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Purification Processes for Generating Cationic Lignin-Acrylamide Polymers

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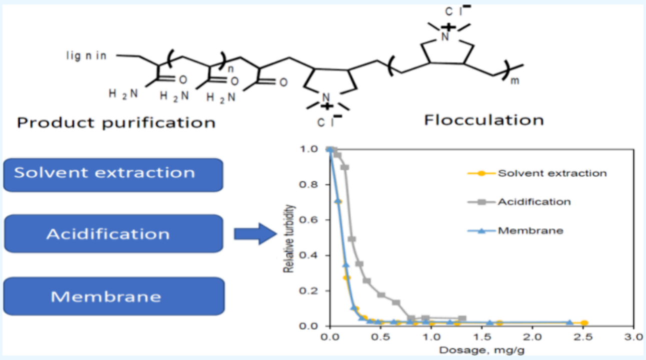
ABSTRACT: Purification is an essential step in many polymerization processes for fabricating highly pure polymers. This study considered various purification methods for purifying the product of lignin, acrylamide (AM), and diallyl dimethylammonium chloride (DADMAC) copolymerization reactions at a laboratory scale. The charge density, yield, molecular weight, and solubility analyses confirmed that ethanol extraction and membrane filtration were the most effective processes for producing lignin-p(AM)-p(DADMAC). The ^{1}H NMR analysis revealed that the membrane dialysis effectively removed unreacted AM and DADMAC monomers from the reaction medium. The produced samples of the ethanol-extraction and dialysis processes had higher solubility and yield compared to the product of the acidification process. Thermogravimetric studies confirmed that the ethanol-extracted and dialyzed samples had a degradation temperature (220 °C) higher than that of the acidified samples (160 °C). The rheological studies confirmed that the viscosities of the polymer solutions were influenced more by the solubility than by the molecular weight of the generated polymers within the molecular weight range examined in this study. The flocculation studies confirmed that the ethanol-extracted and dialyzed polymers were more effective flocculants than the acidified samples for the particles of a kaolinite suspension. Based on the above results, membrane filtration with a larger pore size could be an environmentally friendly method for effectively purifying lignin-p(AM)-p(DADMAC).



1. INTRODUCTION

As an abundant and renewable biomass, lignin can produce value-added products, such as carbon fibers, biosorbents, platform chemicals, adhesives, flocculants, paper-strength additives, and hydrogels.[1−6] The diversity of functional groups in lignin has created opportunities for the polymerization of lignin, which has received attention to induce lignin polymers for potentially replacing petroleum-based products. Various anionic (e.g., acrylic acid), cationic (e.g., 2-[methacryloyloxy]ethyl) trimethylammonium chloride (METAC)), and nonionic (e.g., acrylamide (AM)) monomers have been successfully grafted onto lignin via free radical polymerization to produce value-added products.[6−8]

Polyacrylamide (PAM) is a water-soluble polymer with high flocculating efficiency for water treatment.[9] Grafting the PAM chain onto lignin would improve its solubility and molecular weight (as PAM is water-soluble and lignin is not), which would be beneficial for creating effective lignin-derived flocculants.[6] However, most suspensions have negative charges, and flocculants with cationic groups are more favorable than nonionic ones in aggregating and settling colloids from suspensions. Therefore, polymerization with cationic monomers can be explored to impart positive charges to lignin-p(AM) and improve its flocculation performance. With a high cationic charge density, poly diallyl dimethylammonium chloride (PDADMAC) is one of the effective synthetic polyelectrolytes for flocculation processes and is extensively used in industry.[10] In this paper, two monomers of acrylamide (AM) and diallyl dimethylammonium chloride (DADMAC) were selected for polymerizing with kraft lignin to generate a cationic flocculant.[11]

Generally, the purity of copolymers can improve their efficiency and widen their applications. Several purification processes were utilized as a final step of polymer synthesis for separating the desired products from undesired chemicals such as unreacted monomers, undesired homopolymers, and inorganic salts used in the reaction. Solvents, such as acetone and ethanol, are widely used to purify polymers.[12] Rong and co-workers purified lignin-acrylamide (lignin-AM) polymer using acetone.[6] In another work, lignin-[2-(methacryloyloxy)-ethyl] trimethylammonium chloride (lignin-METAC) was purified using ethanol/water and centrifugation, and the final

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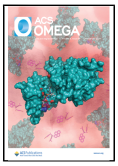

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precipitated lignin-METAC product had no unreacted monomers (i.e., METAC) and homopolymer (i.e., polyMETAC).[8] In another work, a mixture of acetone and ethanol was used for purifying the product of acrylamide-[2-(methacryloyloxy)ethyl] trimethylammonium chloride-methacryloxypropltri-methoxysilane polymer).[13]

Acidification is a commercial process for lignin recovery in the LignoBoost and LignoForce processes.[14−16] Acidification is easy and inexpensive compared to other methods (e.g., membrane separation).[16,17] In the past, attempts were made to separate lignin-acrylic acid (lignin-AA) and lignin-AM from reaction media via acidification.[4,18] Membrane filtration has been an effective method for purifying polymers from reaction mixtures to remove chemicals (e.g., unreacted monomers and inorganic salts) smaller than the molecular weights cutoff of the membrane. As is well-known, filtration with different pore sizes can produce products with altered molecular weights and properties.[19,20] Previously, lignin-glycidyl-trimethylammonium chloride (lignin-GTMAC) and lignin-AM were purified successfully using a membrane with molecular weights cutoff of 1000 g/mol and 12 000−14 000 g/mol, respectively.[3,4,19,20] However, the efficiency of the separation processes was not documented.

This study produced lignin-p(AM)-p(DADMAC) from polymerizing lignin, AM, and DADMAC monomers via free radical polymerization.[21] Then, different ethanol extraction (as a nontoxic solvent), acidification, and membrane dialysis processes were utilized to purify the products. Although different purification processes were used to purify lignin-based polymers in the past,[17,22−24] the effectiveness of altered processes in producing lignin-derived polymers was not compared comprehensively. However, this information will be essential for creating lignin-derived products with different properties for varied applications. This manuscript is the first report to compare the efficiency of the altered purification processes for generating polymeric lignin derivatives with other properties. The effects of varying separation methods on charge density, solubility, and product yield were discussed in this work in detail. Also, the structural and elemental analyses of the separated polymers were comprehensively investigated by using nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), static light scattering (SLS), and rheology analyses. Furthermore, the efficiency of the products as flocculants was assessed by using a dynamic drainage jar (DDJ) in kaolinite systems. The results of this work provide insights into the development of an efficient purification pathway for producing lignin-derived polymers with the desired properties.

2. MATERIALS AND METHODS

2.1. Materials. Softwood kraft lignin was supplied by FPInnovations from the LignoForce pilot plant in Thunder Bay, ON. Diallyl dimethylammonium chloride (65 wt % in water) (DADMAC), acrylamide, sodium persulfate, potassium poly(vinyl sulfate) (PVSK), sodium hydroxide, and kaolinite, all analytical grades, were obtained from Sigma-Aldrich and used without any further purification. Membrane dialysis with molecular weight cuts off, MWCO, of 1, 10, and 25 kg/mol (1, 10, 25 KDa) were purchased from Spectrum-Laboratories.

2.2. Polymerization Process. In this set of experiments, 2.0 g of lignin and 40 mL of water were added to a three-necked glass flask. A specified amount of acrylamide and DADMAC at lignin: AM: DADMAC molar ratio of 5.5:2.4:1 was prepared in the flask, which was the optimum condition based on our previous work,[11] and the pH of the system was adjusted to 2 while stirring at 500 rpm. The reaction mixture was purged with nitrogen for 20 min, and then 30 mg of $Na_2S_2O_8$ was added to the reaction mixture. The mixture was purged with nitrogen for an additional 10 min while stirring at 500 rpm. The reaction was maintained at 90 °C for 2 h to obtain lignin-p(AM)-p(DADMAC). After the reaction, the mixture was cooled to room temperature and purified following different methods.

2.3. Product Purification. Seven different methods were utilized for lignin-*g*-p(AM)-p(DADMAC) purification after reaction, including ethanol extraction (process 1), centrifugation (process 2), acidification (process 3), acidification with aeration (process 4), and membrane dialysis with MWCO of 1 kg/mol (process 5), 10 kg/mol (process 6), and 25 kg/mol (process 7).

For ethanol extraction (process 1), the reaction mixture was cooled to room temperature and mixed with ethanol. In this process, ethanol was added to the reaction medium at a volume ratio of 4:1, making the lignin polymer precipitate. The precipitate was washed with 50 mL of ethanol and dried in an oven at 60 °C until a constant weight. A lower drying temperature positively affected the polymer's properties (e.g., solubility, molecular weight), avoiding the induced polymer's physicochemical instability.[25] In process 2, the reaction mixture was centrifuged at 4000 °C for 10 min, and the precipitate was collected and dried at 60 °C until a constant weight. In process 3, the pH of the reaction mixture was adjusted to 1.5 at 90 °C by adding 25% H_2SO_4. The mixture was stirred at 400 rpm for 30 min and then centrifuged at 4000 rpm for 10 min. The precipitate was collected and dried in an oven at 60 °C until a constant weight. In process 4, the acidification of the reaction mixture was conducted at 90 °C, but the mixture was aerated by an air pump (Topfin Air-1000) at the flow rate of 0.017 L/s while stirring at 400 rpm. Afterward, the sample was centrifuged at 4000 rpm for 10 min, and the precipitate was collected and dried at 60 °C in an oven until a constant weight. In the filtration method (processes 5, 6, and 7), the reaction mixtures were first adjusted to pH 7 with the help of NaOH (1 mol/L) and then kept in the cellulose dialysis tubes obtained from SpectrumLabs and dialyzed against 4 L of deionized water for 48 h. The deionized water was changed every 12 h during this analysis. Then, the sample was collected and dried in an oven at 60 °C until a constant weight was reached.

2.4. Yield, Solubility, and Charge Density. The yield of lignin-p(AM)-p(DADMAC) production was calculated by following eq 1.

$$\text{Yield, \%} = \frac{\text{Mass of copolymer}}{\text{Mass of monomers} + \text{Mass of lignin}} 100 \qquad (1)$$

The mass of the copolymer is the amount of product after purification and drying. The mass of monomers and the mass of lignin are the corresponding masses used in the reaction.

The products' charge density and solubility are essential properties for their use as flocculants.[26] For charge density and solubility measurements, 0.2 g of lignin-p(AM)-p(DADMAC) product collected following the different purification methods was added to 19.8 mL of water. Then, the suspension was shaken at 30 °C and 150 rpm for 2 h and centrifuged at 1000 rpm for 5 min. After centrifugation, the supernatant was collected for charge density and solubility analysis. The sample concentration in the supernatants was determined by drying the supernatant at 105 °C to determine its solubility, which is reported as a weight percentage (wt %).[11] The charge density measurement was performed on the supernatant obtained above by a particle charge detector, Mutek PCD 04 titrator (Arzbergerstrae, Herrsching, Germany), with PVSK (0.005 mol/L) as the titrant.[11] The reported results in this article are the averages of three runs.

2.5. ^{1}H NMR Analysis. The chemical structures of lignin-*g*-p(AM)-p(DADMAC) purified following different methods were recorded by an INOVA-500 MHz instrument (Varian, USA) and analyzed using ^{1}H NMR with a 45° pulse and a relaxation delay time of 1.0 s. First, 0.02 g of the copolymers were dissolved in 1 mL of D_2O at pH 11. The copolymers were completely water-soluble at pH 11.[11] The unreacted AM and DADMAC contents still in the copolymer after purification steps were calculated according to our previous publication.[21]

2.6. Organic Element Analysis. The organic elements of the lignin-p(AM)-p(DADMAC) polymer were detected by a Vario Micro elemental analyzer (Elementar, German). Before the elemental analysis, the samples were dried in an oven at 105 °C overnight to remove any moisture. The carbon, hydrogen, nitrogen, and oxygen contents of 2 mg of lignin-p(AM)-p(DADMAC) separated via different processes were measured following a method described elsewhere.[11] In lignin-p(AM)-p(DADMAC), DADMAC was the only contributor of charges (i.e., a charge density of +1 mequiv/g equals 1 mmol/g of DADMAC). Thus, the content of DADMAC in the copolymer was determined by utilizing the lignin copolymers' charge density (CD) to calculate the overall content of DADMAC followed by deduction of the unreacted DADMAC (obtained previously by NMR) via eq 2. The nitrogen content of kraft lignin was negligible; thus, the nitrogen content in lignin-p(AM)-p(DADMAC) originated from nitrogen in both acrylamide and DADMAC. The AM content in the copolymer was determined by using the nitrogen content of the copolymers to calculate the overall nitrogen-containing components (i.e., total DADMAC and AM content) followed by the deduction of the DADMAC content and the unreacted AM (obtained previously by NMR) using eq 3. DADMAC and AM grafting ratios were calculated according to eqs 4 and 5, respectively.

$$\begin{aligned} C_{\mathrm{DADMAC}} &= C_{\mathrm{DADMAC(o)}} - C_{\mathrm{DADMAC(u)}} \\ &= \frac{\mathrm{CD}}{1000} - \frac{U_{\mathrm{DADMAC}}\%}{M_{\mathrm{DADMAC}}100} \end{aligned} \tag{2}$$

$$\begin{aligned} C_{\mathrm{AM}} &= C_{\mathrm{N(o)}} - C_{\mathrm{DADMAC(o)}} - C_{\mathrm{AM(u)}} \\ &= \frac{\mathrm{N}\%}{14\cdot 100} - \frac{\mathrm{CD}}{1000} - \frac{U_{\mathrm{AM}}\%}{M_{\mathrm{AM}}100} \end{aligned} \tag{3}$$

$$\begin{aligned} &\text{Grafting ratio of DADMAC} \\ &= \frac{\text{Weight of grafted DADMAC}}{\text{Weight of lignin in the polymer}} \\ &= \frac{C_{\mathrm{DADMAC}}M_{\mathrm{DADMAC}}}{1 - C_{\mathrm{DADMAC}}M_{\mathrm{DADMAC}} - C_{\mathrm{AM}}M_{\mathrm{AM}}}100 \end{aligned} \tag{4}$$

$$\begin{aligned} &\text{Grafting ratio of AM} \\ &= \frac{\text{Weight of grafted AM}}{\text{Weight of lignin in the polymer}} \\ &= \frac{C_{\mathrm{AM}}M_{\mathrm{AM}}}{1 - C_{\mathrm{DADMAC}}M_{\mathrm{DADMAC}} - C_{\mathrm{AM}}M_{\mathrm{AM}}}100 \end{aligned} \tag{5}$$

Where CD is the charge density of the polymer (mmol/g); N% is nitrogen content of the copolymer; C_{DADMAC} and C_{AM} are the DADMAC and AM contents (mol/g) in the copolymer, respectively; U_{DADMAC} and U_{AM} are percentages of unreacted DADMAC and AM, respectively; $C_{\mathrm{DADMAC\ (o)}}$ and $C_{\mathrm{DADMAC(u)}}$ are the overall DADMAC contents (mol/g) and unreacted DADMAC contents (mol/g) in the product, respectively; $C_{\mathrm{N\ (o)}}$ is the overall N contents (mol/g) in the product; $C_{\mathrm{AM(u)}}$ is the unreacted AM contents (mol/g) in the product; M_{DADMAC} and M_{AM} are molar mass (g/mol) of DADMAC and AM, respectively.

2.7. Molecular Weight Analysis. The molecular weight and radius of gyration (R_g) of lignin-p(AM)-p(DADMAC) copolymer was determined by a static light scattering (SLS) instrument (Brookhaven Instruments BI-200SM Goniometer System, Holtsville, USA). In this analysis, the samples were prepared in 0.5 M NaOH and 10 mM KNO_3 at 5 different concentrations of 0.5, 1.0, 1.5, 2.0, and 2.5 g/L while stirring at 300 rpm overnight for dissolution. Before measurement, the sample solutions were filtrated twice using 0.45 μm syringe filters to remove impurities. The samples' refractive index increment (d*n*/d*c*) was determined by a differential refractometer (Brookhaven Instruments BI-DNDC, Holtsville, USA) at 25 °C. In the SLS measurement, time-averaged intensity measurements were made at variable angles from 15° to 155° and a wavelength of 637 nm at room temperature. BIC Zimm Plot software calculated the molecular weight and radius of gyration (R_g) in the study.[27]

2.8. Thermogravimetric Analysis. The thermogravimetric analysis of lignin-p(AM)-p(DADMAC) and p(AM)-p(DADMAC) was performed by using a TGA analyzer (TGA i1000 Series System, Wisconsin, USA) to characterize the thermal stability of the samples. The samples were heated from room temperature to 700 °C at a heating flow rate of 20 °C/min under a nitrogen flow rate of 100 mL/min.

2.9. Rheological Analysis. The rheological properties of lignin-p(AM)-p(DADMAC) were analyzed with a DHR-2 rheometer (TA Instruments). In this analysis, 3 wt % concentration of the lignin samples was prepared in deionized water at pH 6.5 and 25 °C. Flow ramp experiments and oscillation measurements were carried out with a standard concentric cylinder cup (with a diameter of 30.37 mm) and a DIN rotor (with a bob diameter of 28.03 mm and bob length of 41.96 mm).

2.10. Flocculation of Kaolinite Suspension. The flocculation performance of lignin-p(AM)-p(DADMAC) in kaolinite suspensions was investigated with a photometric dispersion analyzer (PDA 3000, Rank Brothers, UK) connected to a dynamic drainage jar (DDJ). First, 480 mL of deionized water was poured into the DDJ container fitted with a 70 mm mesh screen and circulated from the DDJ to the PDA through a 3 mm plastic tube. The DC voltage of pure water was recorded when the system reached a steady flow of 20 mL/min, which was regulated by a peristaltic pump throughout the experiment. Then, 20 mL of a 25 g/L kaolinite suspension was added to a DDJ container (to make a 1 g/L kaolinite concentration in DDJ) while being circulated at the flow rate of 20 mL/min and stirred at 200 rpm. This caused a decrease in the initial DC voltage (DC_0) to a new DC voltage (DC_i) in PDA analysis. After a steady state was reached (100 s), the lignin-p(AM)-p(DADMAC) copolymers (5 g/L concentration) were added to the DDJ to induce the flocculation process. A steady state increase in DC voltage was represented as a final suspension DC voltage (DC_f). The degree of flocculation was presented as relative turbidity, calculated from the variation in the DC voltage signals of the PDA analyzer before and after adding lignin derivatives according to eq 6.

$$\tau_r = \frac{\tau_f}{\tau_i} = \frac{\ln\left(\frac{DC_0}{DC_f}\right)}{\ln\left(\frac{DC_0}{DC_i}\right)} \quad (6)$$

Where τ_i is the initial turbidity of kaolinite suspension; τ_f is the final turbidity of kaolinite suspension after adding the flocculant; DC_0 is the initial DC voltage of pure water; DC_i is the DC voltage of kaolinite suspension itself; and DC_f is the DC voltage of kaolinite suspension after adding the flocculant.

3. RESULTS AND DISCUSSION

3.1. ^{1}H NMR Assessment. The ^{1}H NMR spectra of kraft lignin are shown in Figure S1. The peak at 8.3 ppm is attributed to the unsubstituted phenolic protons. The broad resonance is attributed to the substituted phenolic protons (7–7.5 ppm) and aromatic protons (6–7 ppm). The board resonance between 3 and 4 ppm is associated with methyl protons widely present in methoxyl groups of the lignin macromolecule.[28]

The ^{1}H NMR spectra of lignin-p(AM)-p(DADMAC) purified by different methods are described in Figure 1. An enlarged view of the spectral range from 6 to 8 ppm is presented for a better comparison in that region. The weak bulges from 6 to 7.5 ppm are associated with the resonance in the lignin, indicating the presence of lignin in the copolymer.[8] The 5–6.5 ppm peaks are related to allylic groups in the monomers of acrylamide and DADMAC.[29] The resonances in the 3.6–3.8 and 2.8–3.37 ppm range are associated with $-CH_2-$ groups and $N-CH_3$ in DADMAC, respectively. The peaks at 2.65 and 2.24 ppm are attributed to -CH- protons in DADMAC and AM, respectively. The resonance at 1.65 ppm is assigned to $-CH_2-$ protons at the main polymer backbone of P(AM) and P(DADMAC).

In the spectra of ^{1}H NMR (Figure 1), processes 5 to 7 had similar peaks, while processes 2 to 4 shared similar peaks. In Table 1, the concentrations of unreacted AM and DADMAC monomers in the samples were calculated by considering the integrated area of g, h, f, and a, b, respectively, which referred to backbones of AM and DADMAC in the ^{1}H NMR, shown in Figure S2 in the Supporting Information.[29] The peaks at 1.65 ppm related to the backbone of polymers are more evident in the dialyzed samples (processes 5, 6, and 7) and the ethanol-extracted sample (process 1). It is considered that the component ratio of lignin-p(AM)-p(DADMAC) copolymers in these samples was much higher than that in the centrifuged (process 2) and acidified (processes 3, 4) samples. The unreacted monomers left in the products via processes 5 to 7 are much less than the other processes, demonstrating that dialysis was an efficient method for removing the monomers due to the low molecular weight of the monomers that could pass through the membrane pores. As these monomers are reactive and may be environmentally unfriendly (e.g., neurotoxicity, reproductive toxicity, and immunotoxicity of acrylamide),[30] they should be removed from the copolymer

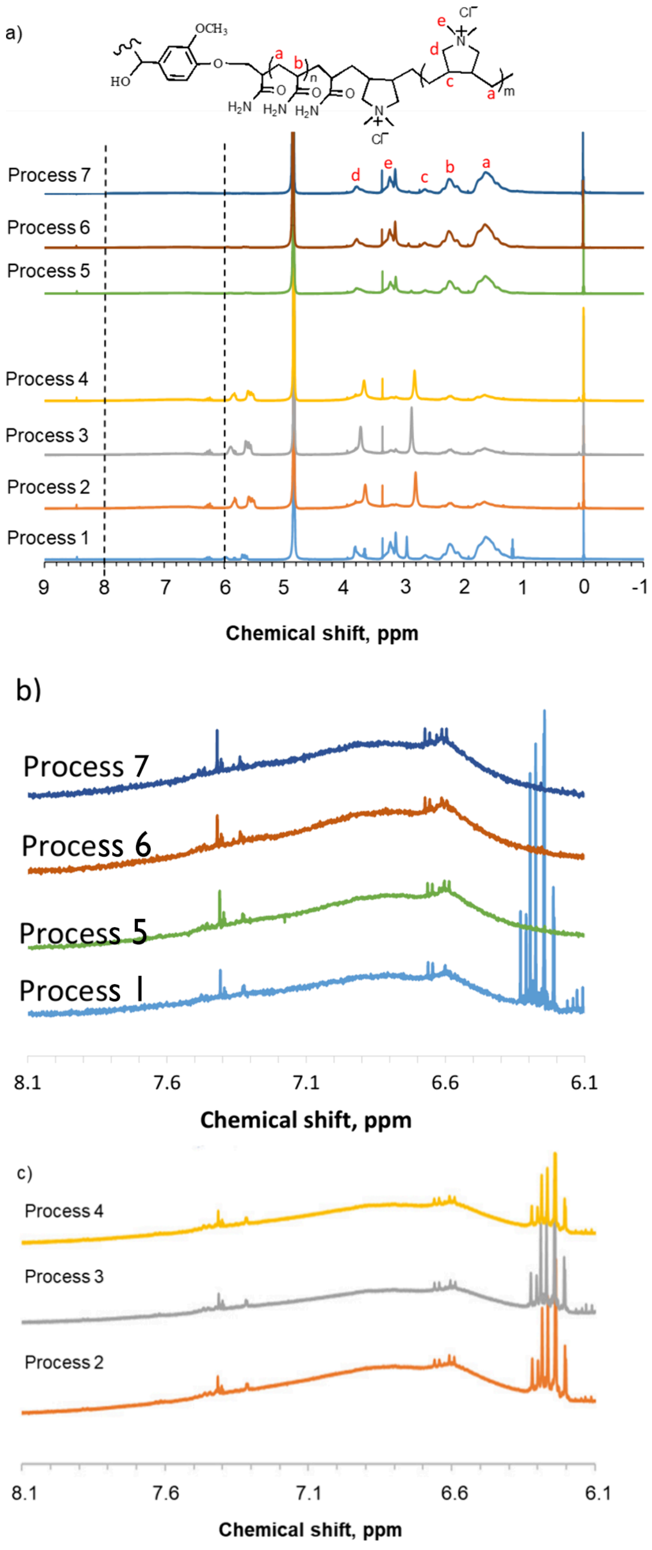


Figure 1. (a) Full ^{1}H NMR spectra of lignin-p(AM)-p(DADMAC) samples purified following different processes; (b) Enlarged view of the ^{1}H NMR spectrum ranging from 6 to 8 ppm for process 1, 5, 6, and 7; (c) Enlarged view of the ^{1}H NMR spectrum ranging from 6 to 8 ppm for process 2, 3, and 4.

Table 1. Concentrations of Unreacted AM and DADMAC Monomer Left in the Samples after Purification Processes

Sample	Unreacted AM, wt %	Unreacted DADMAC, wt %
Process 1	0.13	2.23
Process 2	0.37	4.42
Process 3	0.38	3.88
Process 4	0.20	3.42
Process 5	0.00	0.32
Process 6	0.00	0.40
Process 7	0.00	0.08

product, and the membrane process showed an efficient way for achieving it. Processes 5 to 7 present negligible amounts of AM monomers and a low DADMAC content, while processes 1 to 4 show low AM but some DADMAC residues. AM monomer can easily self-assemble and form p(AM),[31] and thus, its unreacted concentration would be generally lower than that of DADMAC in the reaction mixture after polymerization. Our previous study also confirmed that in the copolymerization of lignin, AM, and DADMAC, AM had a much higher conversion ratio (96%) than DADMAC (68%) because of the higher reactivity of AM.[21] Therefore, fewer AM monomers would be left in the reaction mixture after copolymerization, and the purification processes effectively removed them from the mixtures.

3.2. Yield, Solubility, and Charge Density Characteristics. Figure 2 describes the solubility and yield of lignin-p(AM)-p(DADMAC) purified by following different methods. After the copolymerization reaction, the reaction mixture was subjected to different purification processes to obtain the products. Therefore, no unpurified lignin-p(AM)-p-(DADMAC) was available before any purification process. The sample separated via ethanol precipitation (process 1) generated the copolymer with the highest solubility of 85 wt % and yield of 63 wt %. The samples purified by filtration (processes 5, 6, 7) had a similar solubility and yield to the ethanol-extracted sample (process 1). However, with the increase in the pore opening of filtration, the yield of the product decreased as more copolymers could pass through the filter pores and thus be wasted. In comparison, the yields of the dialysis of unreacted lignin were tested to be 72%, 66%, and 62% for the membranes with MWCO of 1 kg/mol, 10 kg/mol, and 25 kg/mol, respectively.

The acidification methods (processes 3 and 4) seemed to generate products with a lower yield and solubility. The centrifugation itself induced 55 wt % solubility (process 2), and its combination with acidification (processes 3 and 4) further reduced the solubility. The reason could be that acidification resulted in the precipitation of a large portion of unreacted lignin in the purified samples, which can be observed in the TGA profile (Figure 3) and will be discussed in section 3.5. According to Price et al.,[11] softwood kraft lignin is insoluble in water at acidic and neutral pH. Thus, unreacted lignin was probably precipitated and collected after adjusting pH to 1.5 and centrifuging. In addition, due to the better solubility of lignin-p(AM)-p(DADMAC) (40 wt % at pH 2 and 80% at pH 7), the lignin copolymers were partially dissolved at pH 1.5. They would not be fully collected at acidic pH. It is observable that all acidification and centrifugation methods had low effectiveness in separating lignin-p(AM)-p(DADMAC) (Figure 2).

After polymerization, in addition to lignin-p(AM)-p-(DADMAC), the reaction mixture contained several by-products, including lignin-p(AM), p(AM)-p(DADMAC), and p(AM), unreacted lignin, and AM and DADMAC monomers. Lignin-p(DADMAC) and p(DADMAC) would not form under the studied reaction conditions.[21] In the final products, lignin-p(AM)-p(DADMAC), p(AM)-p(DADMAC), and DADMAC monomers contributed to cationic charges, and the rest (i.e., lignin-p(AM), p(AM), unreacted lignin, and AM monomers) had anionic charges. The attachment of DADMAC to lignin or AM contributed to the cationic charge of the copolymer. Except for the centrifugation process (process 2), these results confirmed that the charge density of the samples was similar regardless of the purification process (Figure 2), demonstrating that the major components in the water-soluble part of the final products were lignin-p(AM)-

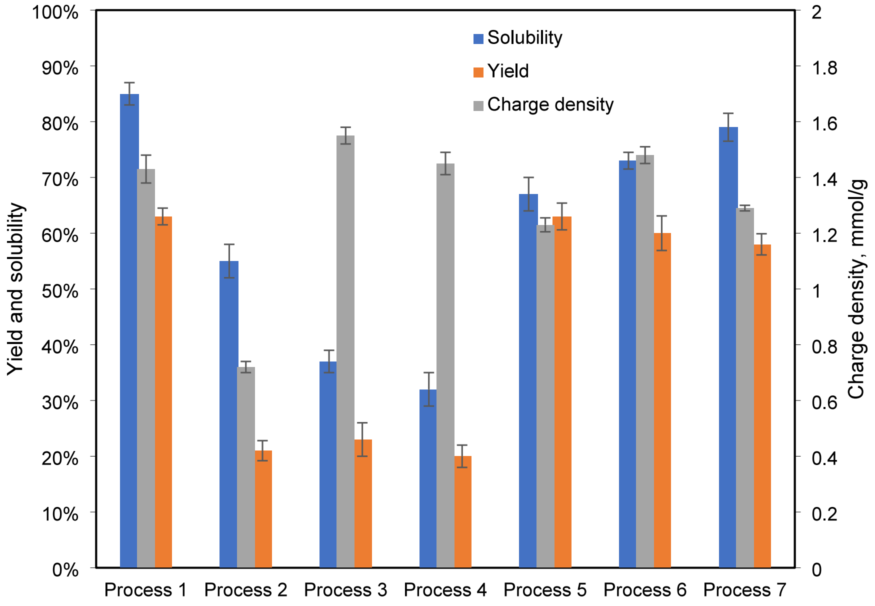


Figure 2. Solubility, yield, and charge density of lignin-p(AM)-p(DADMAC) purified by different methods.

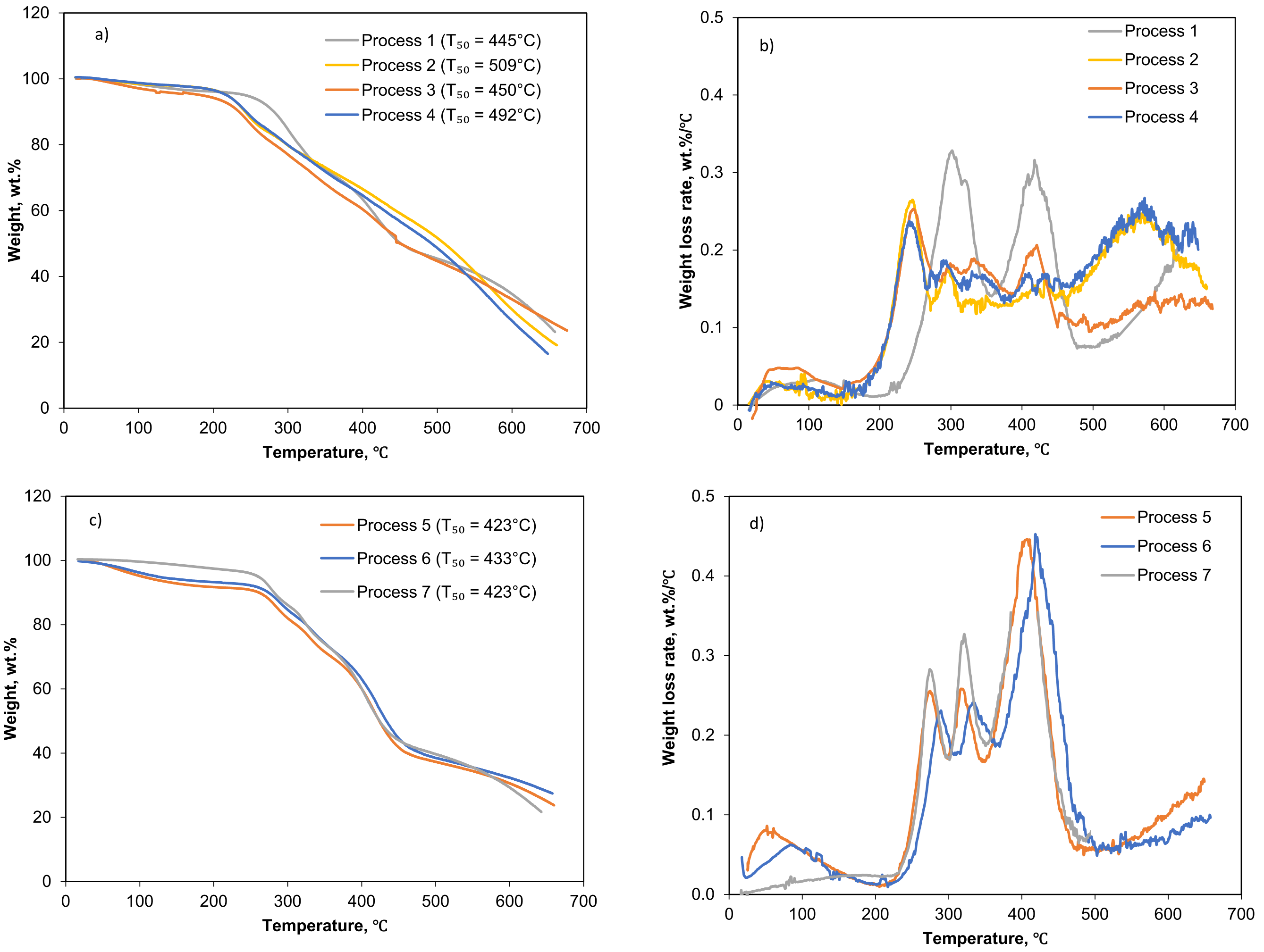


Figure 3. Weight loss (a) and weight loss rate (b) of lignin-p(AM)-p(DADMAC) purified via processes 1−4. Weight loss (c) and weight loss rate (d) of lignin-p(AM)-p(DADMAC) purified via processes 5−7.

Table 2. Lignin, AM, and DADMAC Content in the Final Products

Sample	N, wt %	Grafting ratio of AM, wt %	Grafting ratio of DADMAC, wt %	N_{DADMAC}, wt %	N_{AM}, wt %	C, wt %	DADMAC, wt %	AM, wt %	Lignin, wt %
Process 1	12.3	191	77	2	10.3	51.7	23	52	25
Process 2	4.3	21	9	1	3.3	53.3	12	17	71
Process 3	6	32	35	2.2	3.8	53.8	25	19	56
Process 4	4.8	21	30	2	2.8	54.8	23	14	63
Process 5	11.3	154	62	1.7	9.6	47.1	20	49	31
Process 6	12.5	221	101	2.1	10.5	50.8	24	53	23
Process 7	12.6	228	84	1.8	10.7	50.5	21	55	24

p(DADMAC) and p(AM)-p(DADMAC), which contributed to positive charges. It can be seen that the trend in the charge density of the purified samples was consistent with the DADMAC contents shown in Table 2. The lower charge density of the sample separated by process 2 may be due to fewer DADMAC-containing copolymers in the final product, which was proved in Table 2.

3.3. Molecular Weight Analysis. Table 3 lists the MW and radius of gyration (R_g) of lignin-p(AM)-p(DADMAC) separated by different methods. In determining MW by static light scattering (SLS) measurements, refractive index increment (d*n*/d*c*) is an important parameter.[32] The values for d*n*/d*c* depend on the chemical structure of the polymer and the average MW.[33] As can be seen in Table 3, each MW of the

Table 3. Molecular Weight of Lignin and Lignin-p(AM)-p(DADMAC)

Sample	MW, g/mol	R_g, nm	d*n*/d*c*
Lignin	$(7.90 \pm 2.10)\times10^4$	-	-
Lignin-p(AM)-p(DADMAC)			
Process 1	$(9.32 \pm 0.50)\times10^5$	68 ± 3.8	0.14
Process 2	$(8.86 \pm 0.13)\times10^5$	50.2 ± 1.2	0.18
Process 3	$(2.19 \pm 0.87)\times10^6$	99.3 ± 5.8	0.16
Process 4	$(1.36 \pm 0.04)\times10^6$	56.4 ± 2.4	0.17
Process 5	$(1.26 \pm 0.21)\times10^6$	76 ± 10.0	0.15
Process 6	$(3.74 \pm 0.58)\times10^6$	101.3 ± 9.3	0.16
Process 7	$(8.10 \pm 1.40)\times10^6$	127.1 ± 9.9	0.15

lignin copolymer sample corresponds to a specific value of d*n*/d*c*, which would be affected by the brownish color of the lignin-p(AM)-p(DADMAC) copolymer solutions due to the presence of lignin. It can be seen that a higher lignin concentration (Table 2) in the separated copolymer samples led to a higher d*n*/d*c* value (Table 3). As higher lignin indicated a lower grafting ratio in the copolymer (Table 3), the d*n*/d*c* value of the lignin-p(AM)-p(DADMAC) copolymer increased with increased grafting ratio, which was closely related to both the branching polymer structure and MW of the copolymer. This is why no evident correlation between d*n*/d*c* and MW can be found in this study (Table 3). The centrifugation (process 2) provided the lowest molecular weight, 8.86×10^5 g/mol, while the membrane isolation using the highest MWCO (process 7) generated the highest MW value, 8.1×10^6 g/mol. As centrifugation collects copolymer based on gravitation force, it was the least discriminatory process and thus isolated copolymers with different molecular weights, which induced the average MW of the collected copolymer to be lower than that of other samples. The MW of the samples collected via processes 3 and 4 were larger than that of process 2, indicating that acidification was somehow effective in collecting the copolymer with a higher MW. For the samples collected via processes 5 to 7, the larger molecular weight cutoff allowed more effective removal of smaller molecules, resulting in the larger molecular weight of the separated samples.

It should be mentioned that compared with the lignin-p(AM)-p(DADMAC) polymers, the synthetic polymer, i.e., p(AM)-p(DADMAC) had a larger molecular weight ($(3.15 \pm 0.36) \times 10^7$ g/mol) and higher charge density (2.16 mmol/g),[11] implying that the participation of lignin in the reaction hampered the polymerization progress of AM and DADMAC.[21] The radius of gyration (R_g) of a polymer is a geometrical quantity defined as the average square distance of the chain segments from the center of the mass of the chain of a polymer segment.[34] The R_g is very sensitive to macromolecules' size, geometry, and structure and strongly depends on the degree of polymerization.[35] A strong dependency of R_g on the molecular weight of synthetic polymers was observed in the literature.[36] In Table 3, larger R_g was determined for lignin-p(AM)-p(DADMAC) polymers with larger molecular weights, indicating longer chain lengths. It is noticed that the polymer generated from processes 4 and 5 had a similar MW but different R_g. The large R_g of polymer from process 5 may indicate its more three-dimensional structure. The reason is that the higher yields of dialysis processes (processes 5−7) than that of the acidification processes (processes 3−4) (Figure 2) preserved more lignin-p(AM)-p(DADMAC) fractions with higher MW and chemical structure diversities, resulting in more 3D structures of collected copolymers. Therefore, the relatively higher R_g for processes 5−7 than for processes 1−4 indicated that membrane dialysis preserved more lignin-p(AM)-p(DADMAC) with three-dimensional structure than other purification methods (i.e., ethanol precipitation, centrifuge, and acidification).

3.4. Elemental Analysis. Table 2 indicates each sample's nitrogen content and AM and DADMAC grafting ratio. The sample produced via membrane isolation (processes 5−7) and ethanol extraction (process 1) had a higher nitrogen content and AM than the other samples. As explained in our previous study, the activation energy for AM (65.7 kJ/mol) was slightly lower than that for DADMAC (69.3 kJ/mol) in the lignin-containing copolymerization reaction system.[21] Thus, AM facilitated the production of lignin-p(AM)-p(DADMAC) and extended its MW (Table 3).[31] Logically, the product generated via membrane dialysis with higher nitrogen contents and molecular weights possessed AM and DADMAC grafting ratios higher than those of other purification processes. The copolymers containing low molecular weights (and thus less AM) would probably pass through the pores for purification via membrane filtration. In contrast, only the higher molecular weight copolymer would be collected. The larger the pores of the membranes, the higher the molecular weight of the copolymer it would collect, and such a copolymer would have a higher AM content.

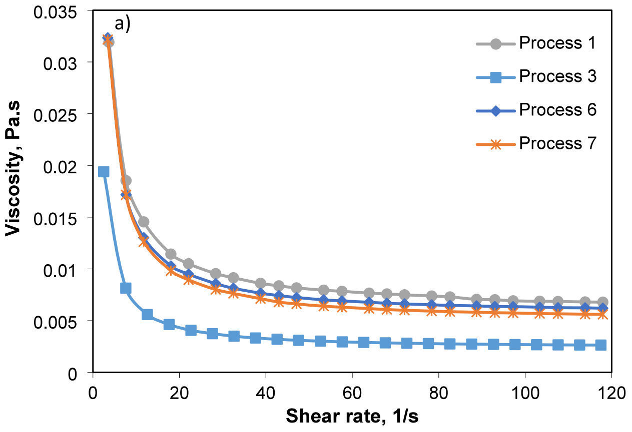
The final products' lignin, AM, and DADMAC contents were estimated via the elemental analysis, and the results are tabulated in Table 2. The grafting ratios were calculated based on the nitrogen content of AM and DADMAC samples. The lignin content in the copolymer was calculated by subtracting AM and DADMAC contents from 100%. The results confirmed that process 2 (centrifugation) would collect the copolymer with a lower DADMAC content. The major differences in components in the separated copolymers by different methods are the AM and lignin contents. The results of AM and lignin are alike in the ethanol-extracted and dialyzed samples since the lignin contents of these samples are approximately 24−31 wt %. The lower solubility of lignin would cause the precipitation of the copolymer with a higher lignin content (56−71 wt %) for isolation by centrifugation (process 2) and acidification (process 3−4). As the process with higher pore size dialysis collected the copolymer with a larger molecular weight, it contained more AM than lignin (Table 1).

3.5. Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was carried out on all of the samples of lignin-p(AM)-p(DADMAC) to study the thermal stability and decomposition of the samples. The thermal stability of polymers is essential, as it depicts how the chemical structure of the copolymer would impact its thermal stability and its possible applications. The thermogravimetric (TG) (weight loss vs temperature) and derivative thermogravimetric (DTG) curves (weight loss rate vs temperature) of the samples are described in Figure 3. Figure 3a illustrates the weight loss of lignin-p(DADMAC)-p(AM) extracted via processes 1 to 4. All copolymer samples were stable at <160 °C, which is related to the loss of moisture and impurities in the sample.[37] The second stage (from 220 to 350 °C) is the decomposition associated with amide and carboxyl groups.[38] In this stage, quaternary ammonium salts in p(DADMAC) of the copolymer break up into ammonia and alkyl halide,[39] while amide groups in p(AM) part of the copolymer break to release water, ammonia, and a small amount of carbon dioxide.[37] The main p(AM) chains may remain interactive as their decomposition temperature is 340−440 °C.[37] The last stage, occurring between 360 and 470 °C, is attributed to the decomposition of p(DADMAC) chains and the breakdown of main p(AM) chains, causing the release of carbon dioxide, water, nitrile compounds, and imides.[37,38]

The sample purified via ethanol extraction and dialysis started to degrade at 220 °C (Figures 3b and 3d), consistent with their similar lignin contents and grafting ratios (Table 2). Compared with the ethanol-extracted or dialyzed samples, all of the acidified samples started to degrade at a lower temperature of 160 °C (Figure 3b). They showed a higher

50% decomposition temperature (T_{50}) (Figure 3) as they contained more lignin (Table 3). The synthetic p(AM)-p(DADMAC) had lower thermal stability (with a T_{50} of 400 °C) than lignin-p(AM)-p(DADMAC) polymers, which is attributed to the presence of kraft lignin in the copolymer.[11] Additionally, T_{50} did not significantly change with molecular weight (Tables 2 and 4). According to the characteristics of TG and DTG curves, it could be concluded that the thermal degradation occurred independent of molecular weight, while the lignin content influenced the degradation of the investigated polymers differently.

3.6. Rheological Studies. As samples generated via processes 1, 3, 6, and 7 generated better results in charge density, solubility, and yield (Figure 2), they were chosen for further analysis. The rheological properties of the selected samples analyzed under flow ramp experiments and dynamic frequency-sweep experiments are shown in Figure 4. The viscosity and shear stress of the samples were recorded at a shear rate range of 0 and 120 1/s in 120 s. The results in Figure 4 indicate a decrease in viscosity following the shear rate reduction, reflecting the samples' shear-thinning behavior.[40] This is consistent with the rheological properties of kraft lignin and p(AM)- p(DADMAC), exhibiting shear thinning behavior shown in our previous study.[11] Generally, viscosity is directly proportional to the molecular weight of the polymer in solution; however, this trend was not seen in Figure 4 as these samples were not soluble. The most important factor affecting the viscosity developed by water-soluble polymers is the solution concentration of the polymer.[41] Process 1, with the lowest MW, induced the highest dynamic viscosity, attributed to its higher solubility of 85% (Figure 2). Process 3 showed the lowest viscosities, resulting from its lowest solubility of only 37% (Figure 2). It was previously reported that the optimal dose of the polymer flocculant in the flocculation process would decrease with the increase in the intrinsic viscosity of the polymer flocculant.[42] Therefore, it is expected that the sample of process 3 would have an optimal dosage higher than that of the samples of 1, 6, and 7. The viscosity measurement of polymer solution is generally crucial for establishing an effective flocculation process.[43]



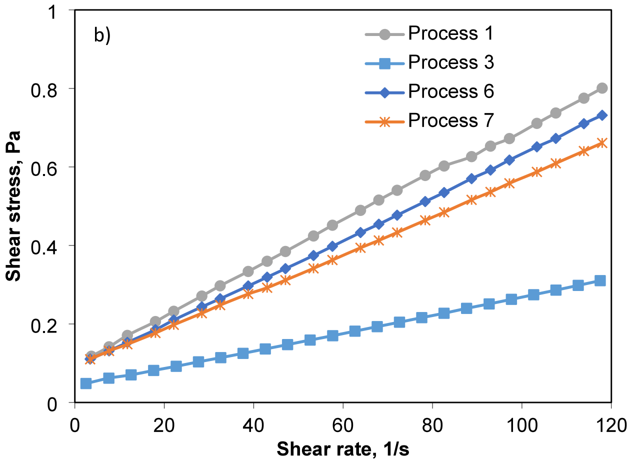


Figure 4. (a) Viscosity and (b) shear stress as a function of shear rate for lignin derivatives in deionized water (3 wt %).

3.7. Flocculation Performance. The application of the selected samples as flocculants for kaolinite suspensions was evaluated, and the results are listed in Figure 5. The results confirmed that all samples, except for sample 3, purified via acidification, had a similar flocculation efficiency. Also, the dialyzed samples with a higher MW and lower charge density (produced via process 7) obtained a higher turbidity removal than the sample generated via process 6. For these samples, the optimum flocculation dosage was 0.5 mg/g, which reduced the turbidity of kaolinite by 97.7%, 96.2%, and 97.3% for process 1, process 6, and process 7, respectively. The acidified sample had an optimal dosage of 0.8 mg/g, generating a turbidity removal of 95.2%. These optimum dosage results are in agreement with the expectations found previously by rheological analysis. Although the optimal dosage (0.2 mg/g) for the p(AM)-p(DADMAC) was lower, its reduction in the relative turbidity (93%) of the kaolin solution was also lower than lignin-p(AM)-p(DADMAC) polymers.[11] The flocculation mechanisms have been reported to involve charge neutralization, bridging, electrostatic patch, and hydrophobic interaction depending on the properties of the flocculants, the interactions between the flocculants and the wastewater components, and the process conditions.[11,44] For instance, in one study, the dominant flocculation mechanism of using a cationic flocculant (dodecyl poly(glucoside)-AM-DADMAC with a cationic degree of 30 mmol/g and dosage of 8.5−9 mg/L) for treating oil-containing wastewater was charge neutralization and hydrophobic association.[45] Another research using AM-

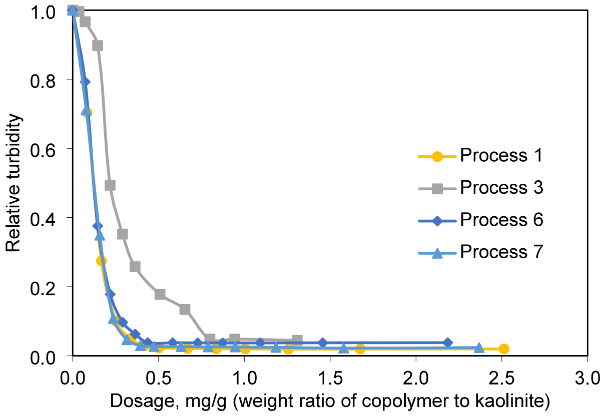


Figure 5. Relative turbidity as a function of lignin-p(AM)-p(DADMAC) dosage (mg/g) in a kaolinite suspension.

DADMAC stated that charge neutralization led to flocculation of kaolin-humic acid wastewater in acidic conditions while bridging and adsorption mainly affected flocculation in alkaline conditions.[46] In the current study, lignin-p(AM)-p(DADMAC) flocculants with high molecular weight could develop bridging with their cationic charges, contributing to charge neutralization in the flocculation process.[47]

3.8. Purification Discussion. Among all seven purification processes, centrifugation (process 2) was the most convenient but least favorable process, as it generated lignin-p(AM)-p(DADMAC) with the lowest charge density (Figure 2b), molecular weight (Table 3), and grafting ratios (Table 2).

Acidification with or without aeration (processes 3 and 4) was relatively complex compared to other purification methods. The acidified samples showed a relatively higher charge density (Figure 2b) and molecular weight (Table 3). However, the solubility and yield of the acidification processes were relatively low (Figure 2a). The acidification process resulted in the precipitation of products with unreacted lignin (Table 2), leading to a higher degradation temperature (Figure 3b). Additionally, the higher amounts of unreacted AM and DADMAC monomers (Table 1) in the acidified samples may limit their applications due to the toxic effects of these monomers, as mentioned previously. The aeration (process 4) increased the process complexity for acidification (process 3) and reduced the solubility, yield, charge density, and molecular weight of the acidified samples. Therefore, aeration is not recommended for purifying lignin-p(AM)-p(DADMAC) by acidification.

Although the ethanol extracted sample exhibited comparably high solubility, yield, and charge density (Figure 2), grafting ratios (Table 2), thermal degradation temperature (Figure 3b), and flocculation efficiency (Figure 5), its lower molecular weight (Table 3) may limit its performance for flocculation applications due to the lowered bridging effect. Also, this process consumes a large quantity of organic solvent, and its products contain relatively higher amounts of unreacted AM and DADMAC monomers (Table 1), which are not environmentally friendly.

The membrane dialysis processes (processes 5 to 7) were indicated to have the highest effectiveness for the separation of lignin-p(AM)-p(DADMAC) in terms of their extremely low unreacted AM and DADMAC monomers (Table 1), a high solubility, yield, and charge density (Figure 2), high molecular weight (Table 2), high grafting ratio with low lignin content (Table 3), high thermal degradation temperature (Figure 3d), and high flocculation efficiency (Figure 5). The membrane with a larger pore size generated products with a higher solubility (Figure 2a) and molecular weight (Table 2), which would improve the flocculation performance through bridging. Furthermore, membrane dialysis processes (processes 5 to 7) and ethanol extraction (process 1) processes had a comparable yield, which was much higher than other processes (Figure 2). The energy consumption of membrane dialysis processes may not be significant. Although the procedure of membrane dialysis is relatively time-consuming, it may be a viable process as it does not involve complex systems., e.g., solvent handling. Also, membrane dialysis would be more environmentally friendly compared to other methods.

4. CONCLUSIONS

The different purification methods of lignin-p(AM)-p(DADMAC) were studied in the work, including ethanol extraction, centrifuging, acidification, acidification with aeration, and membrane dialysis with different pore sizes (processes 1 to 7). The ethanol-extracted or dialyzed samples had higher solubility and yield than the acidified samples, while all of the samples had a similar cationic charge density. The membrane dialysis (processes 5 to 7) presents negligible content of AM monomers and a low DADMAC content, while processes 1 to 4 show much higher AM and DADMAC residues in the products. All the samples had degradation peaks in the range of 220 to 350 °C, and this temperature range would reflect the decomposition of quaternary ammonia groups. The dialyzed samples started to degrade at 220 °C, which was higher than that (160 °C) for acidified samples because acidified samples contained a great number of unreacted lignin. The samples' rheological properties indicated that the polymer solutions' viscosities were independent of molecular weights due to the significant impact of the solubility of the investigated polymers. The flocculation studies showed that the ethanol-extracted and dialyzed samples obtained higher turbidity removal at a lower optimum dosage (0.5 mg/g) than the acidified sample (0.8 mg/g). Therefore, membrane dialysis with a larger pore size was considered the most favorable method due to its effectiveness for separating lignin-p(AM)-p(DADMAC), best product properties and flocculation performance, and environmentally friendliness. This study discussed the efficacy of different polymer purification methods, which are crucial for selecting the purification process and controlling the desired properties of the lignin-based polymeric products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c06904.

One figure (Figure S1) on the ^{1}H NMR spectrum of kraft lignin and one figure (Figure S2) on the ^{1}H NMR spectra of AM and DADMAC monomers (PDF)

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was originally published ASAP on October 15, 2024. Due to a production error, Figure 3b was incomplete. The revised version was reposted on October 18, 2024.