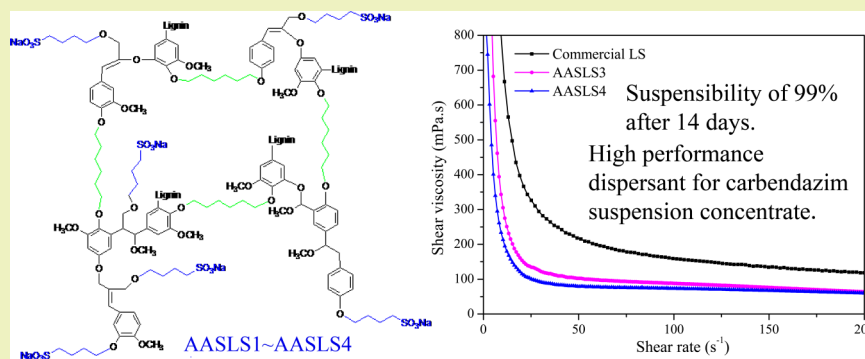


Alkyl Chain Cross-Linked Sulfobutylated Lignosulfonate: A Highly Efficient Dispersant for Carbendazim Suspension Concentrate

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ABSTRACT: A new family of highly water-soluble alkyl chain cross-linked sulfobutylated lignosulfonates (AALSs) with a three-dimensional network structure and naked alkyl sulfonic acid groups were readily prepared by using 1,4-butane sultone (BS) and C₆H₁₂Br₂ by a one step reaction in water, which simultaneously improved the sulfonation degree and molecular weight. GPC, ¹H NMR, FTIR and functional group content tests confirmed their cross-linked chemical structure and efficient nucleophilic substitution reaction mechanism. Furthermore, the dispersion properties of AALSs in a carbendazim suspension concentrate (SC) system were investigated. AALS4 with high molecular weights (*M_w*) and moderate sulfonation degrees showed suspensibility of 99% in 45% carbendazim SC after hot storage at 50 °C for 14 days. Meanwhile, AALS4 also showed smaller SC particle size and better rheological performance than commercial lignosulfonate. The adsorption isotherms and ζ-potential of AALSs on carbendazim SC particles were studied to reveal the dispersion mechanism. The alkyl chain cross-linked structure and long alkyl chain-containing sulfonic acid groups contribute to the excellent dispersion properties on carbendazim SC. Our modification approach for lignin might provide a novel concept and prospective avenue for the design of efficient dispersants.

KEYWORDS: Alkali lignin, Sulfonation, 1,4-Butane sultone, Dispersion, Carbendazim suspension concentrate

INTRODUCTION

It is estimated that about 2.5 million tons of pesticides were used on crops, and the environmental costs accumulated on pesticide overuse all over the world is almost \$100 billion annually.¹ Harmful fungus injures crops severely and brings serious losses of crops annually.² For a long period of time, antifungal agents were chosen to control the fungal diseases of crops. As a well-known antifungal agent, carbendazim is widely used to control a broad range of diseases on fruits, vegetables and field crops.³ However, carbendazim is very resistant to degradation in the environment after overuse. Moreover, the active ingredients of carbendazim contained hydrophobic and aromatic substances, which make this pesticide difficult to be wetted and dispersed in water. Thus, they easily accumulate in crops and cause environmental pollution. Meanwhile, the poor water-solubility and high melting point limit its environment-friendly application considering safety problems.⁴ Therefore, it is important to find some effective methods to solve the process problems in the use of carbendazim. Addition of using dispersing agents, various surfactants such as emulsifiers, is an

effective solution to decrease the usage of carbendazim.⁵ As an environment-friendly, renewable and economical dispersant, lignosulfonate (LS) has great application potential due to its hydrophobic phenyl propane groups and SO₃⁻ groups, which offer π-π interactions and adsorption effects, respectively, on pesticide molecules. Our previous studies also illustrated that the molecular weights and sulfonic group content were the dominant factors that affect the dispersion performance of LS in a pesticide dispersion system.⁶

LS, as a byproduct of the pulping and paper making industry, was produced by sulfonation of industrial lignin. Alkali lignin (AL) is the major component of black liquor of alkaline pulping, and accounts for more than 90% of total industrial lignin. Poor water-solubility and low reactivity severely limit the industrial applications of alkali lignin.⁷ So far, a variety of chemical modification approaches including alkylation graft

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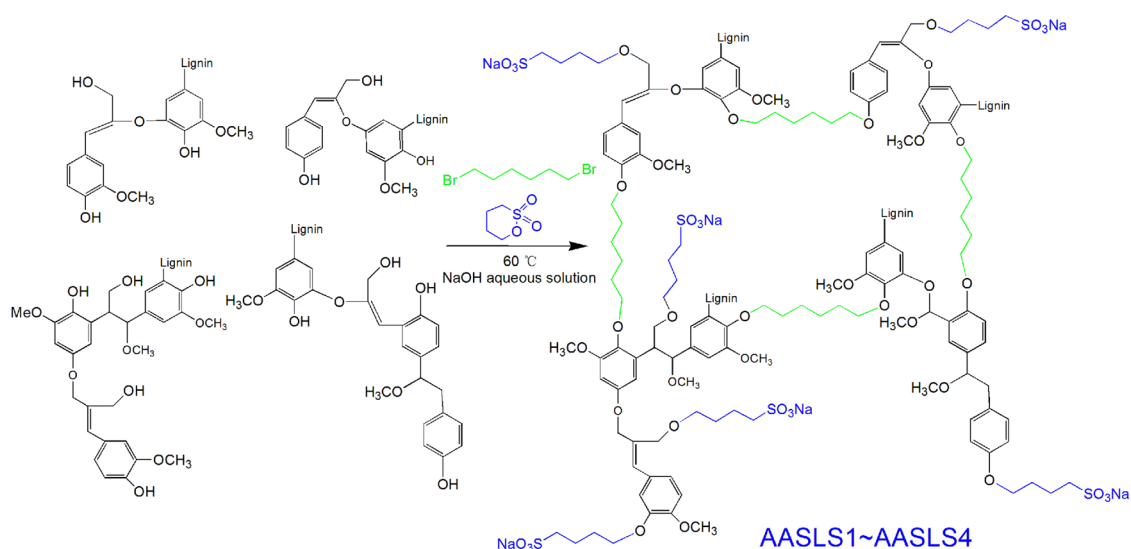


Figure 1. Synthetic route and reaction condition of AASLSs.

Table 1. Effects of 1,4-BS and $C_6H_{12}Br_2$ on the Functional Group Contents and Molecular Weight Distributions of AASLSs

samples	m(AL):m(1,4-BS):m($C_6H_{12}Br_2$)	–OH (mmol/g)	–SO ₃ (mmol/g)	M_w (Da)	M_n (Da)	PDI
AL	1:0:0	2.30	0.00	1900	1000	1.88
AASLS1	1:0.08:0.3	0.72	1.58	6840	2130	3.21
AASLS2	1:0.08:0.45	0.68	1.21	8070	4150	1.95
AASLS3	1:0.15:0.3	0.49	2.66	11850	3280	3.61
AASLS4	1:0.15:0.45	0.15	2.18	13120	4022	3.26
commercial LS		1.89	2.34	10060	2560	3.93

copolymerization and sulfonation have been investigated to make full use of alkali lignin and obtain highly valuable lignin-based anionic surfactants.^{7–9} Sulfonation modification was one of the most efficient ways to improve the properties of lignin because it could enhance surface activity and adsorption ability of alkali lignin, and has been extensively studied and reported.^{10,11}

However, modification methods should also be developed to increase M_w of LS, as M_w is an important factor to improve the dispersion ability. LS with appropriate M_w and sulfonation degree has been widely used in the dispersion of cement, coal-water slurry (CWS), TiO₂ and pesticides in our previous work.^{11–14} LS with high sulfonic degree and M_w exhibited better dispersion performances due to its good water-solubility, electrostatic repulsive forces and appropriate steric repulsive forces.^{12,13} LS with higher sulfonic group content and moderately high M_w exhibited positive effect on the dispersion performance in the system of particles.^{12–16}

To improve the sulfonation degree, we chose 1,4-butane sultone (1,4-BS) as a sulfonation reagent, which had long $-C_4H_8-SO_3H$ alkyl chains after a ring-opening reaction during sulfonation with lignin, and were different from conventional sulfonation reagents formaldehyde and Na₂SO₃. It was well-known that 1,4-butane sultone (1,4-BS) can react with phenolic hydroxyl groups and alcoholic hydroxyl groups to enhance the water-solubility of polymer. For example, a new sulfoalkyl ether cyclodextrin derivatives was synthesized by the way that 1,4-BS reacted with the hydroxyl group of cyclodextrins.¹⁷ In addition, catalyzed by NaOH, the starch could react with 1,4-BS in dimethyl sulfoxide (DMSO) to increase the water-solubility.¹⁸ However, to the best of our knowledge, efficient

sulfonation of lignin using 1,4-BS as a sulfonation reagent has been rarely reported, to date.

Herein, using alkali lignin (AL) as a raw material, we designed and successfully prepared a new family of lignosulfonates (LSs) containing alkyl chain bridging blocks ($-C_6H_{12}-$) and alkyl sulfonic acid groups ($-C_4H_8-SO_3$), which simultaneously increased the M_w and sulfonation degree to overcome the disadvantages in previously reported sulfonation methods. Catalyzed by NaOH, 1,4-BS will directly react with the phenolic hydroxyl groups and alcoholic hydroxyl of AL. However, $C_6H_{12}Br_2$ can react mainly with the phenolic hydroxyl groups of AL. As a result, we obtained AASLSs with the three-dimensional cross-linked structures as proposed in Figure 1. A sulfonation degree of higher than 2.0 mmol/g was achieved, and the M_w values were improved obviously by almost a factor of 7-fold. The combination of the three-dimensional network structure by alkyl bridging and long alkyl chain sulfonic acid groups played an important role to improve its dispersibility. Furthermore, the dispersion and adsorption of AASLSs in carbendazim suspension concentrates (SCs) was investigated and the effects of molecular weights and alkyl sulfonic acid groups were discussed in detail.

EXPERIMENTAL SECTION

Materials. The alkali lignin (AL) supplied by Shuntai Co. Ltd. (Hunan Province, China), was separated from pine wood pulping black liquor by acid precipitation with H₂SO₄. The commercial LS was supplied by Shixian Paper Mill (Jilin Province, China), and the parameters of structure characteristics are shown in Table 1. Commercially available reagents were used without purification, including 1,4-BS and 1,6-dibromohexane, which were purchased from Energy Chemical Co. Ltd. (Shanghai Province, China). Carbendazim, named *N*-(benzimidazolyl-2)methyl carbamate, was an

antifungal agent that had significant anticancer activity, and was provided as a light powder (50 μm) with a minimum purity of 97.8% from Frey Agrochemicals Co. Ltd. (Jiangsu Province, China).

Synthesis of AASLSs. The synthesis details for AASLSs are shown in Figure 1. AL (10 g) was dissolved in 50 mL of aqueous NaOH solution at pH 12. When the lignin was dissolved, different proportions of 1,4-BS, 1,6-dibromohexane and NaOH were fed at 70 $^{\circ}\text{C}$ and the reaction was stopped after stirring for 7 h. The mass ratio of AL:1,4-BS:1,6-dibromohexane was controlled as 1:0.08:0.3, 1:0.08:0.45, 1:0.15:0.3 and 1:0.15:0.45, and the products were named as AASLS1, AASLS2, AASLS3 and AASLS4, respectively. The products were dialyzed by a dialysis membrane (Special Products Laboratory, USA, MWCO of 1000 Da) to remove excessive starting materials and the hydrolyzed product of 1,4-BS and 1,6-dibromohexane, and concentrated by vacuum rotary evaporation. The purified products were further studied with the measurements of Fourier transform infrared (FTIR), ^1H NMR, functional group content, gel permeation chromatography (GPC) test, ζ -potential and dispersion properties.

Fourier Transform Infrared (FTIR) Spectroscopy. The FTIR of samples were recorded between 4000 and 400 cm^{-1} on an Auto system XL/I-series/Spectrum 2000 instrument (Thermo Nicolet Co., Madison, WI, USA). The measurement method was a potassium bromide pressed-disk technique. Squashes were prepared by mixing 200 mg of KBr with 2 mg of samples in an agate mortar. Then the squashes were tableted and tested for infrared spectrum analysis.

^1H NMR Spectra. The ^1H NMR spectra of samples were recorded with 30 mg of each sample dissolved in 0.5 mL of deuterium oxide (D_2O) at room temperature by a DRX-400 spectrometer (400 MHz ^1H NMR frequency, Bruker Co., Ettlingen, Germany). 1 mg of NaOH extra was added into the NMR tube to make AL dissolve in D_2O .

Functional Group Content. The phenolic hydroxyl groups (Ph-OH) content of the samples was measured by an FC method and the pH was 10. The sulfonic groups ($-\text{SO}_3\text{H}$) content of lignin samples was detected by an automatic potentiometric titrator (Type 809 Titrand, Metrohm Corp., Switzerland). With the titrant NaOH standard solution (0.05–0.10 mg/L), the sulfonic groups ($-\text{SO}_3\text{H}$) content was calculated:

$$S = C_{\text{NaOH}}V_{\text{NaOH}}/m \quad (1)$$

where S was the sulfonic group ($-\text{SO}_3\text{H}$) content (mmol/g), C_{NaOH} was the molar concentration of NaOH (mmol/L), V_{NaOH} was the volume of NaOH solution used (L) and m was the weight of lignin sample (g).

Gel Permeation Chromatography (GPC). The molecular weights of samples were determined by a Waters 1515 Isocratic HPLP pump (Waters, USA). The calibration standard was polystyrene sulfonate (PSS) with the M_w range from 2 to 100 kDa, using 0.10 mol/L NaNO_3 solution (pH = 10.4) as the eluent with a flow rate of 0.50 mL/min. All lignin samples were filtered by a 0.22 μm filter.

Preparation of Carbendazim SCs. Carbendazim SC were prepared by wet milling with a planetary ball mill (QM-3SP2, Nanjing University Instrument Factory, China). Carbendazim (45 g), dispersant (3 g) and Milli-Q water (52 g) were mixed and added to a grinding jar filled with zirconium balls (300 g) with a diameter of 10 mm. The rotation rate was set at 400 rpm and ran for 2 h to obtain target particle size lower than 5 μm . The carbendazim SCs (pH = 7) were obtained as per the procedure described above and their dispersion properties were tested.

Dispersibility Measurement of Carbendazim SC. After being sealed and placed in the oven (50 ± 1 $^{\circ}\text{C}$) for 14 days, the dispersibility and stability of carbendazim SC were tested. The particle size distribution of carbendazim SC was tested by an MS2000 laser diffraction particle size analyzer equipped with a Hydro SM wet dispersion unit (Malvern Instruments, U.K.). The dispersion medium was Milli-Q water, and the volume-based meandiameter was reported as the average particle size.

Suspensibility tests of carbendazim SC were performed according to Collaborative International Pesticides Analytical Council (CIPAC) Method MT161. The remaining tenth of the suspension was assayed

gravimetrically after it was dried, and the total suspensibility was calculated. Each sample was measured in triplicate.

Rheological Measurement of Carbendazim SC. After being sealed and placed in the oven (50 ± 1 $^{\circ}\text{C}$) for 14 days, the rheological measurement of carbendazim SC with different dispersants was performed employing a rheometer (Haake MARS III, Thermo Fisher Scientific, USA) equipped with a cylindrical rotor of CC26 Ti at (25 ± 0.1 $^{\circ}\text{C}$). The shear rate range was 0–200 s^{-1} . The viscosity value was recorded at a shear rate 100 s^{-1} of carbendazim SC. Each sample was measured in duplicate.

Determination of Adsorption Amount on the Surface of Carbendazim Particles. The adsorption amounts of different dispersants on carbendazim surface were determined as the difference between the concentrations of dispersants solutions before and after adsorption equilibrium. The measurement procedures were conducted as following steps. 0.5 g of carbendazim powder was placed in a beaker and 50 mL of samples solution with a given concentration (0.0–1.6 g/L) were added into it, the mixture was shaken for 6 h at 30 $^{\circ}\text{C}$. After 12 h of equilibration, the samples were centrifuged at 10000 rpm for 10 min. Then concentration of the supernatant was determined using a UV/vis spectrometer (UV-2450, Shimadzu Corp., Japan) at the wavelength of 280 nm at the value of pH 7.0 at room temperature. The adsorption amount of samples on the carbendazim surface was expressed as

$$\Gamma(\text{mg/g}) = (C_0 - C_t + C_{\text{control}})V/m \quad (2)$$

where Γ (mg/g) is the mass of samples adsorbed on the carbendazim surface, C_0 (g/L) is the mass concentration of original samples fraction solution, C_t (g/L) is the mass concentration of adsorption equilibrium samples solution, C_{control} (g/L) is the mass concentration of control sample, V (mL) is the total volume of solution and m (g) is the mass of carbendazim.

ζ -Potential Measurement. The ζ -potential of carbendazim particles were determined as a function of concentration of different AASLS3, AASLS4 and commercial LS solutions. The aqueous suspensions containing 0.5 wt % carbendazim powder and different samples dosages were prepared using the same method for carbendazim SC described above. The ζ -potential measurement was conducted by an apparatus from Zeta PALS. The ζ -potential analyzer (Brookhaven, Corp., USA) was at room temperature and the pH was 7.0. Each sample was determined for 10 times, and the average value was obtained.

RESULTS AND DISCUSSION

FTIR Analyses. A comparison of the FTIR spectra of AL with the AASLSs clearly revealed differences in the frequency range and fingerprint region (Figure 2a), which came from the successful introduction of alkyl chain and alkyl sulfonic acid groups into AL. Compared with AL, AASLSs had strong absorbance of the areas of S—O and S=O stretching at 1042 and 653 cm^{-1} (A_{1042} , A_{653}). It reflected that a lot of sulfonic groups had been introduced in AASLSs by alkyl sulfonic. Vibrations at 1202 cm^{-1} (A_{1202}) was attributed to the phenyl C—O—C ether bond stretching, which clearly indicated the introduction of alkyl chain. AASLSs had strong absorbance of the areas of methylene stretching vibrations from alkyl chain at 2935 cm^{-1} (A_{2935}), which reflected efficient reaction of alkyl chains with alkali lignin. Additionally, AASLSs had weak absorbance of the areas of phenolic group stretching at 3444 cm^{-1} (A_{3444}), which indicated that alkyl groups were bonded with the phenolic hydroxyl groups.

^1H NMR Analyses. For the in-depth elucidation of structural features of AASLSs, the ^1H NMR spectra of AL and AASLSs with quantitative samples in D_2O are presented in Figure 2b. Compared with AL, the dramatic increase of aliphatic proton signals such as 2.76, 2.92 and 3.51 ppm came from the efficient coupling of $-\text{C}_4\text{H}_8-\text{SO}_3\text{H}$ groups. Aliphatic

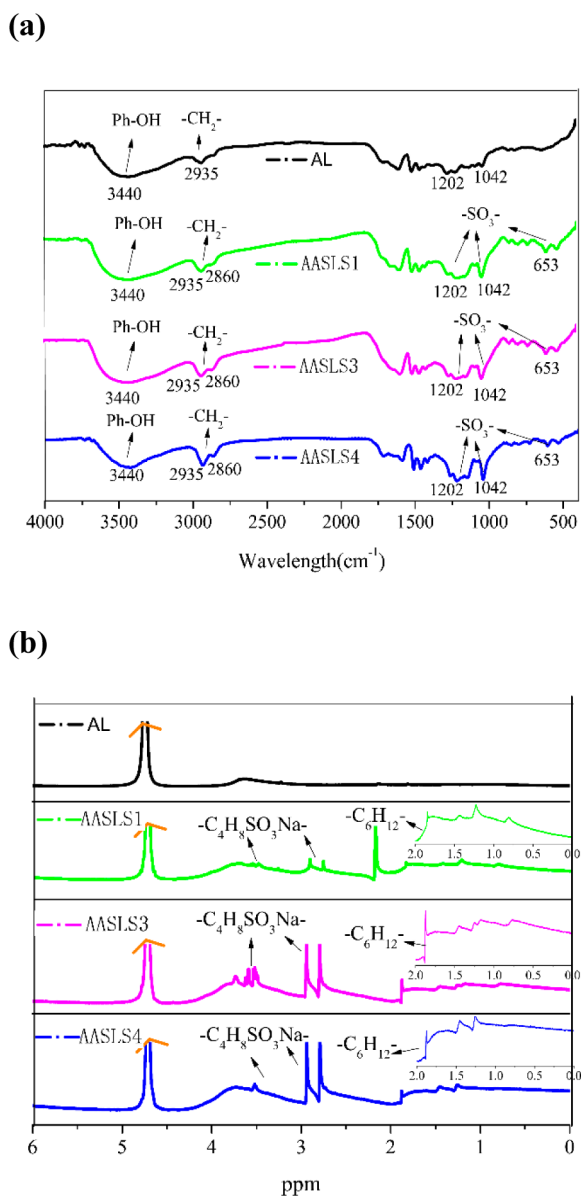


Figure 2. Spectroscopic analyses of AL and AASLSs: (a) FTIR spectra, (b) ^1H NMR spectra in D_2O .

proton signals at 1.24, 1.41 and 1.71 ppm were ascribed to $-\text{C}_6\text{H}_{12}-$ groups. All the signal intensities of the aliphatic protons exhibited significantly increase due to both the alkyl sulfonic acid groups and alkyl chain of AASLSs.

Functional Group Content Analyses. The content of sulfonic group and phenolic hydroxyl groups of AASLSs were analyzed, and the results are listed in Table 1. There was a direct relationship between the mass ratio of $m(\text{AL}):m(1,4\text{-BS}):m(\text{C}_6\text{H}_{12}\text{Br}_2)$ and consumption of phenolic hydroxyl groups and sulfonation degrees of AL. With the increasing amounts of 1,4-BS and $\text{C}_6\text{H}_{12}\text{Br}_2$, the content of phenolic hydroxyl groups contents of AASLSs decreased significantly, from 2.30 to 0.15 mmol/g, which showed that phenolic hydroxyl groups were one of the main reactive sites.

Meanwhile, sulfonation was also one of the dominant factors for the decrease of phenolic hydroxyl groups. The sulfonation degree of AASLS1 increased obviously, up to 1.58 mmol/g, when the $m(\text{AL}):m(1,4\text{-BS})$ was 1:0.08 only, and the content of phenolic hydroxyl groups decreased from 2.30 to 0.72

mmol/g. With the same amount of 1,4-BS and an increased amount of $\text{C}_6\text{H}_{12}\text{Br}_2$, such as $m(\text{AL}):m(1,4\text{-BS}):m(\text{C}_6\text{H}_{12}\text{Br}_2)$ from 1:0.08:0.3 to 1:0.08:0.45, the sulfonation degree decreased to 1.21 mmol/g. It could be explained by the competitive reaction of $\text{C}_6\text{H}_{12}\text{Br}_2$ with 1,4-BS on the phenolic hydroxyl groups of AL. The sulfonation degree of AASLS3 increased significantly by increasing the $m(1,4\text{-BS})$ and was up to 2.66 mmol/g when $m(\text{AL}):m(1,4\text{-BS})$ was 1:0.15, which was even higher than that of graft-sulfonation by acetone and formaldehyde (2.48 mmol/g).

Gel Permeation Chromatography (GPC) Analyses. The weight-average molecular weights (M_w), the numerical-average molecular weights (M_n) and the polydispersity (M_w/M_n) of the AASLSs, AL and commercial LS are listed in Table 1. The molecular weight distribution of AASLSs and LS are shown in Figure 3. The molecular weights distribution of AASLSs are appropriately narrow from Figure 3.

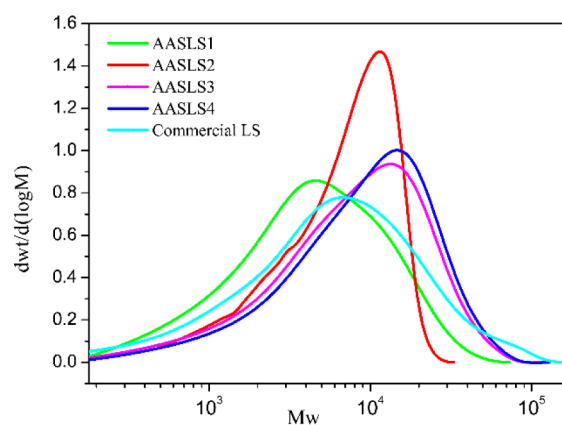


Figure 3. Effect of 1,4-BS and 1,6-dibromohexane on M_w distributions of AASLSs.

As shown in Table 1, with increased the proportion of $\text{C}_6\text{H}_{12}\text{Br}_2$, the M_w of AASLSs had increased step by step. When AL was coupled by increasing the amount of $\text{C}_6\text{H}_{12}\text{Br}_2$, a more extensive increase of M_w was observed. On one hand, 1,4-BS enhanced the water-solubility of AASLSs, which was good to the further M_w increase of AASLSs without cross-linking. On the other hand, 1,4-BS and $\text{C}_6\text{H}_{12}\text{Br}_2$ competed to react with the phenolic hydroxyl groups, so excessive 1,4-BS might not be conducive to the further reaction between $\text{C}_6\text{H}_{12}\text{Br}_2$ and the phenolic hydroxyl groups. The effects of $m(1,4\text{-BS})$ and $m(\text{C}_6\text{H}_{12}\text{Br}_2)$ on M_w are listed in Table 1.

The M_w of AASLS1 increased by a factor of 3.6-fold for AL when the mass ratio of $m(\text{AL}):m(1,4\text{-BS}):m(\text{C}_6\text{H}_{12}\text{Br}_2)$ is only 1:0.08:0.3. At the same amount of $\text{C}_6\text{H}_{12}\text{Br}_2$, the M_w of AASLSs increased when the amount of 1,4-BS was increased, such as $m(\text{AL}):m(1,4\text{-BS}):m(\text{C}_6\text{H}_{12}\text{Br}_2)$ from 1:0.08:0.3 to 1:0.15:0.3. It showed that an increase of 1,4-BS was conducive for the alkyl chain coupling polymerization of AASLSs due to the enhanced water-solubility, which promoted the reaction between $\text{C}_6\text{H}_{12}\text{Br}_2$ and phenolic hydroxyl groups. The M_w increased with increase of $m(\text{C}_6\text{H}_{12}\text{Br}_2)$ with the same amount of $m(1,4\text{-BS})$. As shown in Table 1, the M_w of AASLS4 increased to 13 120 Da when the ratio of $m(\text{AL}):m(\text{C}_6\text{H}_{12}\text{Br}_2)$ increased to 1:0.45. It showed that this was an efficient approach to increase the M_w of AL using $\text{C}_6\text{H}_{12}\text{Br}_2$ to polymerize lignin molecules. Alkylation on phenol hydroxyl groups is a widely studied modification way for lignin-based

Table 2. Dispersion Properties of Carbendazim SC with Different Dispersants after Hot Storage at 50 °C for 14 days^a

dispersant	dosage of dispersant (%)	SC (%)	partical size (μm)	suspensibility (%)	apparent viscosity (mPa·s)
AASLS1	3	42.44	1.903		3.54
AASLS2	3	43.13	1.732		3.83
AASLS3	3	48.28	1.487	99.38 \pm 0.32	87.63
AASLS4	3	50.44	1.479	99.56 \pm 0.19	73.01
commercial LS	3	47.56	9.273	86.74 \pm 0.52	159.34

^aThe carbendazim SC prepared with AASLS1 or AASLS2 after hot storage at 50 °C for 14 days was stratified, and carbendazim settled to the bottom, so the suspensibilities of the two samples were not tested.

polymers, but it usually decreases the water-solubility of LS, which limits its application in an aqueous solution system.^{19,20} In our study, we used alkyl chains to couple the LS molecules and obtained a polymer with acceptable solubility.

Dispersion Property of Carbendazim SC. The main dosage forms of carbendazim were wetttable powders, water dispersible granules and suspension concentrates. In this study, AL, AASLSs and commercial LS were selected to prepared carbendazim SC. When preparing 45% carbendazim SC with 3% dispersants, it was found that carbendazim SC prepared with AASLSs or commercial LS were capable to flowing, but carbendazim SC prepared with AL did not disperse and flow. So, AL could not be used as the dispersant of the carbendazim SC. Carbendazim SC prepared with AASLS1 or AASLS2 was difficult to flow and stratified. It can be explained with the following aspects: With relatively low M_w and sulfonic acid group content of AASLS1 and AASLS2, the steric hindrance and electrostatic repulsion between the carbendazim particles and AASLS1 or AASLS2 were weak and easy to aggregate. With appropriately high M_w and sulfonic acid group content, AASLS3, AASLS4 or commercial LS will adsorb on the particle surface and will weaken the aggregation of particles through the electrostatic repulsive forces and improve its wettability and dispersibility. However, AL has poor water-solubility and low M_w , which is not conducive to adsorb on the particle.

The average particle sizes and suspensibility of carbendazim SC prepared with AASLS3, AASLS4 or commercial LS are shown in Table 2. The average particle sizes of carbendazim SC prepared with the first two were below 1.5 μm , but with commercial LS was up to 9.273 μm . The particle size distributions of carbendazim particles with AASLSs or commercial LS solutions were shown in Figure 4a. AASLS3 or AASLS4 illustrated the standard normal distributions, whereas commercial LS presented similar bimodal distributions with a large portion of particles whose diameters were even larger than 100 μm . After hot storage at 50 °C for 14 days, the suspensibilities of carbendazim SC prepared with AASLS3 or AASLS4 showed no change, which were 99.38% and 99.56%, respectively, were higher than that of commercial LS, which was 86.74% only, indicating the AASLS3 and AASLS4 showed better dispersion performance for carbendazim SC than commercial LS.

Rheological Behavior of Carbendazim SC. Carbendazim SC prepared with AL, AASLS1 or AASLS2 showed bad dispersion performance, so the viscosity curve of them was not tested in our study. The viscosity curve and flow curve of carbendazim SC prepared with AASLS3, AASLS4 or commercial LS are presented in Figure 4b. As Figure 4b shows, the shear viscosity of carbendazim SC decreased by increasing the shear rate until a steady state was approached and showed a typical shear thinning behavior. The apparent viscosity of carbendazim SC with AASLS3 or AASLS4 was

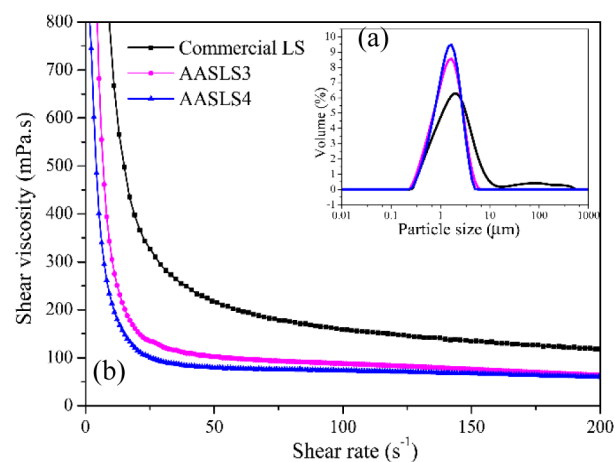


Figure 4. (a) Particle size distributions of carbendazim particles with AASLSs and commercial LS solutions. (b) Shear viscosity curve of 45% carbendazim SC prepared with 3% AASLSs and commercial LS.

87.64 and 73.01 mPa·s only, which was less than that with commercial LS, showing good dispersion properties and utilization potentiality for carbendazim SC. The alkyl chain cross-linked structure of AASLS3 and AASLS4 flipped to make the long alkyl chain-containing sulfonic acid bared and open to the water, then a water film was formed, which made the apparent viscosity of carbendazim SC with AASLS3 or AASLS4 lower.

Adsorption Amount on the Surface of Carbendazim Particles. The dispersive ability of AASLS3 and AASLS4 was determined by the adsorption on carbendazim particles. AASLS3 and AASLS4 could improve the electronegativity of particle by adsorbing on the particles surface to form steric effect and electrostatic repulsion among particles and keep suspensions stability. The adsorption amount on the surface of carbendazim particles is shown in Figure 5.

The adsorption amounts of AASLS3 and AASLS4 on the carbendazim particles were appreciably higher than that of the commercial LS below the concentration of 0.8 g/L. Moreover, AASLS3 and AASLS4 showed much more adsorption amounts, which were up to 25.44 and 28.13 mg/g, much higher than 13.59 mg/g of commercial LS at a high concentration of 1.2 g/L. It was clear that the adsorption amount of AASLS4 on the carbendazim particles was more than that of AASLS3 at each concentration. The results can be explained by the difference of the M_w of the dispersants. With the three-dimensional network structure, the M_w of AASLS4 was higher than that of AASLS3 and it was more beneficial for AASLS4 to disperse carbendazim particles. Similarly, the M_w values of AASLS3 and AASLS4 were larger than that of commercial LS, so commercial LS showed a weak adsorption force on the carbendazim particles surface. AASLS4 showed a higher adsorption amount than those of the

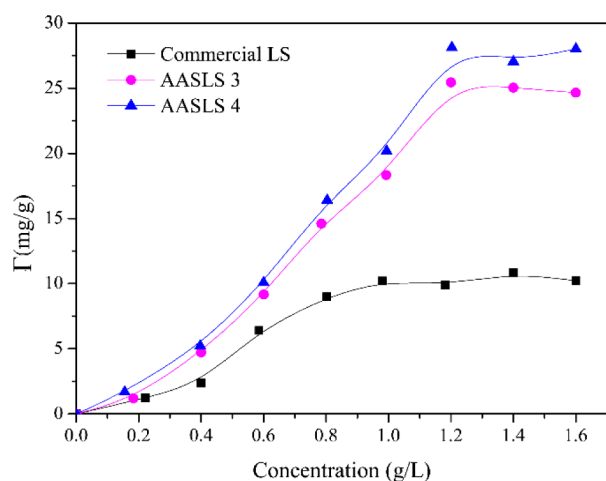


Figure 5. Adsorption isotherms of AASLSs and commercial LS on carbendazim powder surface.

other two at each concentration. Moreover, compared with commercial LS, the alkyl bridging three-dimensional network structures of AASLS3 and AASLS4 also made a great contribution to the efficient adsorption on the carbendazim particles.

Modeling of Adsorption Isotherms. The Langmuir adsorption model, which is often used to describe the physical mechanism of the adsorption, was also used in our work. The experimental data for AASLS3, AASLS4 and commercial LS adsorption on carbendazim were calculated by using the linear formula of the Langmuir adsorption model:

$$\Gamma^{-1} = (\Gamma_{\max}K)^{-1} \times C^{-1} + \Gamma_{\max}^{-1} \quad (3)$$

where C is the adsorbate equilibrium concentration, Γ_{\max} is the theoretical monolayer capacity of adsorption amount on the adsorbent surface, Γ is the experimental adsorption amount and K is the Langmuir adsorption isotherm constant (L/g).

The linear fitting of the experimental adsorption data by the Langmuir adsorption model is shown in Figure 6, and the fitting results are shown in Table 3. As presented in Table 3, R^2 is the correlation coefficient, which all were all above 0.9. Thus, the significant adsorption process of commercial LS, AASLS3

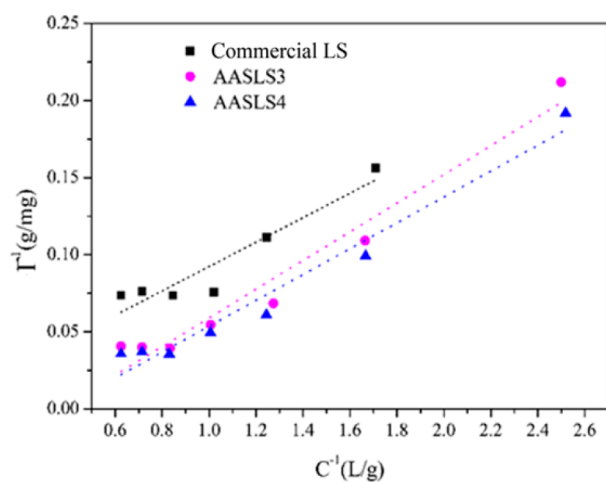


Figure 6. Fitting of experimental adsorption data with Langmuir adsorption model.

Table 3. Langmuir Fitting Parameters of the Adsorption Isotherms

lignosulfonate samples	Γ_{\max} (mg/g)	K (L/g)	R^2
commercial LS	13.89	1.92	0.9067
AASLS3	35.71	6.53	0.9527
AASLS4	37.04	6.42	0.9594

and AASLS4 were characteristic to the Langmuir adsorption model. Moreover, compared with commercial LS, AASLS3 and AASLS4 showed a higher value of Γ_{\max} which indicated that they had a higher adsorption capacity on the carbendazim surface due to the alkyl chain cross-linked structure and long alkyl chain-containing sulfonic acid groups. It was further confirmed the contribution of the three-dimensional network structure by alkyl bridging of AASLS3 and AASLS4, which made the high adsorption amount on the carbendazim particles.

ζ -Potential of Carbendazim Particles. The effects of AASLS3, AASLS4 and commercial LS on the ζ -potential of carbendazim particles were investigated, and the results are shown in Figure 7. The ζ -potential of carbendazim particles is very important to affect the stability of a carbendazim suspension.

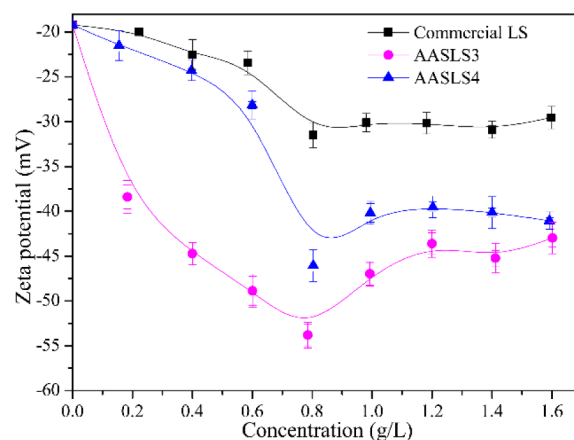


Figure 7. Effect of AASLSs and commercial LS concentrations on ζ -potentials.

As shown in Figure 7, the ζ -potential absolute value of carbendazim increased first and then decreased when the concentrations of AASLS3, AASLS4 and commercial LS were increased. AASLS3 reduced the ζ -potential most efficiently among the three dispersants at each concentration. From Table 1, the sulfonic degree of AASLS3 was higher than those of commercial LS and AASLS4, which was the reason for that AASLS3 showed the lowest ζ -potential among them. The long alkyl chains of AASLS4 may twist and make parts of the alkyl sulfonic groups naked, contributing to the ζ -potential-improving effects, which were better than those of commercial LS.

At the concentration of 0.8 g/L, the ζ -potential absolute value of carbendazim reached the maximum of AASLS3 (-53.81 mV), AASLS4 (-46.04 mV). However, the amount of adsorption on the carbendazim particles in the concentration did not reach a maximum, but with the increasing trend by increasing concentrations. It might be attributed to soft alkyl sulfonic groups entwined and parts of sulfonic groups wrapped in the molecular structure of the three-dimensional network.

CONCLUSIONS

Highly water-soluble alkyl chain cross-linked sulfobutylated lignosulfonates (AASLSs) with a three-dimensional network structure and naked alkyl sulfonic acid groups were readily prepared by using 1,4-BS and $C_6H_{12}Br_2$ in one step, which simultaneously improved the sulfonation degree and molecular weight. AASLSs were systematically investigated by functional group content, GPC and 1H NMR, IR to study the fundamental properties. Moreover, in carbendazim suspension concentrate, AASLS4 showed a highly improved dispersion property such as suspensibility of 99% in 45% carbendazim SC after hot storage at 50 °C for 14 days. The adsorption isotherms and ζ -potential of AASLSs on carbendazim SC particles were studied to reveal the dispersion mechanism. The alkyl chain cross-linked structure and long alkyl chain-containing sulfonic acid groups contribute to the excellent dispersion properties. Our modification approach for lignin might provide a novel concept and prospective avenue for the design of efficient dispersant, which exhibited potential applications in future. This modification approach also provided new concept and promising avenue for the design of efficient dispersants.

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Notes

The authors declare no competing financial interest.

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