and pulping industries produce a vast amount of by-products during the stage of its production. Lignin, being one of the by-products, is often considered as waste [1-4] and not having proper utilization. An estimated 50 million tons of lignin were generated every year [5-6] with less than 10% being satisfied exploited [3, 7]. Inappropriate disposal of lignin into the water source gave rise to an escalation in carbon oxygen demand (COD) [8-11] as well as a contribution towards water pollution on the environment. The exploration of lignin is still the main topics of research even though it is reported lacking in the proper applications [12-14]. The majority of lignin are burned to produce fuel. Meanwhile, some industries utilize lignin to generate the steam, electricity, and heat [15-17]. Even though the fuel made provides more energy than cellulose, this activity will exacerbate global warming since carbon dioxide is released into the environment and will facilitate the pollution of air [13]. Recycling or modification of lignin into useful products is the best ways to minimize the waste and foster revenue for the industries [1].

Lignin as the second largest polymer after the cellulose [18-20] is amorphous, polyphenolic and is a highly cross-linked polymer [1, 6, and 14]. Lignin is a three-dimensional polymer, polymer with infinite molecular weights and high surface area [20-22]. It is consist of 16-30% [5-6, 23] of the total biomass, and this percentage depends on the species and extraction methods. Lignin bonded to xylan (hardwood) and galactoglucomann (softwood) through covalent bonds [24-25]. The main advantage of lignin is that it is capable of withstanding extreme weather conditions, vigorous chemical reactions and it also has exceptional resistance to microorganism [25-26].



Nowadays the modification of polymer into value-added product seems to be more attractive to the scientists. The change of lignin can increase the number of functional groups and consequently, increases the specific chemical moieties [27-28]. The functional groups that initiated by lignin such as carboxyl, amine, hydroxyl, methoxyl and aldehyde introduce variations in the modification [14, 19, 29]. Besides that, lignin also reported having the ability to be as an adsorbent for metal ions removal [30]. Unmodified, modified and hybrid lignin show high capacity to remove metal ions such as lead, mercury, cadmium, copper, zinc, nickel, chromium, and cobalt [2-3, 5-23]. Though the lignin mechanism for the adsorption is still not well understood, the capability of lignin to adsorb the metal ions is even getting prominent considerations [5-6]. Up-to-today the discovery of lignin are shifted to more broadening and value-added products such as antibacterial, drug delivery, carbon fibre nanoparticles, epoxy resin, polyurethane foams and biodegradable film [26,31-34]. Lignin can also be used to replace commercial chelating agent since it is low toxicity, biodegradable, inexpensive and due to its continuous availability [24-25, 35-36].

Lignin-based macro-monomer published in several articles. The macro-monomer can improve the chemical and physical properties of the lignin. Recently, many researchers have reported the synthesis of a macro-monomer with different types of lignin such as biobutanol lignin [37], organosolv lignin [38], and hydroxypropyl lignin [39-40]. The macro-monomer synthesis from lignin with methacryloyl chloride remains an attractive topic among researchers where the protocol to produce this specific type of monomer has been highlighted [41]. However, during their recent studies, it found that the chemical used have not undergone further purification.

In this present study, we investigated the effect of chemicals purification and the ratio of lignin to a methacryloyl chloride and its influence onto the lignin segments. To the best of our knowledge, this goal has never attained yet. The monomer is synthesis similarly to the previous studies with some minor modifications [41]. The monomer produced is then characterized portrayal by using Fourier Transformed Infrared spectroscopy (FT-IR) and Nuclear Magnetic Resonance ($^1\text{H-NMR}$). The results show that noise and impurities successfully removed in the monomer produced after the purification of the chemicals.

2. Experimental

2.1. Materials

Alkali lignin (AL), triethylamine (TEA), tetrahydrofuran (THF) and methacryloyl chloride (MAC, 97%) were supplied by Sigma-Aldrich Korea Ltd. All this chemical were utilized without any purification. Prior used for the synthesis of lignin methacrylate, MAC was used with and without purification.

2.2. Preparation of lignin methacrylate (LMA) monomer

First, 0.1 g of lignin was dissolved in 40 mL THF. Then, 100.0 g of TEA was added under continuous stirring. Next, 100.0 g of MAC solution was added dropwise into the solution. Upon completion, the flask was immediately sealed, and the esterification process was performed at room temperature for 24 h. Then, the resultant TEA salt precipitate was separated using the filtration process, and the remaining THF solution was turned into a concentrate via the evaporation process. The resultant residue was dissolved in chloroform and an aqueous amount of sodium hydrogen carbonate. After that, water was used to rinse the remaining salts and methacrylic acid from the synthesized salt.

Finally, the final product was dried over magnesium sulfate and was evaporated under vacuum for 24 h. The resulting product was labeled as LMA monomer. Two different mass ratios of lignin and MAC were studied in this experiment which is 1:100 and 1:200. Besides, the purification effect of MAC on the lignin framework also was investigated.

2.3. Physico-chemical characterisation

Fourier Transform Infrared (FT-IR) measurements for all samples were recorded in the range between 4000 and 400 cm^{-1} by the spectrometer (Spectrum GX, Perkin Elmer). 1 mg of sample was mixed with 100 mg of KBr pellet during the preparation. The FT-IR spectra were then set to the transmission mode, and the analysis was performed at resolution 2.0 cm^{-1} . The nuclear magnetic resonance ($^1\text{H-NMR}$) spectra for LMC were recorded by a nuclear magnetic resonance spectrometer (Varian NMR Systems 500MHz) using DMSO-d_6 as the solvent. For the $^1\text{H-NMR}$, the samples of LMA (100 mg) was dissolved in 0.5 ml of DMSO-d_6 for analysis of purposes.

3. Results and discussion

3.1. Characteristics of purified and unpurified methacryloyl chloride (MAC)

The interaction of MAC and lignin was investigated by the studies on the purification effect of MAC. The reaction scheme of LMA synthesis is shown in Fig. 1.

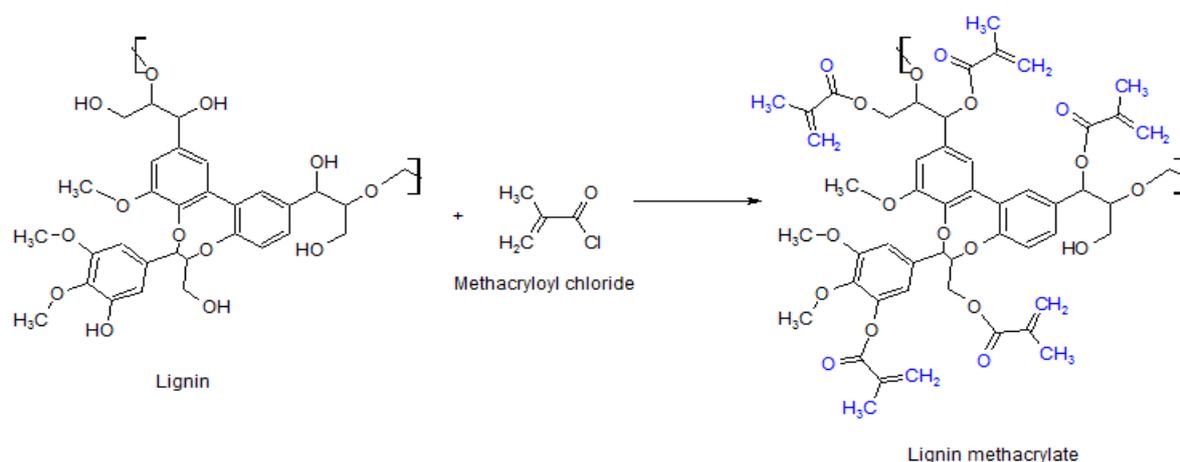


Fig. 1. The reaction scheme for the synthesis of lignin methacrylate

Fig. 2 showed the FT-IR spectra of the standard and purified MAC. At a band of 3200–3500 cm^{-1} regions, the conventional MAC spectra (a) had absorption peaks at 3460 cm^{-1} , which is assigned to OH stretching band. Meanwhile, the purified MAC spectra (b) shows that the stretching band of the hydroxyl group was disappeared. The appearance of new peaks in this region at 3552 cm^{-1} , 3479 cm^{-1} and 3420 cm^{-1} were assigned to the methyl group ($-\text{CH}_3$) of MAC segments. Also, we noted that the peak intensity at 1617 cm^{-1} bending mode of the carbonyl group of MAC segments became stronger and more apparent as compared to that of with FT-IR spectra in (a). This evidence implied that the OH group of monomethyl ether hydroquinone segments successfully removed from MAC by the distillation process. After the purification, it found that all the hydroxyl groups are coming from AL and not from the MAC. The $^1\text{H-NMR}$ spectra for purified MAC in DMSO-d_6 shown in Fig. 3.

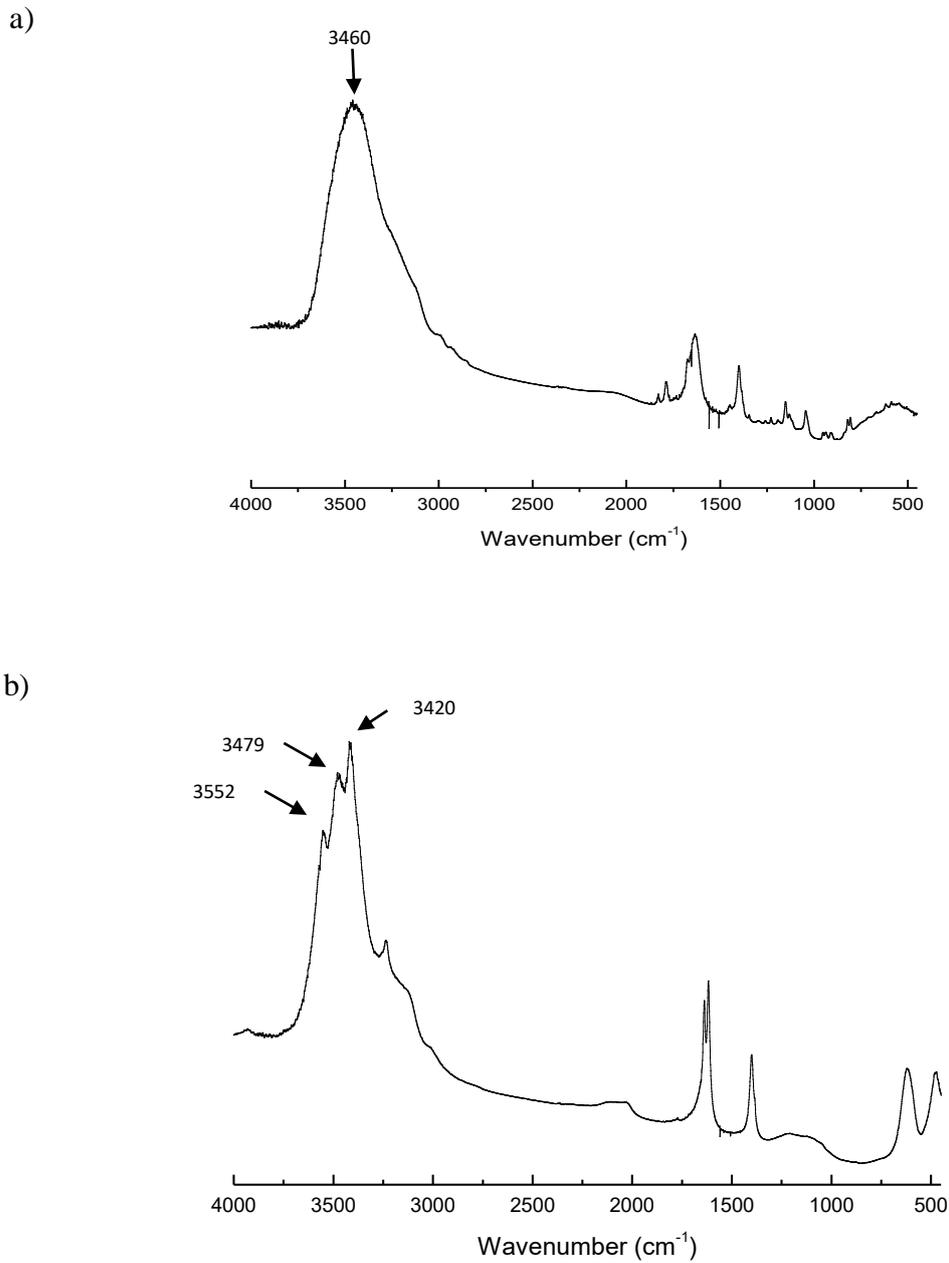


Fig. 2. Comparison of FT-IR spectra of a) conventional and b) MAC with purification.

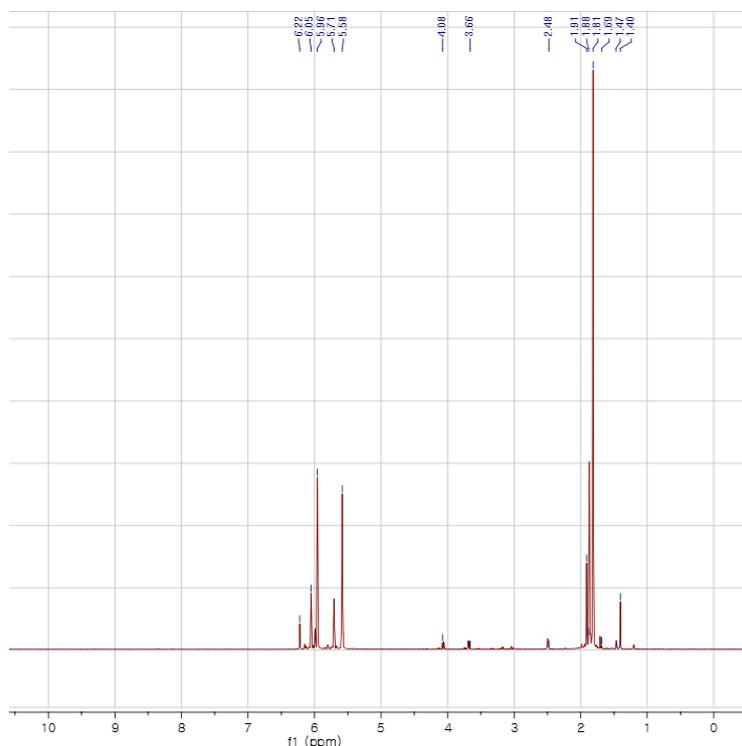


Fig. 3. ^1H -NMR spectra of alkali lignin

3.2. Characteristics of lignin methacrylate (LMA) by FT-IR spectroscopy

FT-IR spectra of lignin methacrylate prepared at a mass ratio of 1:100 and 1:200 between lignin and MAC were compared and used to confirm the presence of the MAC segments in the lignin framework.

As per shown in Figs 4 and 5, the IR band appeared at 1725 cm^{-1} and 1637 cm^{-1} . These bands assigned to $\text{C}=\text{O}$ stretch which originates from MAC segments while $-\text{C}=\text{C}-$ stretch from a vinyl group respectively. In the framework of LMA, it found the group of $-\text{C}=\text{O}$ from MAC was present. The vinyl stretch together with ester group also observed at 1637 cm^{-1} and 1298 cm^{-1} respectively. The vinyl group intensity at 3235 cm^{-1} increases meanwhile, the band at 3500 cm^{-1} for hydroxyl group was unable to be detected in both cases of LMA, which explains the occurrence of interaction between MAC within the lignin structure. These indicated that the LMA was successfully synthesized using esterification process.

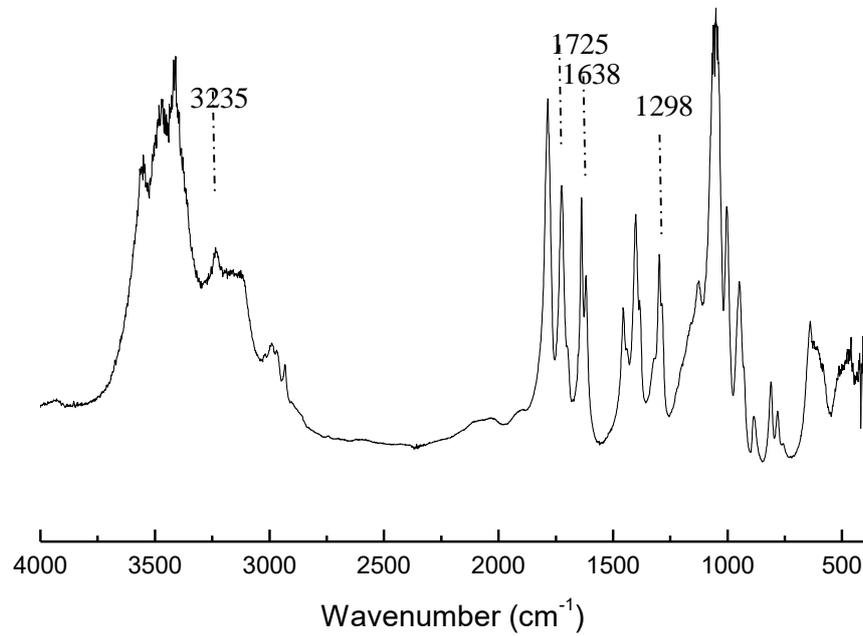


Fig. 4. FT-IR spectra of lignin methacrylate (LMA) with the ratio (1:100 wt%)

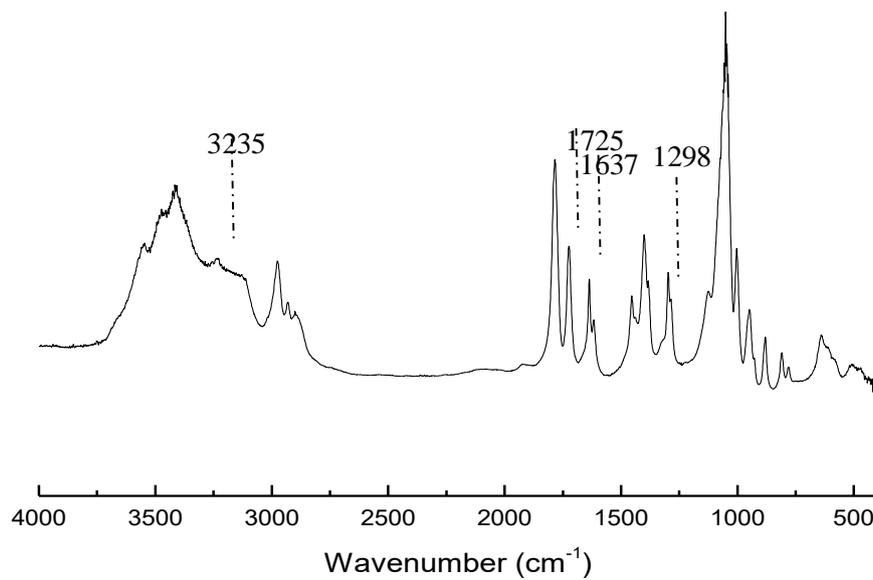


Fig. 5. FT-IR spectra of lignin methacrylate (LMA) with the ratio (1:200 wt%)

The comparison of LMA with a different mass ratio of 1:100 and 1:200 using purified and unpurified of MAC investigated by using FT-IR analysis. Fig. 6 shows that the peak at the range 1290 cm^{-1} representing ester group as a product of the reaction between MAC and lignin. The height of this product can indicate in the FT-IR spectra after purification process. The LMA monomer formation verified by the absence of some characteristic signals of a hydroxyl group and the appearance of the double bond signals in the IR spectra. Besides that, it observed that in the LMA monomer, there are two indications of absorption bands which can show at 953 cm^{-1} (C-H bending of a vinyl group) and another one at bands at 1637 cm^{-1} (C=C stretching vibration). These two bands verify the formation of lignin methacrylate from the primary reaction between lignin and MAC.

a)

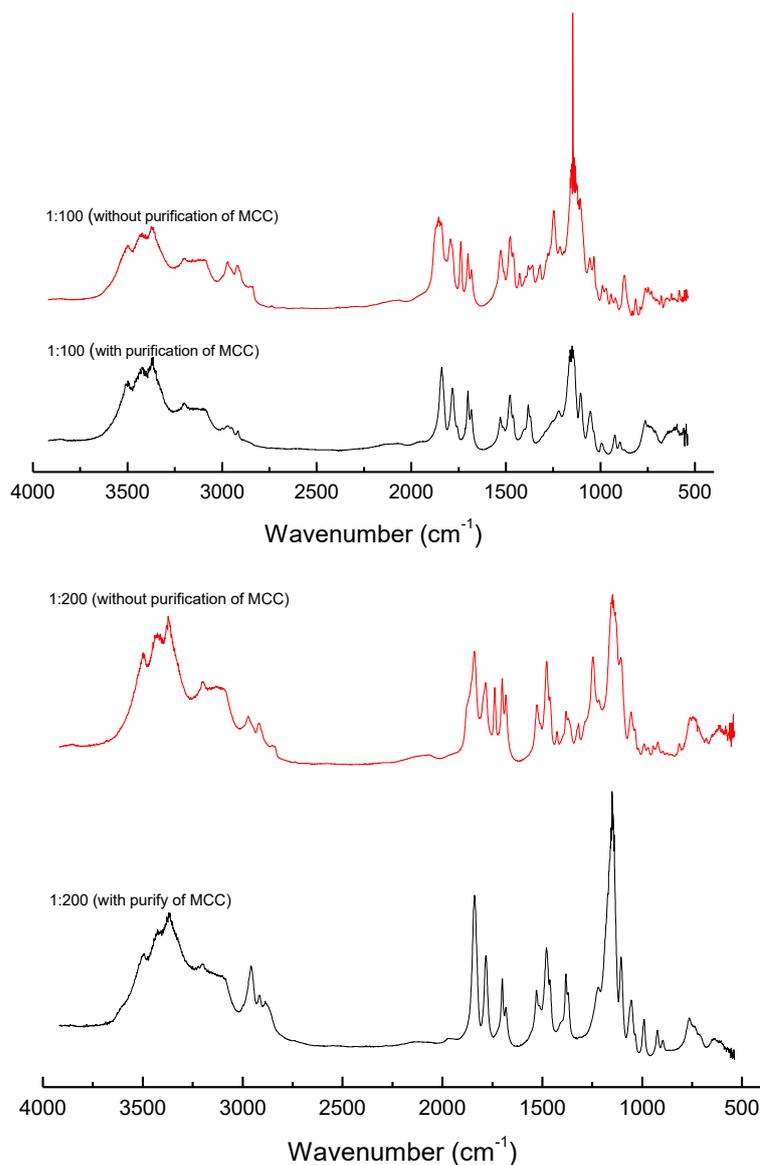


Fig. 6. FT-IR of LMA with mass ratio 1:100 (a) and 1:200 (b) with and without purification

3.3. Characteristics of lignin methacrylate by $^1\text{H-NMR}$ spectroscopy

The interaction behavior between MAC and lignin structure analyzed by using NMR spectroscopy. Fig. 7 presents a comparison of the $^1\text{H-NMR}$ spectra for lignin methacrylate of the different ratio of MAC with and without purification. Fig. 7 a (ii) and b (ii) show that the signals at 6.24 and 6.02 ppm were indicated the vinyl protons in the lignin methacrylate. However, the intensity of vinyl proton peak in spectra a (i) and b (i) is lower compared to that of lignin methacrylate with the purification of MAC. The peak at 1.93 ppm for both ratios of lignin methacrylate show the presence of protons in the aromatic group from the lignin segments. Meanwhile, as for the lignin methacrylate without purification of MAC, the impurities can be detected at the region of 1.93 ppm as shown in spectra a (i) and b (i). The signal presence at 6.02 ppm (1H), 6.24 ppm (2H), 1.93 ppm (3H, $-\text{CH}_3$) and 2.51 ppm (2H, $-\text{CH}_2$) and 3.59-3.58 ppm (1H, $-\text{C-O-CH}$) prove the formation of lignin methacrylate (LMA).

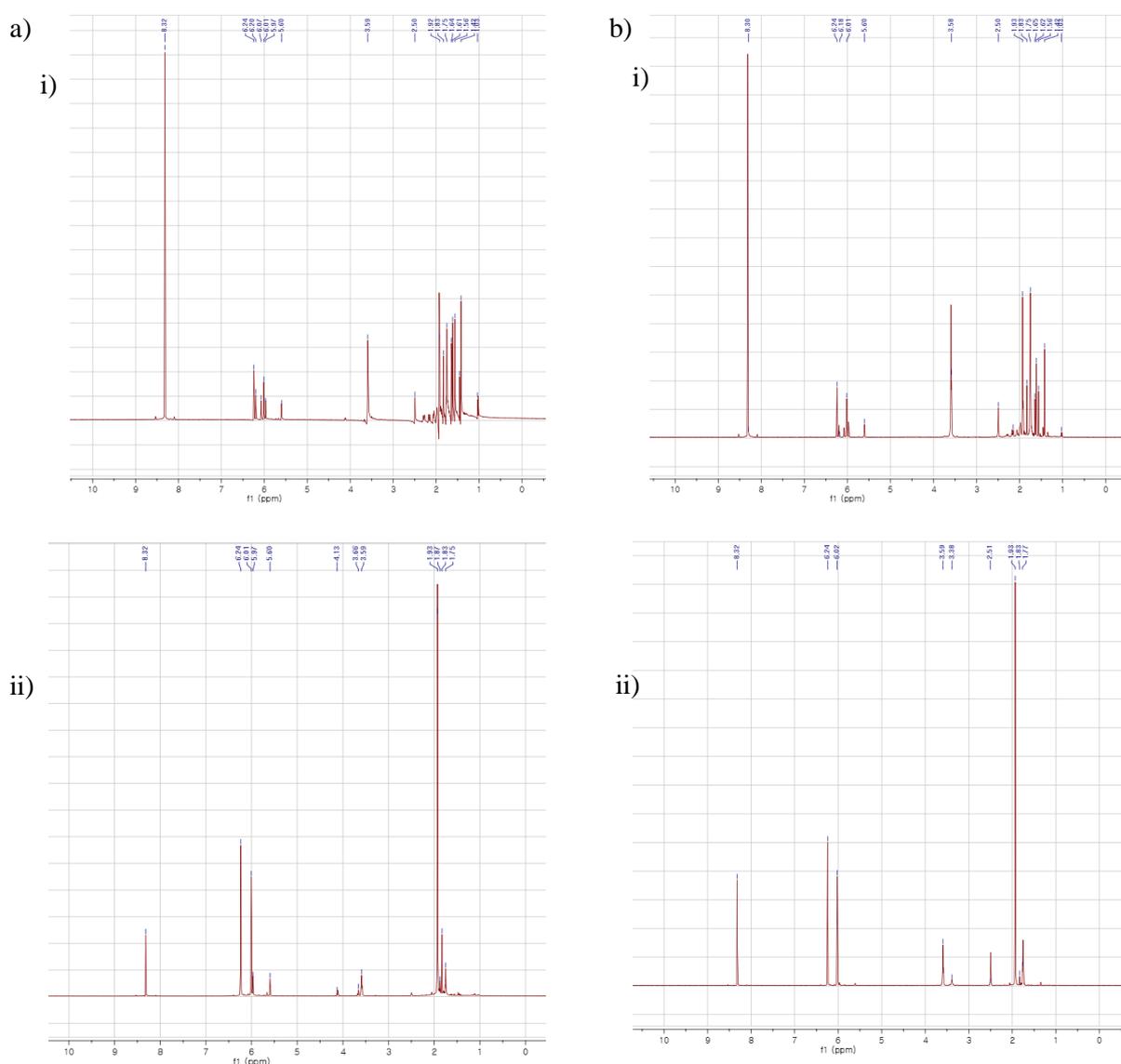


Fig. 7. ^1H NMR of LMA at mass ratio 1:100 (a) and 1:200 (b) with (i) and without (ii) purification of MAC

4. Conclusions

A new monomer, lignin methacrylate (LMA) was successfully synthesized by the condensation of methacryloyl chloride (MAC) with alkali lignin (AL) in the presence of triethylamine (TEA) in anhydrous tetrahydrofuran under N₂ gasses at room temperature. FT-IR spectra show that the purification of MAC is successfully removed the hydroxyl groups from the stabilizer (monomethyl ether hydroquinone). After the purification, we found that all the hydroxyl groups are coming from the AL segments and not from MAC solvent. The final product which is lignin methacrylate does not show any hydroxyl groups in the FT-IR spectra shows the reaction successfully enhanced by the individual response between AL and MAC. FT-IR spectra also indicate that vinyl group from MAC segments successfully interact with lignin structure for both ratio 1:100 and 1:200. However, the peak of the ester group detected with the purification of MAC. The LMA with a ratio of 1:200 then was considered as the best parameter in the production of lignin methacrylate with the purification of MAC solvent. The ¹H-NMR result provides evidence that the purification of MAC will reduce the noise and impurities when compared to the one in the case of without purification. Both results from FT-IR and ¹H-NMR show that the purification of MAC is crucial and plays a significant role in the lignin segment during the synthesis of better LMA macromonomer.

5. Acknowledgments

This work was supported by the Majlis Amanah Rakyat (MARA) and National Research Foundation of Korea (NRF, 2017R1A2B3006770, 2017M3D1A1039421), KU-KIST Graduate School of Converging Science and Technology and a Korea University Grant.

References

- [1] Garcia-Valls R Hatton T A 2003 Metal ion complexation with lignin derivatives *Chem. Eng. J.* **94** 99-105
- [2] Wysokowski M Klapiszewski L Moszynski D Bartczak P Szatkowski T Majchrzak I Siwinska- Stefanska K Bazhenov V V Jesionowski T 2014 Modification of chitin with kraft lignin and development of new biosorbents for removal of cadmium (II) and nickel (II) ions, *Mar. Drugs* **12** 2245-2268
- [3] Sciban M B Klasnja M T Antov M G 2011 Study of the biosorption of different heavy metal ions onto Kraft lignin *Ecological Engineering* **37** 2092-2095
- [4] Stewart D 2008 Lignin as a base material for materials applications: chemistry, application and economics *Ind. Crops Prod.* **27** 202-207.
- [5] Guo X Zhang S Shan X-Q 2008 Adsorption of metal ions on lignin *J. Hazard. Mater.* **151** 134-142
- [6] Mohan D Pittman Jr C U Steele P H 2006 Single, binary and multi-component adsorption of copper and cadmium from aqueous solutions on Kraft lignin-a biosorbent *J. Colloid Interface Sci.* **297** 489-504
- [7] Liu X Zhu H Qin C Zhou J Zhao J R Wang S 2013 Adsorption of heavy metal ion from aqueous single metal solution by aminated epoxy-lignin *BioResource* **8**(2) 2257-2269.
- [8] Wu Y Zhang S Guo X Huang H 2008 Adsorption of chromium (III) on lignin *Bioresource Technol.* **99** 7709-7715
- [9] Maldhure A V Ekhe J D 2011 Preparation and characterizations of microwave assisted activated carbons from industrial waste lignin for Cu(II) sorption *Chem. Eng. J.* **168** 1103-1111
- [10] Gao Y Yue Q Gao B Sun Y Wang W Li Q Wang Y 2013 Preparation of high surface area-activated carbon from lignin of papermaking back liquor by KOH activation for Ni(II) adsorption *Chem. Eng. J.* **1** 217345-353
- [11] Lv J Luo L Zhang J Christie P Zhang S 2012 Adsorption of mercury on lignin: combined surface complexation modelling and X-ray absorption spectroscopy studies *Environ. Pollut.* **162** 255-261
- [12] Merdy P Guillon E Aplincourt M Dumonceau J Vezin H 2002 Copper sorption on a straw lignin: experiments and EPR characterization *J. Colloid Interface Sci.* **245** 24-31
- [13] Lu Q-F Huang Z-K Liu B Cheng X 2012 Preparation and heavy metal ions biosorption of graft copolymers from enzymatic hydrolysis lignin and amino acid, *Bioresource. Tech.* **104** 111-118
- [14] Mohammad Ibrahim M N Wan Ngah W S Norliyana M S Wan Daud W R 2009 Copper (II) biosorption on soda lignin from oil palm empty fruit bunches (EFB) *Clean* **37**(1):80-85
- [15] Dizhbite T Zakis G Kizima A Lazareva E Rossinskaya G Jurkjane V Telysheva G Viesturs U 1999 Lignin-a useful bioresource for the production of sorption-active materials, *Bioresource. Tech.* **67**(3) 221-228
- [16] Kriaa A Hamdi N Srasra E 2010 Removal of Cu(II) from water pollutant with Tunisian activated lignin prepared by phosphoric acid activation *Desalination* **250** 179-187
- [17] Harmita H Karthikeyan K G Pan X J 2009 Copper and cadmium sorption onto Kraft and organosolv lignins, *Bioresource. Tech.* **100** 6183-6191
- [18] Wysokowski M Klapiszewski L Moszynski D Bartczak P Szatkowski T Majchrzak I Siwinska-Stefanska K Bazhenov V V Jesionowski T 2014 Modification of chitin with Kraft lignin and development of new biosorbents for removal of cadmium (II) and nickel (II) ions *Mar. Drugs.* **12** 2245-2268

- [19] Lalvani S B, Hubner A, Wiltowski T S 2000 Chromium adsorption by lignin, *Energy. Sour.* **22**:45-56.
- [20] Sciban M B, Klasnja M T, Antov M G 2011 Study of the biosorption of different heavy metal ions onto Kraft lignin, *Ecol. Eng.* **37** 2092-2095
- [21] Demirbas A, 2007 Adsorption of Co(II) and Hg(II) from water and wastewater onto modified lignin, *Energy Sour. Part A* **29** 117-123
- [22] Acemioglu B Samil A Alma M H Gundogan R 2003 Copper (II) removal from aqueous solution by organosolv lignin and its recovery *J Appl. Polym. Sci.* **89** 1537-1541
- [23] Thakur V K Thakur M K 2015 Recent advances in green hydrogels from lignin: a review, *International J. Biol. Macromol.* **72** 834-847
- [24] Celik A Demirbas A 2005 Removal of heavy metal ions from aqueous solutions via adsorption onto modified lignin from pulping wastes, *Energy. Sour.* **27** 1167-1177
- [25] Demirbas A 2004 Adsorption of lead and cadmium ions in aqueous solutions onto modified lignin from alkali glycerol delignification, *J. Hazard. Mater. B* **109** 221-226.
- [26] Wang J Manley R St J Feldman D 1992 Synthetic polymer-lignin copolymers and blends *Prog. Polym. Sci.* **17** 611-646
- [27] Gregorova A Sedlarik V 2016 Characterization of structural and physical properties of dichloromethane-and methanol-fractionated Kraft lignin and its adsorption capacity of Cu(II) and Ni(II) ions, *Desalin. Water Treat.* 10655-10663
- [28] Ge Y Qin L Li Z 2016 Lignin microspheres: an effective and recyclable natural polymer-based adsorbent for lead ion removal, *Mater. Design.* **95** 141-147
- [29] Lalvani S B, Wiltowski T S Murphy D Lalvani L S 1997 Metal removal from process water by lignin, *Environ. Technol.* **18** 1163-1168
- [30] Albadarin A B Al-Muhtaseb A H Al-Laqtah N A Walker G M Allen S A Ahmad M N M 2011 Biosorption of toxic chromium from aqueous phase by lignin: mechanism, effect of other metal ions and salts, *Chem. Eng. J.* **169** 20-30
- [31] Tan E Vermerris W 2015 Recent developments in polymers derived from industrial lignin, *J. Appl. Polym. Sci.* 42069-42069
- [32] Laurichesse S Averous L 2014 Chemical modification of lignins: towards biobased polymers, *Prog. Polym. Sci.* **39** 1266-1290
- [33] Lora J H Glasser W G 2002 Recent industrial applications of lignin: a sustainable alternative to renewable materials *J. Polym. Env.* **10** 39-48
- [34] Feldman D Lacasse M Beznacuk L M 1996 Lignin-polymer systems and some applications *Prog. Polym. Sci.* **12** 271-299
- [35] Basso M C Cerrella E G Cukierman A L 2014 Cadmium uptake by lignocellulosic materials: effect of lignin content, *Sep. Sci. Technol.* **39** 1163-1175
- [36] Crist D R Crist R H Martin J R 2003 A new process for toxic metal uptake by a Kraft lignin *J. Chem. Technol. Biotechnol.* **78** 199-202
- [37] Liu X Wang J Yu J Zhang M Wang C Xu Y Chu F 2013 Preparation and characterization of lignin based macromonomer and its copolymers with butyl methacrylate *J. Bio. Macromol.* **60** 309-315
- [38] Rials T G Glasser W F 1989 Multiphase materials with lignin: IV. Blends of hydroxypropyl cellulose with lignin, *J. Appl. Polym. Sci.* **37** 2399-2415
- [39] Ciemniecki S L Glasser W G 1988 Multiphase materials with lignin: 2. Blends of hydroxypropyl lignin with poly(vinyl alcohol), *Polymer* **29**(6) 1030-1036
- [40] Ciemniecki S L Glasser W G 1988 Multiphase materials with lignin: 1. Blends of hydroxypropyl lignin with poly(methyl methacrylate) *Polymer* **29**(6) 1021-1029
- [41] Cunha C D Deffieux A Fontanille M 1993 Synthesis and polymerization of lignin-based macromonomers. III. Radical copolymerization of lignin based macromonomers with methyl methacrylate *J. Appl. Polym. Sci.* **48** 819-831