

In Situ Copolymerization Studies of Lignin, Acrylamide, and Diallyldimethylammonium Chloride: Mechanism, Kinetics, and Rheology

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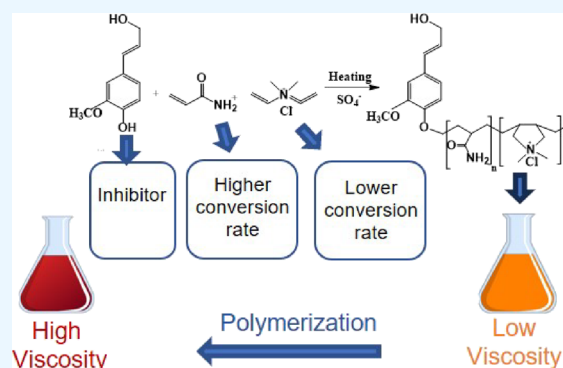
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ABSTRACT: In this work, free-radical polymerization of kraft lignin, acrylamide (AM), and diallyldimethylammonium chloride (DADMAC) was studied in detail. In situ nuclear magnetic resonance (NMR), rheological analysis, and particle size techniques were conducted to understand the physicochemical characteristics of this copolymerization system. The copolymerization of lignin–AM and lignin–DADMAC had activation energies of 65.7 and 69.3 kJ/mol, respectively, and followed the first-order kinetic model, which was monitored by in situ ^1H NMR results. The highest conversions of AM and DADMAC were 96 and 68%, respectively, in the copolymerization of lignin, AM, and DADMAC at the molar ratio of 5.5:2.4:1, pH 2 and 85 °C. The results illustrated that the participation of AM in the reaction was essential for polymerizing DADMAC to lignin due to less steric hindrance of AM than DADMAC facilitating its bridging performance. The monomer conversion ratio and dynamic rheology of the reaction system indicated that lignin acted as an inhibitor in the copolymerization reaction. The particle size analysis of the reaction mixtures reflected the alteration in the size of particles from coarse particles ($>300\ \mu\text{m}$) to fine particles (<10 and $10\text{--}50\ \mu\text{m}$) and suspension to colloidal systems when the reaction progressed. The oscillation study of the reaction media confirmed the gradual increase in the viscosity of the reaction media, illustrating the crosslinking of lignin, AM, and DADMAC.



1. INTRODUCTION

Lignin is an under-utilized component of woody biomass and has a complex three-dimensional polymeric structure. It was reported that the chemical pulping industry generates over 70 million tons of lignin every year worldwide.¹ Despite its widespread availability, only 5% of the lignin generated by the pulping industry was recovered and sold for commercial applications.¹ In contrast, the remaining 95% was either burned as a fuel source or disposed of.¹ To diversify the use of lignin in sustainable product development, lignin has been converted to other value-added products, such as lignin nanoparticles, battery binders and electrodes, emulsion stabilizers, carbon fibers, biosorbents, chemical reagents, adhesives, flocculants, paper-strength additives, gene carriers, and hydrogels.^{2–4} Among them, the use of lignin for flocculant productions seems promising as challenges associated with cleaning water are a global health problem.

The current coagulants/flocculants for wastewater treatment rely heavily on either inorganic salt (i.e., alum, FeCl₃) or petroleum-based synthetic polymers, including poly(acrylamide) (PAM), cationic poly(acrylamide) (CPAM), and anionic poly(acrylamide) (APAM). Although these materials are efficient, inorganic salts are toxic and produce large quantities of sludge, and synthetic polymers are

nonbiodegradable and their respective monomers can be harmful.⁵ The diversity of functional groups in lignin has also created opportunities for producing lignin-based flocculants for use in various industrial wastewater effluents.⁶ The polymerization of lignin and acrylamide can lead to a more environmentally friendly flocculant than PAM. In this regard, lignin–acrylamide polymers are usually neutral or negatively charged, only suitable for flocculating cationic material, such as cationic dyes.^{7,8}

Generally, a flocculant with higher cationic charges could remove more negatively charged colloids from wastewater. To produce cationic lignin, glycidyl trimethylammonium chloride (GTMAC) was grafted on hardwood lignin to create a highly cationic lignin-based polymer suitable for sulfate removal and kaolin settling.⁹ Cationic lignin–GTMAC could also facilitate water purification by the agglomeration of viruses and other microorganisms in water.¹⁰ Also, lignin was copolymerized

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with cationic monomers to produce cationic lignin-based flocculants/coagulants. In another work, lignin-based dimethylamine–acetone–formaldehyde copolymer (L-DAF) was synthesized for the removal of anionic dyes (Acid Black 1, Reactive Red 2, and Direct Red 23) via coagulation–flocculation.¹¹ Previous studies also demonstrated that [2-(acryloyloxy) ethyl]trimethylammonium chloride (ATAC) or [2-(methacryloyloxy)ethyl]trimethylammonium methyl sulfate (METAM) were two cationic monomers rendering lignin flocculants.¹² On the other hand, grafting the PAM chain onto lignin would improve lignin's solubility and molecular weight, which would be beneficial for lignin-derived flocculant fabrications.⁷ To make lignin with a high molecular weight and cationic charge density, the modification of lignin with acrylamide (AM), diallyldimethylammonium chloride (DADMAC), or [2-(methacryloyloxy)ethyl]trimethylammonium chloride (METAC) was studied in two-component systems.^{13,14} In this regard, a lignin-based cationic macromolecule was produced by polymerizing DADMAC and AM on lignin.¹³ In this system, for the first time, lignin was polymerized with AM and DADMAC in an aqueous medium rather than the organic solvents to produce cationic water-soluble flocculants for wastewater treatment systems.¹⁵ It was reported in our previous work that compared with other cationic flocculants used in wastewater treatment systems (12 mg/L pAM), the synthesized lignin-AM-DADMAC flocculant required a lower dosage (1 mg/L) to achieve an acceptable removal without the need of a dual-polymer system due to its relatively high molecular weight and a comparable charge density.¹⁵ Despite the promising flocculation results, the fundamentals and preparation process of generating a cationic lignin–AM–DADMAC copolymer in three-component systems have not been studied in detail. In this regard, the physicochemical characteristics of lignin polymerization with AM and DADMAC reactions are unavailable. Still, it is essential to investigate the mechanism of polymerization, which further helps tailor lignin-derived copolymers with different compositions for various applications.

In situ polymerization analysis has been considered an advanced technique for understanding the kinetic of polymerization systems. For example, the polymerization of *n*-butyl acrylate in an aqueous suspension,¹⁶ which was studied in an in situ form by nuclear magnetic resonance (¹H NMR) and scanning electron microscopy (SEM), was determined to follow a first-order kinetic model. In another work,¹⁷ the in situ ¹H NMR analysis of the copolymerization reaction of methyl methacrylate (MMA) and DADMAC revealed monomer consumptions for determining the reactivity of monomers in the reaction. As NMR can provide real-time data on the monomer concentrations,^{17–21} in situ NMR monitoring was followed in this work to determine the details of the monomer conversions in the copolymerization reaction of lignin, AM, and DADMAC as one objective.

The structural characteristics of polymers, microemulsions, or surfactants and their molecular interactions can be studied by monitoring the rheological behavior, e.g., viscoelasticity parameters, of materials in solutions.²² In this respect, the rheological properties of the reaction mixture during the polymerization reaction can reflect the network formation or cross link of monomers in the solution media.^{23–25} For example, the gradual increase in the viscosity of the system during the polymerization of *N*-isopropylacrylamide was an indicator of the formation of entanglements within polymer

chains.²⁵ The rheological studies, such as viscosity profile during polymerization, provide real-time monitoring and control of polymerization processes.²⁶ In this work, in situ rheological studies were utilized to understand the mechanism of polymerization of lignin, AM, and DADMAC as another objective.

This paper selected two monomers of AM and DADMAC to graft with softwood kraft lignin since these monomers are routinely used for producing uncharged and charged water-soluble polymers. Furthermore, the kinetics of three component systems of lignin, AM, and DADMAC was studied in detail. Also, the physicochemical characteristics of the polymerization of softwood kraft lignin, AM, and DADMAC were investigated in an in situ format by ¹H NMR and rheometer. Also, the information provided by a focused beam reflectance measurement (FBRM) assisted with understanding the particle size variations in the solutions during the polymerization. This analysis offered fundamental evidence of lignin polymerization for generating cationic lignin-derived polymers, which is crucial for reaction monitoring and system control, enabling the development of copolymers with desired compositions for specific end-use applications, e.g., flocculation systems.

2. MATERIALS AND METHODS

2.1. Materials. Softwood kraft lignin was supplied by FPIInnovations from its LignoForce pilot plant facilities in Thunder Bay, Ontario. DADMAC (65 wt % in water), AM, sodium persulfate, sodium hydroxide, KNO₃, sulfuric acid, deuterioxide, and 3-(trimethylsilyl) propionic-2,2,3,3-d₄ acid sodium salt, all analytical grades, were purchased from Sigma-Aldrich and used without further purification. Ethanol (95 vol % in water) was obtained from Fisher Scientific.

2.2. Copolymerization. In this set of experiments, 2.0 g of lignin and 40 mL of water were added to a three-neck flask. The specified amounts of AM and DADMAC were added to the flask to generate a 5.5:2.4:1 molar ratio of lignin:AM:DADMAC (i.e., equivalent to a 6.67:1.06:1 weight ratio based on the molar mass (196 g/mol) of C9 unit of lignin),²⁷ which was the optimum based on our previous work,¹⁵ and the pH of the suspension was adjusted to 2 while stirring at 500 rpm. The reaction mixtures were purged with nitrogen for 20 min, and then 30 mg of Na₂S₂O₈ was added to the reaction mixtures. The mixture was purged with nitrogen for an additional 10 min, while stirring at 500 rpm. The reactions were carried out at 85 °C for 2 h to obtain a lignin–AM–DADMAC copolymer. After the reaction, the mixture was cooled to room temperature and mixed with 400 mL of ethanol, which induced the precipitation of the copolymer. The precipitated copolymer was washed with 50 mL of ethanol and then dried in a freeze-dryer for 24 h. For comparison, the copolymerization of AM with DADMAC (i.e., pAM–DADMAC), lignin with AM (i.e., lignin–AM), lignin with DADMAC (i.e., lignin–DADMAC), and homopolymerization of the AM monomer (i.e., pAM) and DADMAC monomer (i.e., pDADMAC) were performed under the same reaction conditions stated above.

2.3. Molecular Weight. The molecular weights of lignin, pAM–DADMAC, and lignin–AM–DADMAC were analyzed by a static light scattering (SLS) system (Brookhaven Instruments BI-200SM) that was attached to a goniometer system (Holtsville, USA). In this analysis, the samples were prepared in 0.5 M of NaOH and 10 mM of KNO₃ at five

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 with 0.45 μm syringe filters to remove impurities. The refractive index increment of the lignin derivative samples (dn/dc) was determined by a differential refractometer (Brookhaven Instruments BI-DNDC, Holtsville, USA), which was 0.13 for pAM–DADMAC and 0.14 for lignin–AM–DADMAC. In the molecular weight measurement using SLS, time-averaged intensity measurements were made at variable angles from 15 to 155°. The light scattering data that depended on concentrations and angles was fitted into the equation using the Zimm Plot software of the instrument.^{28,29}

2.4. In Situ Copolymerization Reaction in an NMR Instrument. In this experiment, lignin and monomers were dissolved in D_2O under the conditions stated in Section 2.2 in nuclear magnetic resonance (NMR) tubes. After adding the initiator, 1 mL of the reaction mixture was added to the 5 mm NMR tube. The sample cavity of the NMR instrument was equilibrated at desired reaction temperatures by the temperature control unit of the NMR instrument, and the tubes containing the reaction mixtures were placed into the cavity. The copolymerization reaction was conducted in the NMR tubes at different reaction temperatures from 60 to 85 °C for 2 h. The sample was scanned every 10 min by an INOVA-500 MHz machine (Varian, USA) for ^1H NMR analysis. The concentration of monomers during the copolymerization reaction was determined via ^1H NMR analysis.

The copolymerization degree of lignin is difficult to measure because of its heterogeneous structure, as it contains various substructures arranged randomly. Therefore, the copolymerization process was studied based on the conversion ratio of AM and DADMAC monomers calculated considering their initial and final concentrations in the polymerization reaction system. To determine the concentration of AM and DADMAC, the areas under the peaks associated with different groups of AM (peak g, h, f) and DADMAC (peak a and b) were determined as shown in Figure S1a and calibrated with that of the internal standard, 3-(trimethylsilyl)propionic-2,2,3,3- d_4 acid sodium salt (TMS).³⁰ Figure S1b shows the ^1H NMR spectra for the copolymerization of lignin, AM, and DADMAC as a function of time at 85 °C, as an example. The initial and final concentrations of AM and DADMAC monomers in the ^1H NMR spectrum (at 0 and 120 min, respectively) were calculated by considering the integrated area of g, h, f, and a, b, respectively in Figure S1b. The conversion rate of each monomer was calculated based on the amounts of consumed monomers determined by the difference between initial and final concentrations of AM and DADMAC monomers during the polymerization reaction.

2.5. Rheology. **2.5.1. Dynamic Viscosity of the Polymerization System.** The viscosity changes of a solution containing monomers could indirectly indicate the difference in the molecular weight of polymers generated during polymerization. The rheological behavior of the copolymerization and homopolymerization reactions were monitored by conducting the polymerization reactions inside the chamber of a rheometer, DHR-2 (TA Instruments Co., USA), using a cylinder cup (with a diameter of 30.37 mm) and a vane rotor (with a bob diameter of 28 mm and a bob length of 42 mm) in an in situ manner. In this case, the reaction mixture containing 2 g of lignin and monomers (molar ratio of lignin:AM:DADMAC: 5.5:2.4:1) with the initiator was mixed manually in a 40

mL glass flask at pH 2, purged with nitrogen for 30 min, and then transferred to the cup of the rheometer and blended at 100 rpm for 2 h. The rheometer monitored the viscosity change of the system. In addition, the rheology of copolymerization of lignin, AM, and DADMAC was studied from 60 to 85 °C for 2 h.

2.5.2. Dynamic Viscosity and Zeta Potential of Lignin Solution. The rheometer determined the dynamic viscosity of lignin solutions in the pH range of 2–11. The concentration of lignin solution was 0.025 g/mL. The procedure to prepare lignin samples was the same as the polymerization process but without any monomers of AM and DADMAC. The zeta potential of the lignin solutions was measured by a zeta potential analyzer (NanoBrook Omni, Brookhaven Instruments).

2.5.3. Oscillation Study during and after Polymerization. The rheological behavior of the produced lignin–AM–DADMAC copolymer was studied using the oscillation technique of the rheometer at 85 °C using the same cylinder cup and a DIN rotor (with a bob diameter of 28.03 mm and a bob length of 41.96 mm). The reaction media's linear viscoelastic region (LVR) was studied for selecting the proper strain and stress results, which were 159% and 46.5 Pa for strain and stress, respectively (Figure S2 in the Supplementary Material). The time sweep test ran under the strain of 10%, and the stress during the process did not exceed 15 Pa to ensure that the linkage formation would not be destroyed during the test. To observe the accurate viscoelastic behavior of the polymer, the mutation number ($N_{\text{mu}} = t_{\text{exp}} \times \frac{\partial \ln(x)}{\partial t}$, $x = G'$ or G'') was introduced to ensure the time of measurement has to be lower than the characteristic evolution time of the system.³¹ Thus, the angular frequency, $\omega = 10 \text{ rad/s} = 1.59 \text{ Hz}$, was set in the experiment to have a mutation number lower than 0.1 as recommended. The frequency sweep experiment was studied right after the reaction at 85 °C and 10 rad/s.

2.6. In Situ Particle Size Distribution Measurement. An FBRM system (Mettler-Toledo AutoChem, USA) was also used to study the copolymerization and homopolymerization processes in real time. This instrument detects the chord length of the particles in the polymerization reaction systems in real time.³² Due to the sensitivity of the FBRM probe to the concentration of analysis media, the reaction systems were diluted by adding an extra 40 mL of water and the other conditions were kept the same as the original reaction (i.e., the molar ratio of lignin:AM:DADMAC = 5.5:2.4:1, pH 2, reaction time: 2 h). After adding the initiator, the reaction mixture was purged with nitrogen for 10 min and then the FBRM probe was put into the mixture while blending at 200 rpm. The reaction temperature was adjusted to 70 °C. The beaker was sealed by parafilm during the measurement to isolate the reaction system, and the FBRM instrument was used to monitor the entire 2 h of the copolymerization process.

The particle size of the unmodified kraft lignin at different pH was determined by a Malvern Mastersizer 2000 instrument (Worcestershire, UK). In this analysis, the kraft lignin suspensions (1 g/L) were adjusted to various pH values (i.e., pH 2, 4, 7, 9, 11). About 10 mL of these suspensions was taken and added to 600 mL of deionized water, which was adjusted to the corresponding pH values. The diluted samples were directly used for measuring the particle size distribution at the stirring rate of 250 rpm in the detection range of 0.02–2000 μm .

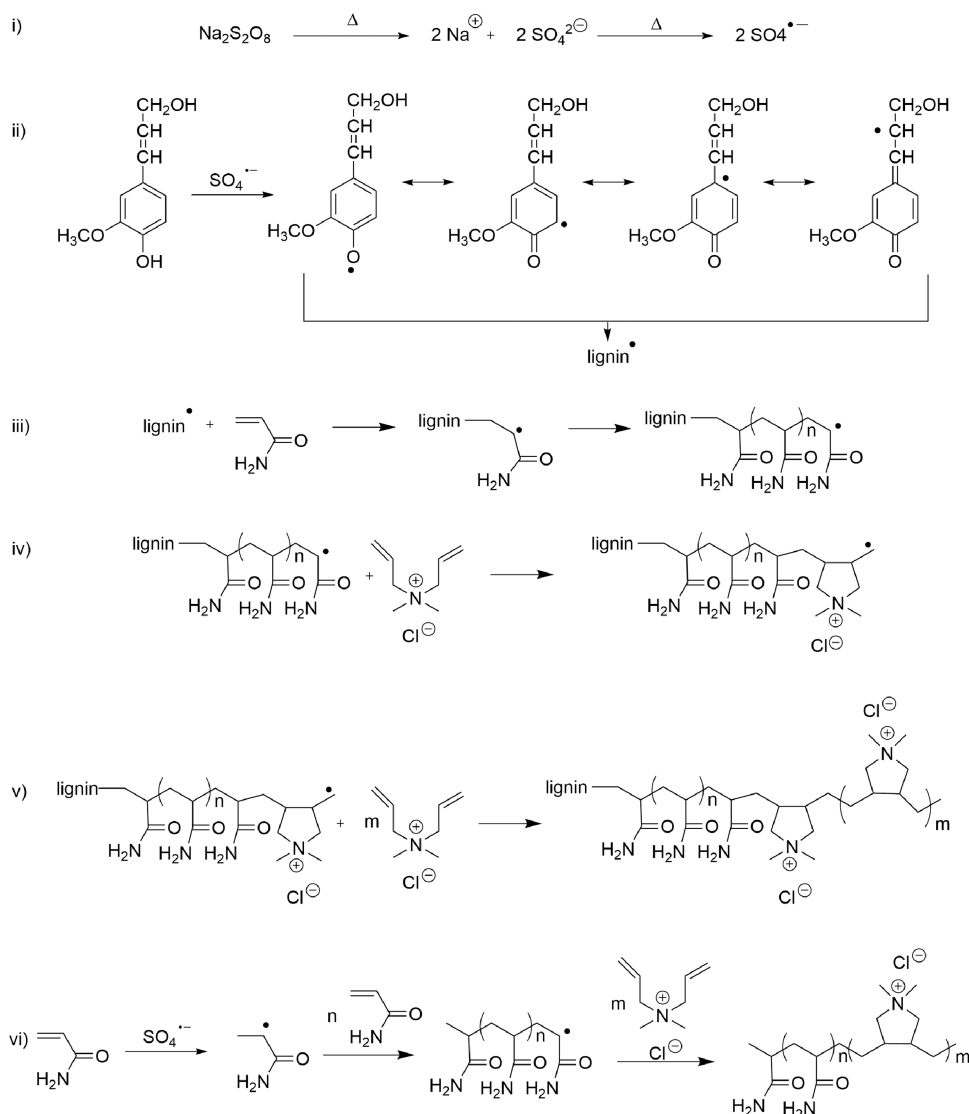


Figure 1. Copolymerization scheme of lignin, AM, and DADMAC initiated by $\text{Na}_2\text{S}_2\text{O}_8$ in a free radical system.¹⁵ Reprinted with permission from Price, J. T.; Gao, W.; Fatehi, P. Lignin-g-poly(acrylamide)-g-poly(diallyldimethylammonium chloride): synthesis, characterization and applications. *ChemistryOpen* 2018, 7, 645–658. [10.1002/open.201800105](https://doi.org/10.1002/open.201800105). Copyright 2018 John Wiley & Sons, Inc.

3. RESULTS AND DISCUSSION

3.1. Mechanism of Copolymerization. The reaction mechanism of lignin, AM, and DADMAC was a free-radical polymerization, and $\text{Na}_2\text{S}_2\text{O}_8$ was used as the initiator (Figure 1). The major chain formation in a free-radical polymerization is composed of free-radical generation, initiation, propagation, and termination, in which free radicals can react in different manners involving addition, coupling, disproportionation, abstraction, fragmentation, and transmutation.³³ In this reaction, sodium persulfate is thermally decomposed into sulfate radical anions, $\text{SO}_4^{\bullet\ominus}$. Then, the free radicals are transferred to lignin, AM, or DADMAC monomers in the reaction media.¹⁵ The free radicals transferred to lignin generate phenoxyl radicals by abstracting unstable hydrogen in phenyl-hydroxyl groups.³⁴ In coniferyl alcohol groups of lignin, the radicals derived from hydroxyl groups on the phenyl ring instead of aliphatic groups due to the higher stability of phenoxyl radicals.³⁵ In the addition stage, the phenoxyl radicals attached to AM monomers form lignin-pAM chains, which are then covalently bound with DADMAC monomers to

generate the final product, lignin-AM-DADMAC. The free-radical sites in both AM and DADMAC monomers were methylene groups on their backbone. In the propagation stage, the stability of a radical is not changed by adding monomer units to the radical but is altered by the group substituent, implying that every chemical has its unique propagation rate constant.³³ The propagation rate constant (k_p) of AM monomers at 50 °C is 2×10^4 L/(mol·s), which is much greater than k_p of DADMAC monomers, 90 L/(mol·s).³⁶

For this reason, lignin radicals react with AM more preferably than with DADMAC. Furthermore, lignin-AM-DADMAC was not the only copolymer formed in the reaction media and the propagation of AM-DADMAC was also achieved. Finally, the free-radical polymerization was terminated by coupling or disproportionation,³³ in which lignin-AM-DADMAC radicals and AM-DADMAC radicals combined into lignin-AM-DADMAC copolymers or broke into copolymers or homopolymers.

The presence of lignin in radical polymerization was reported to either promote or inhibit polymerization in

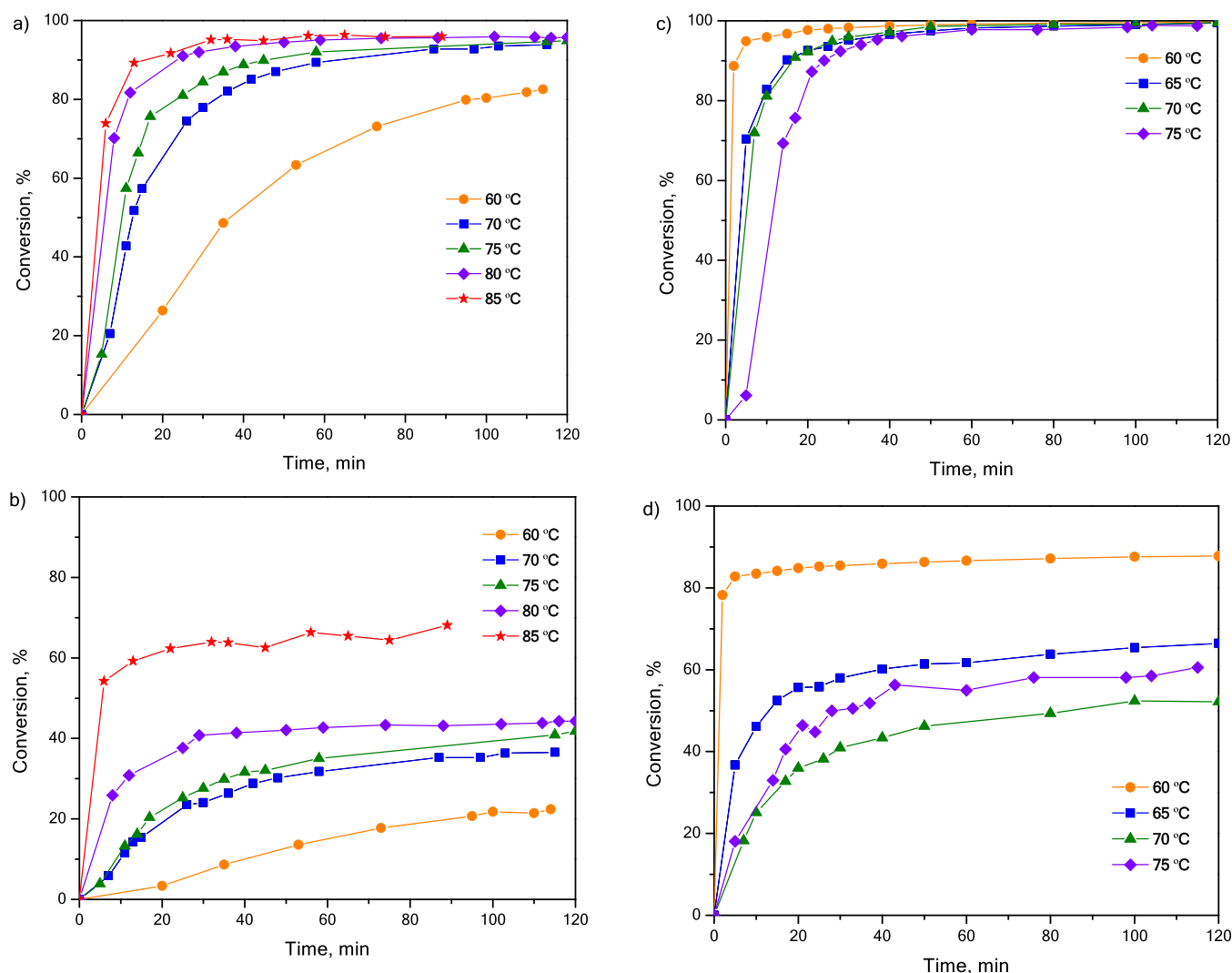


Figure 2. Monomer conversion ratio of (a) AM and (b) DADMAC in the copolymerization process of lignin, AM, and DADMAC (LAD) at different temperatures. Monomer conversion ratio of (c) AM and (d) DADMAC in the copolymerization process of AM and DADMAC without lignin (AD) at different temperatures.

previous studies.^{37–40} As a chain transfer reagent in free-radical polymerization,⁴¹ lignin promotes the molecular weight development of the polymer. However, in this study, the lignin-containing copolymer had a lower molecular weight (6.53×10^5 g/mol) and a lower charge density (1.43 meq/g) than the lignin-free AM–DADMAC copolymer (molecular weight of 2×10^6 g/mol and charge density of 1.88 meq/g), indicating that lignin inhibited the polymerization of the two monomers. The reason for this phenomenon could be that, in the initiation stage of the lignin-containing reaction, many phenoxy radicals may be generated, but these radicals are more stable than the other monomers. Thus, lignin does not promote the polymerization reaction as effectively as the other monomers.⁴¹ The quinoid structure of lignin may influence the molecular weight of the resulting copolymer.³⁸ The formation of covalent bonds between lignin and AM may provide steric hindrance for the growing chains of AM or DADMAC, especially that of DADMAC, due to its relatively low reactivity.

3.2. Kinetics of Copolymerization. The conversions of AM and DADMAC in the copolymerization process of AM and DADMAC with lignin at different temperatures are shown in Figure 2a and b, respectively. Overall, the highest conversion

ratio of DADMAC was 68%, which was lower than that of AM, 96%. Generally, the conversion of AM is faster than that of DADMAC at any temperature. The increase in temperature improved the conversion rates of both monomers, and the rate change was more dramatic for AM than for DADMAC. The reactivity ratio (i.e., the preference of propagation) of DADMAC was reported to be between 0.03 and 0.12, and that of AM was between 6 and 7 in the polymerization reaction of AM and DADMAC in water.^{42–44} Therefore, the lignin–AM–DADMAC copolymer contained more AM with a greater reactivity ratio than DADMAC with a lower reactivity ratio.⁴⁵ AM monomers are depleted quickly in the early stage of copolymerization, followed by the attachment of DADMAC monomers.⁴⁵ The reactivity ratio of DADMAC is close to 0, indicating that it prefers cross-propagation to homopropagation.⁴⁵ Non-polar AM has less steric hindrance than DADMAC. Thus, it can readily participate in the polymerization reactions to form high molecular-weight polyelectrolytes.³⁰ DADMAC with small reactivity has bulky and charged organic side groups promoting self-inhibition and electrical repulsion⁴⁶ and hampering the progress of the polymerization reaction. For comparison, the copolymerization of AM and

DADMAC without lignin was studied, as shown in Figure 2c and d, respectively. The conversion rate calculations depicted opposite trends for the conversion of AM and DADMAC with temperature, and the monomers were consumed faster as temperature decreased. AM monomers' conversion ratio reached a relatively stable value in 5 min at 60 °C and in 40 min at 75 °C. DADMAC monomers had a similar trend except at 70 °C. For the copolymerization system without lignin, the polymerization of AM was reported to be highly exothermic,^{47,48} leading to decreasing monomer conversion rates in the copolymerization system as the reaction temperature increased. On the contrary, the polymerization system with lignin were found to be endothermic.^{15,49,50} The formation of radicals is accelerated at a higher temperature, which promotes the chain transfer and termination.³⁷ Also, at a higher temperature, the viscosity of the reaction solution is known to reduce, facilitating the access of monomers onto the lignin backbone. The reaction at 60 °C generated the highest conversion ratio of AM and DADMAC monomers, which were respectively 100 and 88% (i.e., higher than that in the lignin–AM–DADMAC copolymers), demonstrating that lignin acted as an inhibitor of the polymerization in these reactions. The presence of stable radicals in the macromolecules might be the reason for this behavior.³⁸ However, at each temperature, the addition of lignin reduced the conversion ratio of DADMAC (e.g., from 60 to 42% at 75 °C) more than that of AM (e.g., from 99 to 95% at 75 °C) (Figure 2), suggesting that lignin has a more significant impact on the conversion ratio of DADMAC monomers than that of AM monomers.

The homopolymerization processes of AM and DADMAC and the copolymerization of lignin with AM or DADMAC in two-component systems were studied under the same reaction conditions of the copolymerization, and the results are shown in Figure 3. AM monomers in the homopolymerization reacted more rapidly than those in the copolymerization. They reached a 100% conversion ratio at the equilibrium stage. AM monomers had the lowest conversion rate when reacting with lignin, which indirectly indicates that the involvement of DADMAC in the copolymerization improved the reaction ratio of AM and lignin (Figures 2 and 3). DADMAC monomers did not form pDADMAC, prohibiting the progress of lignin–DADMAC (Figure 3b). Therefore, the participation of AM is required for the reaction of lignin and DADMAC.

The overall conversion ratio of AM and DADMAC monomers was calculated following eq 1:³⁰

$$X(t) = f_{AM}^0 X_{AM}(t) + f_{DADMAC}^0 X_{DADMAC}(t) \quad (1)$$

where $X(t)$ is the overall conversion ratio; f_{AM}^0 and f_{DADMAC}^0 are the initial mole fractions of AM and DADMAC monomers, respectively; and $X_{AM}(t)$ and $X_{DADMAC}(t)$ are the individual conversion rates of AM and DADMAC, respectively. The overall conversion ratio of monomers is shown in Figure 4a,b as a function of time at different temperatures, which were calculated considering the results in Figure 3. For the three-component system of lignin, AM, and DADMAC, the overall monomer conversion ratio of 77% was reached in 30 min at 85 °C (Figure 4a). The higher reaction temperature generated a higher conversion ratio. The trend of the overall conversions in Figure 4a is very similar to the plot of DADMAC conversion in Figure 2b. In the two-component system of AM and DADMAC (Figure 4b), the lowest reaction temperature revealed the highest overall conversion ratio, which is similar

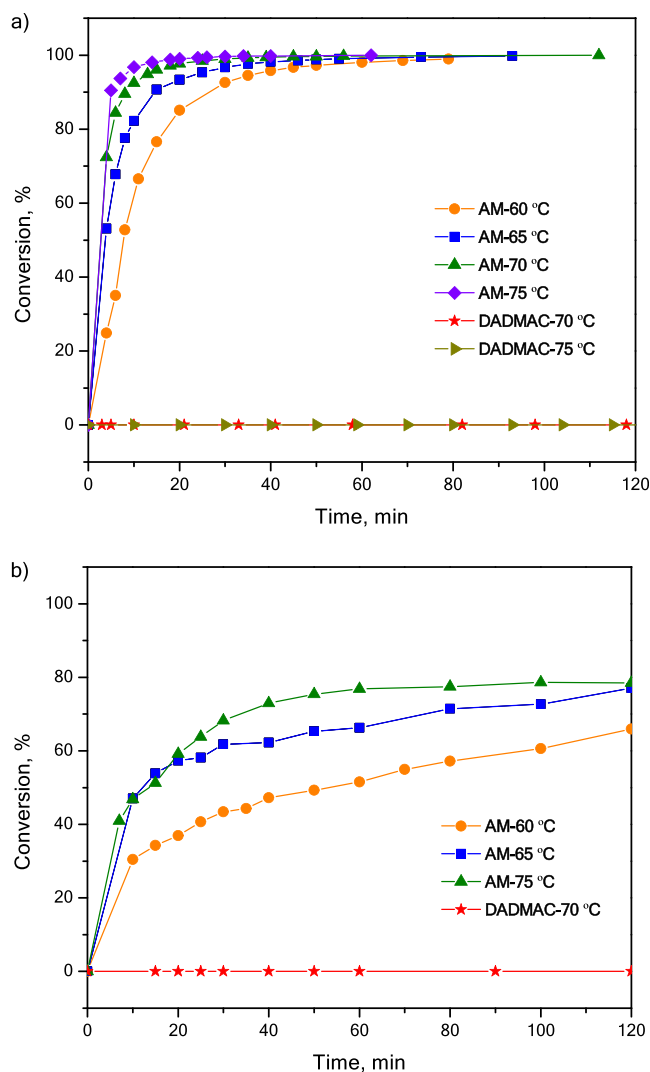


Figure 3. Monomer conversion ratio of AM and DADMAC in (a) the homopolymerization process to generate pAM or p-DADMAC and (b) the copolymerization to form lignin–AM or lignin–DADMAC at different temperatures.

to the trend in the plot of DADMAC conversion in Figure 2d. These results confirm that DADMAC played a major role in the overall conversion of monomers in copolymerization in the presence and absence of lignin.

The consumption rates of monomers are shown in Figure 4c,d as a function of time at different temperatures. The consumption rate, R_p , defined as overall conversion over reaction time, $X(t)/t$, reached the maximum value in 10 min except at 60 °C. In both reaction systems of lignin–AM–DADMAC and AM–DADMAC, the reaction can be defined into two stages: auto-acceleration and self-deceleration. In the first stage (auto-acceleration), the copolymerization ratio rapidly increased to the maximum value. Then, R_p started to reduce but the conversion ratio increased. In this stage, the polymers in the reaction medium probably had low reactive mobility and the intermolecular bonds were converted to intramolecular covalent bonds.⁵¹

The activation energy of the copolymerization reaction for lignin–AM–DADMAC, lignin–AM, and AM–DADMAC productions and of the homopolymerization for pAM was calculated based on the monomer conversion ratios at different

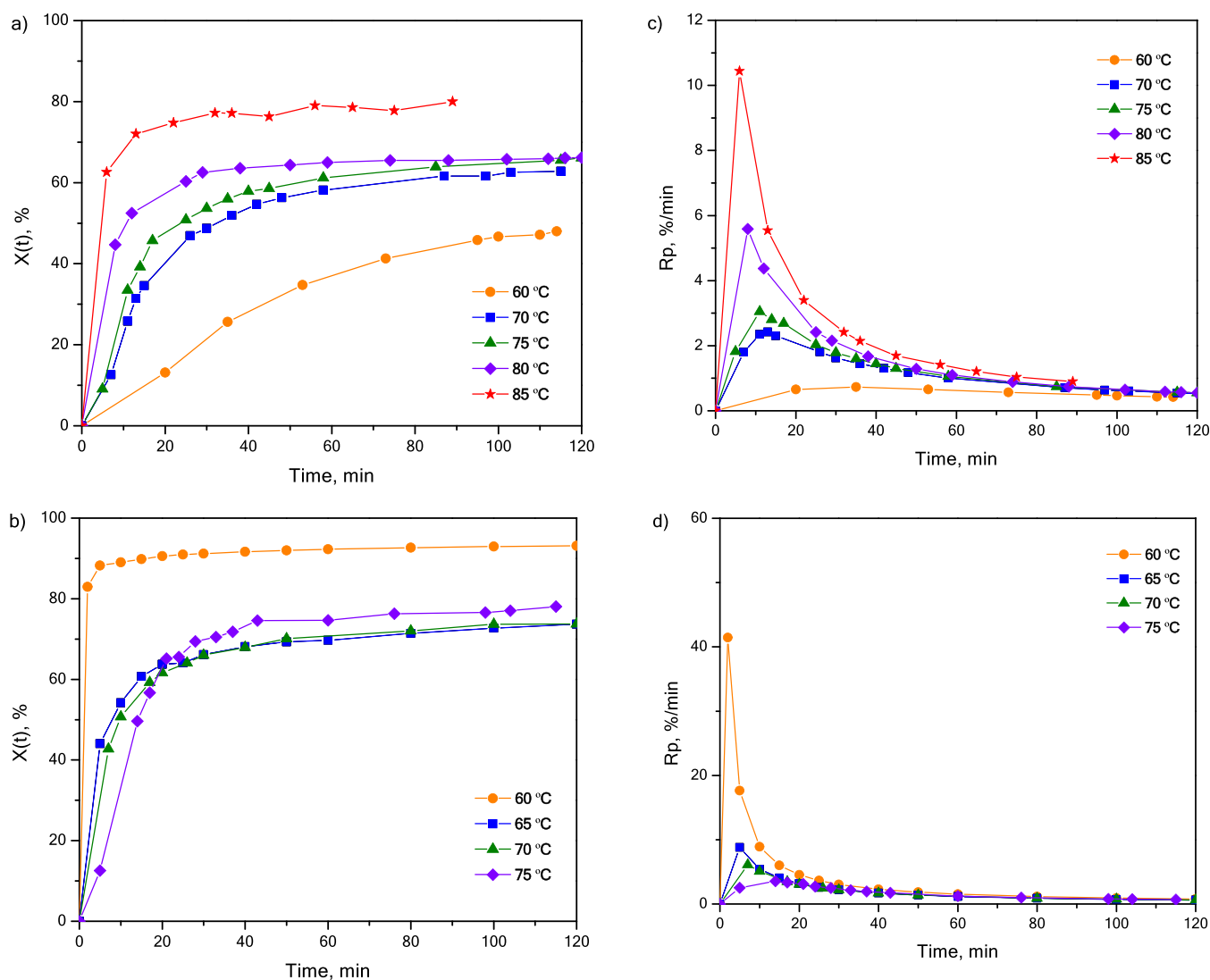


Figure 4. Overall monomer conversion ($X(t)$) for the systems of AM and DADMAC (a) with lignin and (b) without lignin. Consumption rate (R_p) for the systems of AM and DADMAC (c) with lignin and (d) without lignin.

reaction temperatures (Figures 2 and 3), and the results are shown in Figure 5. The copolymerization of monomers in Figure 5a–d was fitted into the first-order kinetics described in eqs 2 and 3. Then, the activation energy was determined using eq 4.³¹

$$-\frac{d[\text{Mo}]}{dt} = K([\text{Mo}] - [\text{Mo}]_f) \quad (2)$$

$$Y = \ln \frac{[\text{Mo}]_0 - [\text{Mo}]_f}{[\text{Mo}] - [\text{Mo}]_f} = Kt \quad (3)$$

$$K = Ae^{-E_a/RT} \quad (4)$$

where $[\text{Mo}]$ is the monomer concentration at time t ; $[\text{Mo}]_0$ is the initial monomer concentration; $[\text{Mo}]_f$ is the final monomer concentration when the equilibrium is achieved; K is the reaction rate constant; A is the collision frequency factor; and E_a is the activation energy. The activation energy for AM and DADMAC in the lignin-containing copolymerization reaction systems can be identified by the plot of $\ln(K)$ versus $1/T$ (Figure 5e), which are 65.7 and 69.3 kJ/mol, respectively. The slightly lower activation energy of AM led to a higher

conversion ratio of AM than that of DADMAC because DADMAC required more activation energy to react.³⁶ As DADMAC could not produce pDADMAC (Figure 3) and its activation energy was higher than AM, it can be stated that the presence of AM was necessary for the copolymerization reaction. Under the same reaction conditions, the activation energy of AM in the pAM system (93.4 kJ/mol) is higher than that (65.7 kJ/mol) in the copolymerization reaction of lignin–AM–DADMAC. The activation energy of AM in the lignin–AM system is 90.4 kJ/mol, which is slightly lower than that (93.4 kJ/mol) of pAM. These results imply that AM preferably reacts with lignin due to its lower activation energy with lignin than with itself.

3.3. Shear-Induced Viscosity Analysis. Figure 6a describes the changes in the viscosity of the reaction media for the production of lignin copolymers and homopolymers during the polymerization reactions. Generally, the viscosity of reaction media increased as time elapsed for the production of copolymers. The increase in the viscosity clarifies the stiffening of the system due to an early-stage reaction.⁵² The viscosity for the polymerization of lignin, AM, and DADMAC increased gradually and reached its maximum in 30 min, representing the

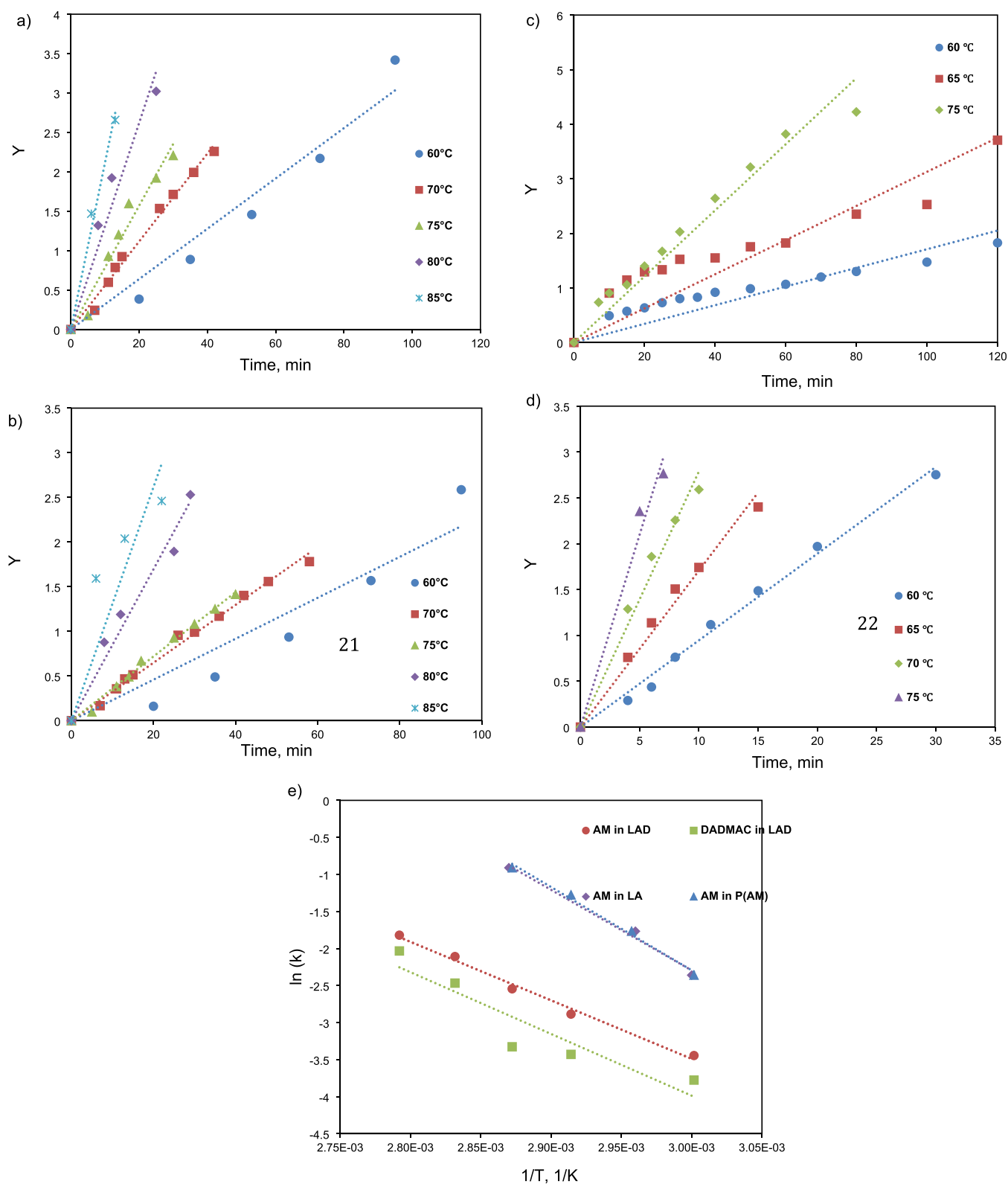


Figure 5. Arrhenius plot for (a) AM and (b) DADMAC in the copolymerization of lignin-AM-DADMAC, (c) AM in lignin-AM, and (d) AM in pAM (Y is expressed in eq 3). (e) The plot of $\ln(K)$ versus $1/T$ for determination of activation energy.

formation of the linear polymer.²⁶ It was discussed that the viscosity enhancement was caused by the formation of entanglements between linear polymer chains.²⁶ The formation of pAM-DADMAC and pAM indicated a much steeper increase in the viscosity owing to the chemical crosslinking and

subsequent gel formation.⁵³ The viscosity of the lignin-free copolymerization system was 10 times as much as that of the lignin-containing system. This behavior reflects the higher molecular weight of the generated polymers in the reaction mixture of the lignin-free system (AD in Figure 6a) than that

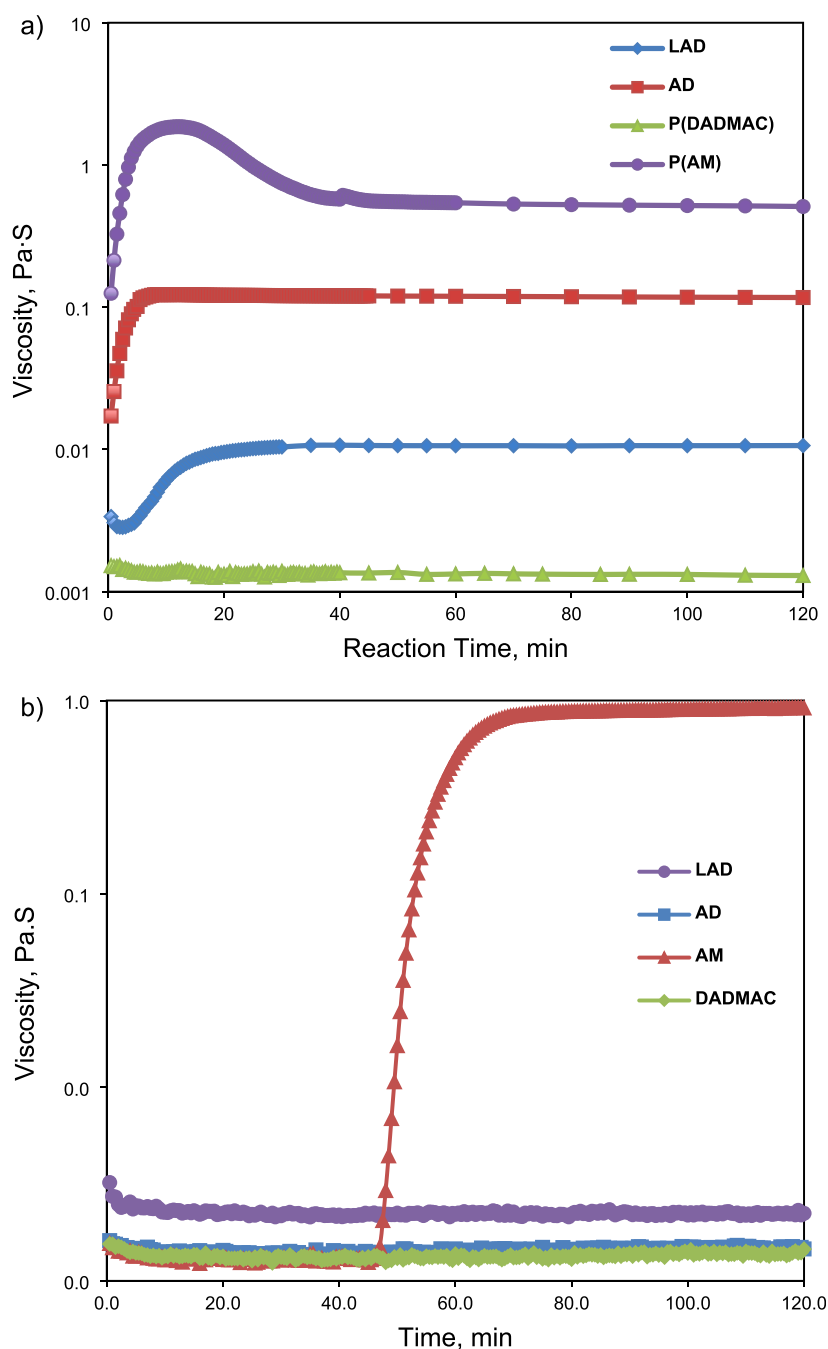


Figure 6. Viscosity changes of lignin–AM–DADMAC (LAD), AM–DADMAC (AD), pDADMAC, and pAM reaction systems (a) with initiator and (b) without initiator as a function of time (measurement conditions: the molar ratio of lignin:AM:DADMAC = 5.5:2.4:1, pH 2, 85 °C, 100 rpm, 2 h).

of the lignin-containing system (LAD in Figure 6a), which agrees with the higher molecular weight of the pAM–DADMAC copolymer (2×10^6 g/mol) than the lignin–AM–DADMAC copolymer (6.53×10^5 g/mol). For the homopolymerization system containing AM, the viscosity increased at the beginning of the reaction and then decreased after 10 min of the reaction. The molecular weight of the pAM solution in the first 10 min was 1.88×10^6 g/mol, which was greater than that after 2 h of reaction (1.67×10^6 g/mol). This behavior confirms that the degradation of pAM molecules causes a decrease in viscosity. Nagashiro and Tsunoda reported that the viscosity decrease of pAM molecules in aqueous solutions was attributed to the change in the dissolved state or

shear degradation.⁵⁴ It is also noticeable that the viscosity change was dramatic for the two-component system of AM and DADMAC or a single system of AM. The lignin-containing system had a slower pace in the viscosity increase (Figure 6a). These results may show that the homopolymerization of AM or copolymerization of AM and DADMAC was quick. Still, the presence of lignin in the system reduced the polymerization rate. This behavior may be related to the stability of phenol radicals of lignin and their resistance in participating or initiating the polymerization reactions. The reaction system containing only DADMAC did not have a noticeable viscosity change. The reaction progress (Figure 3)

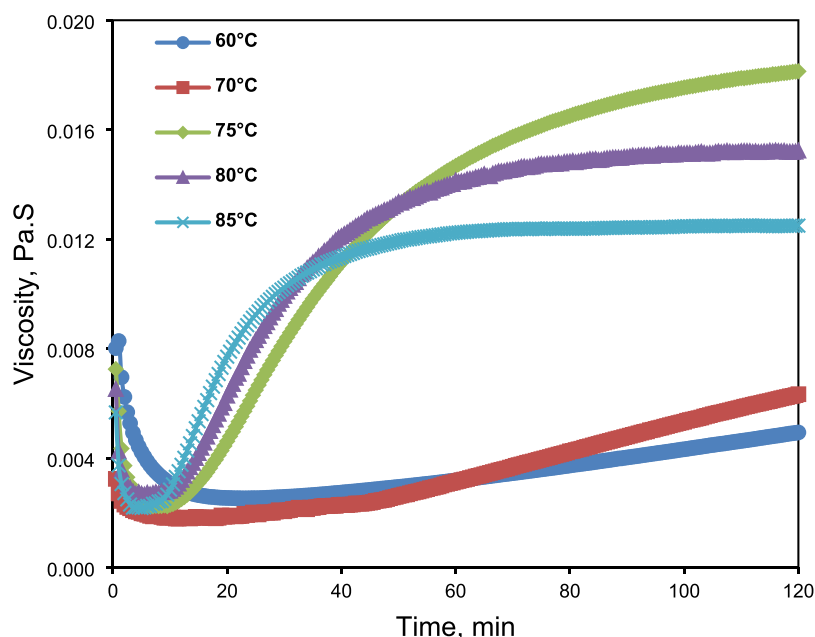


Figure 7. Viscosity changes of the reaction system containing lignin, AM, and DADMAC at different reaction temperatures (measurement conditions: the molar ratio of lignin:AM:DADMAC = 5.5:2.4:1, pH 2, 100 rpm, 2 h).

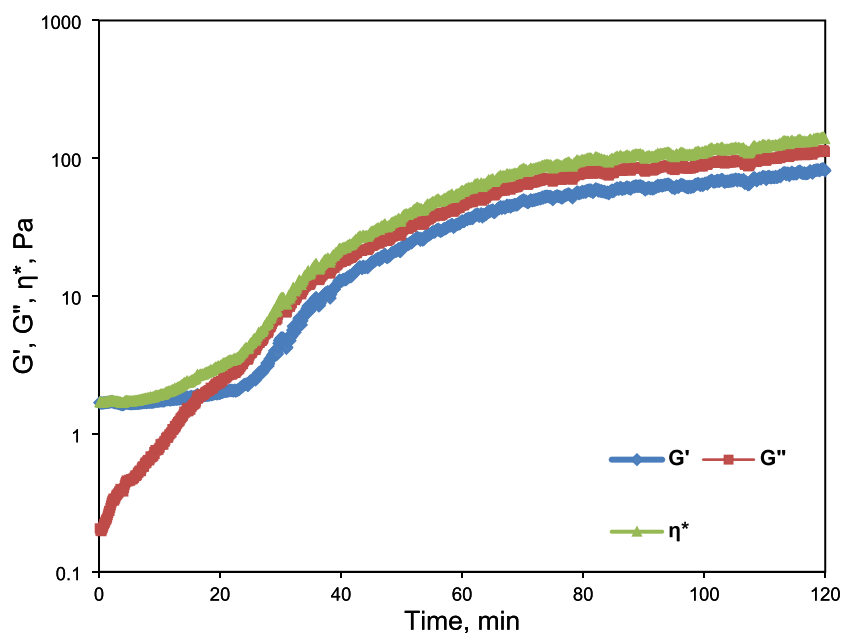


Figure 8. In situ polymerization of lignin with AM and DADMAC monomers in a rheometer chamber. Storage and loss modulus and complex viscosity as a function of reaction time during the polymerization process (measurement conditions: the molar ratio of lignin:AM:DADMAC = 5.5:2.4:1, pH 2, 85 °C, 100 rpm, 2 h).

implied that the homopolymerization of DADMAC did not proceed under the conditions studied in the rheometer.

Furthermore, Figure 6b describes the copolymerization and homopolymerization systems of lignin, AM, and DADMAC without the initiator. Except for the AM system, the rest had no change in viscosity. AM started to form pAM after 45 min when the reaction temperature was higher than its melting point of 84.5 °C.⁵⁵ AM easily polymerizes at its melting point in solution or under ultraviolet light.⁵⁵ Candau et al.⁵⁶ also found that AM could polymerize even in the absence of an initiator due to impurities (e.g., oxygen, peroxides, and emulsifier) present in the reaction medium. The results in

Figure 6b report that the initiator is essential for the copolymerization processes of AM and DADMAC with and without lignin.

The reaction of the system containing lignin experienced a small viscosity drop within 5 min of reaction in Figure 6a, which is perhaps associated with the thixotropy phenomenon defined as the breakage of lignin agglomerates caused by the applied shears at the beginning of the reaction (Figure S3).⁵⁷

3.4. Viscosity Analysis at Different Temperatures. The viscosity of the reaction media containing lignin, AM, and DADMAC was studied at different temperatures and time intervals, and the results are shown in Figure 7. The thixotropic

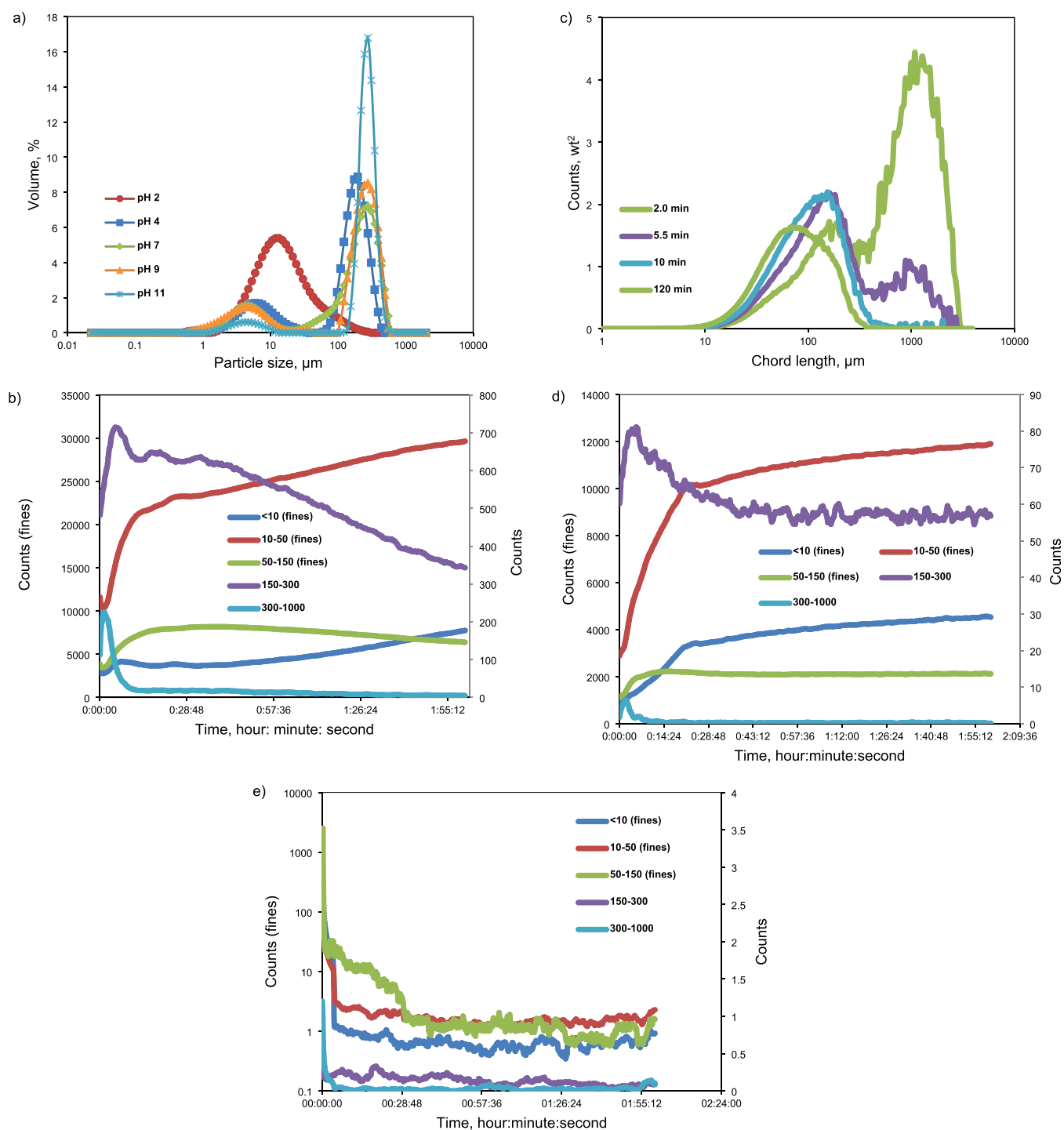


Figure 9. (a) Particle size distribution of lignin at different pH. (b) Particle size variations of the three-component reaction mixture of lignin, AM, and DADMAC (LAD) during the polymerization process. (c) Chord length distribution of the LAD reaction media. Particle size variations of the two-component reaction mixtures of (d) lignin with AM and (e) AM with DADMAC (measurement conditions: the molar ratio of lignin:AM:DADMAC = 5.5:2.4:1, pH 2, 70 °C, 200 rpm, 2 h).

behavior of all samples is evident in the first 5 min of the experiment. It is also seen that the system had a slower rate of viscosity gain but with overall higher viscosity at 75 °C than other temperatures. Theoretically, as these reactions are generally endothermic, a higher reaction temperature provides a higher conversion ratio of monomers to form larger polymers, hence the higher viscosity of the reaction mixtures.⁵⁰ Meanwhile, the temperature increase itself could decrease the viscosity, and the partial hydrolysis of the copolymers at a

higher temperature may occur,³⁷ which may cause a slower rate of viscosity gain. It is also noted that the viscosity of the system first increased rapidly and then became stabilized. The reason could be that the reaction proceeded very quickly at the beginning and the formation of larger molecules hindered the progress of the reaction in the later stage, slowing down the reaction rate and hence viscosity increase.

3.5. Rheological Analysis. The rheometer investigated the oscillation response of the three-component reaction

mixture of lignin, AM, and DADMAC. The change in the storage (G') and loss (G'') modulus (called elastic and viscous modulus), as well as the complex viscosity (η) of the reaction mixture, was analyzed at 85 °C in Figure 8. The elastic and viscous moduli and complex viscosity had a similar trend, illustrating the crosslinking of monomers in the reaction medium.²⁴ Furthermore, the gradual increases in the G' and G'' verified the growing chain of polymers in the reaction, and this growth continued after the monomer conversion rate reached its maximum (Figure 2a) in the polymerization process.⁵⁸ At the beginning of the reaction, the viscosity increased rapidly, which might be attributed to the main chain growth and network formation taking place.²⁴ The increasing rate of viscosity slowed down, which was most likely due to the lowered monomer conversion rate in the later stage of copolymerization (Figure 2a). During the stabilization period, the rate of aggregation and breakdown within the microstructural network is in equilibrium.⁵²

3.6. Particle Size Analysis. The particle size distribution of lignin at different pH is investigated, and the results are shown in Figure 9a. Lignin at different pH (except pH 2) showed bimodal distributions from 1 to 10 μm and from 100 to 1000 μm . The first peak of 1–10 μm was probably the size of kraft lignin particles, and the second peak of 100–1000 μm was caused by aggregation of the particles in suspension systems.⁵⁹ Lignin at pH 2 only had a unimodal distribution from 1 to 100 μm owing to the less solubility of lignin and its further aggregation to the larger size.¹⁵

Figure 9b and c show the size of particles during the polymerization process of lignin with AM and DADMAC. It is found that the size of particles in lignin–AM–DADMAC solution became stable after 5 min, confirming the results of the rheometer illustrated in Figure 6a. In the first 10 min time of the reaction, the number of coarse particles (those greater than 300 μm) became negligible, suggesting particle dissociation and breaking, which is in agreement with the thixotropy phenomenon causing the viscosity drop at the beginning of the reaction (Figure 6a). The decrease in the number of coarse particles (greater than 300 μm) and the increase in the number of fine particles (<10 and 10–50 μm) indicated the solubility improvement of the sample owing to the formation of the copolymers. During the reaction, the distribution of particle size displayed wide multimodality in the first 5 min. Then, the size shifted to a single peak in the finer particle size range (Figure 9c), indicating that the reaction mixture changed from a suspension to a colloidal system along with the formation of the lignin copolymer.

As illustrated in Figure 9d, the particle size of lignin–AM also showed a decrease in the number of coarse particles and an increase in the number of fine particles before 5 min. After 30 min, the number of particles with different sizes stabilized, which is consistent with the viscosity trend for lignin–AM in Figure 6a, implying that the breakdown and aggregation of the microstructure is almost in equilibrium. For the AM–DADMAC in Figure 9e, a very limited number of coarse particles was observed in the absence of lignin and there was almost no change in particle size after 10 min. The change of particle in the first 10 min may be caused by shear mixing. These results suggest that (1) the copolymerization of AM and DADMAC would not induce a significant particle size change since they are both water-soluble monomers and generate water-soluble polymers; (2) the copolymerization of lignin and AM follows the same trend as that of lignin, AM, and

DADMAC; and (3) the change in particle size of the systems (Figure 9a) originates from the solubilization of lignin when lignin reacts with AM (Figure 9e).

4. CONCLUSIONS

Through free-radical polymerization, kraft lignin was synthesized with AM and DADMAC in an acidic environment. In the lignin–AM–DADMAC (LAD) polymerization system, the conversion ratio of AM (96%) was much greater than that of DADMAC (68%) because of the higher reactivity of AM. The temperature elevation improved the conversion rates of both AM and DADMAC monomers, and the rate change was more dramatic for AM than for DADMAC. This is also confirmed by the lower activation energy of AM (65.7 kJ/mol) than DADMAC (69.3 kJ/mol) in the LAD system. The comparison of the monomer conversion ratio between the AM–DADMAC (AD) polymerization system and the LAD system demonstrated that lignin acted as an inhibitor of the copolymerization and lignin has a greater impact on the conversion ratios of DADMAC monomers than that of AM monomers. The zero-monomer conversion ratio of DADMAC in the lignin–DADMAC system and DADMAC homopolymerization system showed that DADMAC neither formed homopolymers nor directly reacted with lignin. The shear-induced viscosity analysis also proved these results. The viscosity of the lignin-containing reactions all reduced in the first 5 min, which might be attributed to the thixotropic behavior caused by dissociation and breaking of lignin agglomerates. The reaction at 75 °C had an overall higher viscosity than other temperatures. The slower rate of viscosity gains at 85 °C than 75 °C throughout the reaction process could be attributed to the lower viscosity of the reaction system or copolymer degradation at a higher temperature. The elastic and viscous moduli verified the growing chain of polymers in the reaction, and this growth continued after the monomer conversion rate reached its maximum. The particle size analysis of the reaction mixtures reflected a decrease in the number of coarse particles (greater than 300 μm) and the increase in the number of fine particles (<10 and 10–50 μm), indicating the solubility improvement of the sample owing to the formation of the copolymers. When the reaction progressed beyond 5 min, the particle size and viscosity analyses reflected the alteration from a suspension to a colloidal system due to the shift in the particle size from coarse to fine particle ranges.

■ ASSOCIATED CONTENT

Data Availability Statement

The datasets related to this work can be available upon request from the corresponding author.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c02296>.

H NMR spectra of monomers, linear viscoelastic region of lignin–AM–DADMAC, and shear stress vs shear rate figure of the copolymer (PDF)

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Author Contributions

X.W.: methodology, data collection and analysis, writing—original draft. W.G.: investigation, validation, writing—review and editing. B.L.: co-supervision, writing—review and editing. P.F.: funding acquisition, resources, supervision.

Notes

The authors declare no competing financial interest.

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