

Article

Synthesis of a Ternary Polysulfonate Dispersant and Its Suspension Performance

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Abstract: Allyl alcohol polyoxyethylene ether (APEG), hydroxyethyl methacrylate (HEMA) and styrene sodium sulfonate (SSS) were used as monomers to obtain a APEG-HEMA-SSS comb-like polymer, which was employed as the polysulfonate dispersant for pendimethalin suspensions in this paper. The comb-like polymer has an anionic polysulfonate backbone, hydrophilic APEG side chains and sulfonic acid groups, which makes the dispersant absorb easily on the surface of pendimethalin particles. The polysulfonate dispersant with good dispersion performance was screened out by orthogonal experiments. The surface tension, zeta potential, particle size and dynamic contact angle of the pendimethalin suspension with APEG-HEMA-SSS as dispersant were investigated. The dispersant improves the dispersibility and wettability of the pendimethalin suspension observably.

Keywords: polysulfonate dispersant; suspension; pendimethalin; dispersion properties; environmental material



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1. Introduction

A dispersant refers to a type of surfactant which can stably disperse solids or liquids in an incompatible medium through a certain charge repulsion principle or polymer steric hindrance effect. Dispersion for lipophilic materials in water is an important part of the production process of many materials, and the dispersant is one of the important components of many environmental materials. Pendimethalin (as show in Figure 1) is a widely used aniline selective herbicide with long-lasting efficacy. However, in practice, it has been found that high-content pendimethalin suspension has bad stability during storage, and it is prone to problems such as thickening, deposition, agglomeration, water-separation and so on, thereby affecting the efficacy of the pendimethalin suspension, and the rational use of highly active dispersants are an effective way to improve the stability of high content pendimethalin suspension [1]. In this work, pendimethalin was used as a model compound to test the suspension performance of the self-synthesized dispersant.

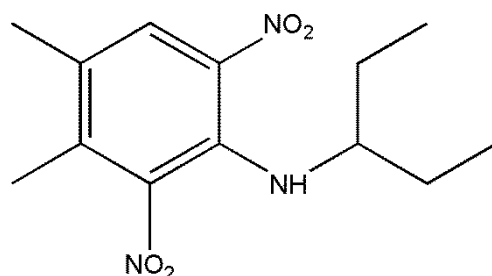


Figure 1. Pendimethalin structure.

At present, studies on the dispersing effect of a high concentration of pendimethalin suspension are still relatively few. The traditional small molecule dispersants can disperse

the pendimethalin, but it is easy to desorb from the surface of the granules to cause the granules to re-aggregate. Polysulfonate dispersants are anionic dispersants, which can form a hydrogen bond with some functional groups on the surface of granules. The dispersion of granules by steric hindrance and electrostatic repulsion can effectively compensate for the deficiency of the small molecule dispersant and improve the stability of suspensions [2,3]. Polysulfonate dispersants have a special comb-like carbon skeleton structure and strong affinity on the crystal surface to inhibit the growth of the crystal. This special structure guarantees a good dispersion property [4]. The improved molecular structure helps to maximize the target performance and meet the specific requirements of different applications. At present, many scholars have studied the relationship between the structure and properties of polysulfonate dispersants [5,6]. Wang et al. studied the effect of different lengths of solvation chains on dispersion properties [7]. Ran et al. found that medium-length side chains have the best dispersion properties for Al_2O_3 suspensions [8]. Omid Akhlaghi et al. studied the effect of polysulfonate dispersants on the rheological properties and stability properties of Al_2O_3 suspensions [9]. Xing Wen et al. prepared a comb polysulfonate dispersant for imidacloprid suspensions, and found that excessive dispersant will affect the stability of the suspension system [10]. Sun Tingting et al. prepared polystyrene-maleic anhydride sodium sulfonate copolymers with different molecular weights and studied the effects on the average particle size, Zeta potential and pH of 20% diflufenbuzon suspension [11]. Wang Lidong et al. synthesized acrylic acid (AA)-sodium styrene sulfonate (SSS)-maleic anhydride (MA) dispersant, and studied the dispersion effect on inorganic BaSO_4 and organic pesticide imidacloprid [12]. Lots of research has shown it is very important to develop high-performance dispersants in new materials [13–16].

In this work, Allyl alcohol polyoxyethylene ether (APEG), hydroxyethyl methacrylate (HEMA) and styrene sodium sulfonate (SSS) were used as monomers to obtain a APEG-HEMA-SSS comb-like polyme. a novel polysulfonate comb-like polymer was successfully employed as the dispersant for pendimethalin suspensions. The structure of the dispersant introduced various functional groups of ester group, hydroxyl group, and sulfonic acid group. The polysulfonate dispersant structure contained a lipophilic group such as a benzene ring and a methyl group which can be adsorbed on the surface of the pendimethalin particles well, the polyoxyethylene ether chain can play a steric hindrance, and the sulfonic acid ions supply the electrostatic repulsion. The separation effect of pendimethalin granules and the physicochemical properties of synthetic dispersants were tested. This work provides valuable theoretical and experimental support for the application of polysulfonate dispersants in suspensions.

2. Materials and Experiments

2.1. Materials

Styrene sodium sulfonate, anhydrous ethanol and sodium hydroxide of analytical grades and tetrahydrofuran with chromatographic purity were purchased from Aladdin Reagent Co. (Shanghai, China). Methyl allyl alcohol polyoxyethylene ether (APEG) and hydroxyethyl methacrylate with industrial grade were applied by Jining huakai resin Co. Ltd. (Jining, China). Ammonium persulfate with analytical grades was purchased from Wuxi prospect chemical reagent Co. Ltd. (Wuxi, China). Dow corning 1410 with industrial grade was purchased from Guangzhou zhongwan new material Co. Ltd. (Guangzhou, China).

2.2. Experiments

2.2.1. Synthesis of Polysulfonate Dispersant

Water, ethanol, hydroxyethyl methacrylate and sodium p-styrene sulfonate were added into a flask. Methacryl polyoxyethylene ether and ammonium persulfate solution were added. The reactions were protected with nitrogen and the temperature kept at 70 °C. The products were purified by dialysis bag. Terpolymers were obtained after being dried in a vacuum freeze dryer [2,5,6]. Figure 2 shows the synthetic route of the polysulfonate

dispersant. The structure of the polysulfonate dispersants was analyzed by Fourier infrared spectroscopy and ^1H NMR.

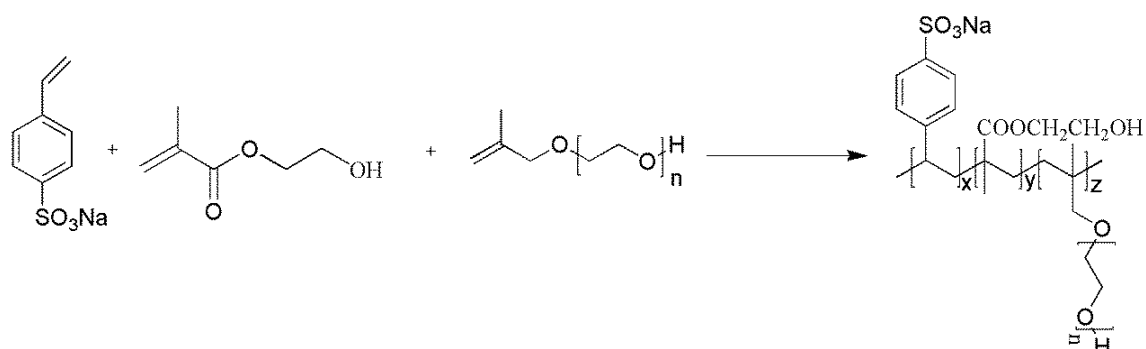


Figure 2. Synthetic route of the polysulfonate dispersant.

2.2.2. Characterization

The molecular structure was characterized by Fourier transform infrared spectroscopy (FTIR) and ^1H NMR spectroscopy. The average molecular weights of the polysulfonate dispersants were determined by gel permeation chromatography (GPC). The mobile phase consisted of tetrahydrofuran, and the standard sample was polystyrene.

The suspension rate was measured by the following steps: (1) 1.00 g polysulfonate dispersant was added to a 250 mL stopper bottle, and 10 mL deionized water was used to dissolve the polymer; (2) 2.50 g pendimethalin fine powder and 250.00 mL water were mixed into the bottle, and the bottle was placed vertically in water at 30 °C for 30 min; (3) 225.00 mL of the suspension was removed, and the remaining 25.00 mL of the suspension was transferred to a Petri dish, dried to constant weight, and the mass M of the residue was recorded to calculate the suspension ratio according to the Equation (1) [2]. The total mass of the dispersant and the pendimethalin granules was 3.50 g.

$$\text{Suspension rate} = \frac{3.50 - M}{3.50} \times \frac{10}{9} \times 100\% \quad (1)$$

Flow point was used to judge the suspension performance of the dispersants. pendimethalin powder was added into a beaker, and 5% polysulfonate surfactant aqueous solution was added drop-wise. The ratio of the quality of the dispersant aqueous solution and the quality of the dimethylpultomy medicine is a flow point. The flow point was measured repeatedly three times, and the average flow point value was calculated. The surface tension of the polysulfonate dispersant solution with different mass concentrations was measured at 25 °C. The surface tension and concentration curves were used to obtain the critical micelle concentration (CMC).

Zeta potential of pendimethalin suspensions were tested, based on the 35% pendimethalin suspension with KCl solution. Then zeta potential of pendimethalin suspensions was determined at 20 °C.

The particle size of pendimethalin suspension was measured before and after the heat storage by a scattering photometer analyzer (Mastersizer2000, Malvern, UK). The storage condition was set at (54 ± 2) °C for 14 days.

3. Results and Discussion

3.1. Optimization of Synthesis Conditions

The synthesis conditions were screened by an orthogonal method, as Tables 1 and 2 shown. The experimental results showed that the sequence of factors affecting the flow point of pendimethalin particles was: HEMA:SSS molar ratio > temperature > initiator > APEG:SSS molar ratio > reaction time. Among all the experiments, the 12th showed the best dispersion effect of pendimethalin and the flow point was 1.5413.

Table 1. Levels and factors of $L_{16}(4^5)$ orthogonal experiments.

	HEMA:SSS	APEG:SSS	Initiator/%	Temp/°C	Time/h
1	3.2	1.2	4	70	2
2	6.3	1.0	8	80	3
3	9.5	0.8	10	90	4
4	12.7	0.6	12	100	5

Table 2. The results of $L_{16}(4^5)$ orthogonal experiments.

Factors	1	2	3	4	5	Flow Point
	HEMA:SSS	APEG:SSS	Initiator	Temp	Time	
1	1	1	1	1	1	1.9510
2	1	2	2	2	2	2.1256
3	1	3	3	3	3	2.0836
4	1	4	4	4	4	1.9761
5	2	1	2	3	4	2.0732
6	2	2	1	4	3	2.1373
7	2	3	4	1	2	1.7619
8	2	4	3	2	1	1.9325
9	3	1	3	4	2	2.0212
10	3	2	4	3	1	1.5818
11	3	3	1	2	4	1.7815
12	3	4	2	1	3	1.5413
13	4	1	4	2	3	1.953
14	4	2	3	1	4	1.7843
15	4	3	2	4	1	2.1013
16	4	4	1	3	2	2.0932
I	2.034	2.000	1.991	1.760	1.892	
II	1.976	1.907	1.960	1.948	2.000	
III	1.731	1.932	1.955	1.958	1.929	
IV	1.983	1.886	1.818	2.059	1.904	
R	0.303	0.114	0.173	0.299	0.108	

The dispersion stability of the pendimethalin suspension depended on the structure and charge amount of the dispersant. The structure of the polysulfonate dispersant can be divided into two parts: one part is an anchor group, which can be closely adsorbed on the surface of the pendimethalin particles to prevent desorption between the dispersant and the particles; the other part is the solvation chain, which has a good compatibility with the dispersion medium [14]. The dispersion effect of pendimethalin particles depends largely on the electrostatic interaction and steric hindrance from the dispersant. There are strong hydrogen interactions between the $-NH-$ polar groups of pendimethalin and the polar groups of $-C=O$ of the polysulfonate dispersant. Pendimethalin is hydrophobic, and the aromatic-ring-containing polysulfonate dispersant is adsorbed via hydrophobic interaction or $\pi-\pi$ stacking. The sulfonic acid group of the polysulfonate dispersant is negatively charged, and provides an electrostatic effect. The PEO side chain forms a hydrophilic solvent layer, and provides the space steric effect.

3.2. Characterization and Performance

3.2.1. Fourier Transform Infrared (FTIR) Analysis

In Figure 3, 3490 cm^{-1} is the $-OH$ stretching vibration, 2889 cm^{-1} is the $-CH$ stretching vibration, 1738 cm^{-1} ester $C=O$ stretching vibration, 1038 cm^{-1} is the $S=O$ asymmetric stretching vibration in the sulfonic acid group, and the special absorption peaks of the ether bond of $1130/948/848\text{ cm}^{-1}$ are the fingerprint area of the benzene ring in sodium p-benzenesulfonate. The synthesized polysulfonate dispersant has no absorption peak in the region of $1600\sim 1660\text{ cm}^{-1}$ ($C=C$ stretch vibration), which indicates that the $C=C$ double

bond disappears, and the monomers undergo polymerization to form the terpolymer polysulfonate dispersant.

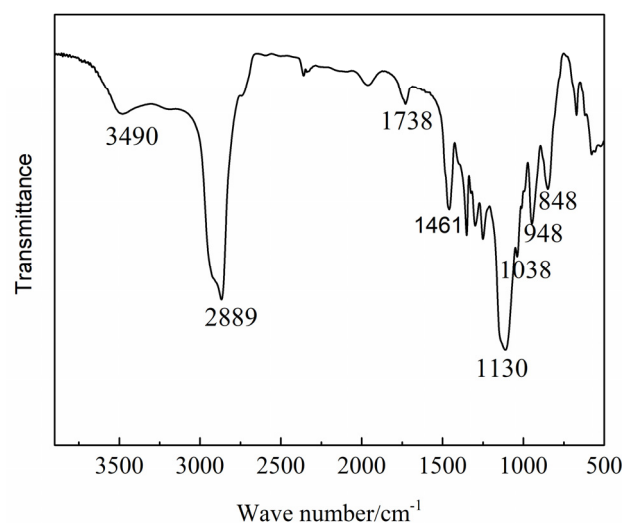


Figure 3. Infrared spectrum of the polysulfonate dispersant.

3.2.2. ¹H Nuclear Magnetic Resonance (NMR) Analysis

As demonstrated in Figure 4, the 2.52 ppm chemical shift comes from DMSO solvent. For APEG-HEMA-SSS, 7.0~7.8 ppm were the chemical shift of H protons in the benzene ring. 3.41~3.73 and 3.38 ppm were the chemical shift of H protons from $-\text{OCH}_2\text{CH}_2$ and $-\text{CH}_2$ attached to the ether bonds; 4.07 ppm was the chemical shift of H protons of $-\text{CH}_2\text{CH}_2$ attached to the ester bonds. In the main chain, $-\text{CH}_3$, $-\text{CH}_2$ and $-\text{CH}$ connected to the side chains gave ¹H NMR signals at 1.22~1.33 ppm and 1.42~1.56 ppm.

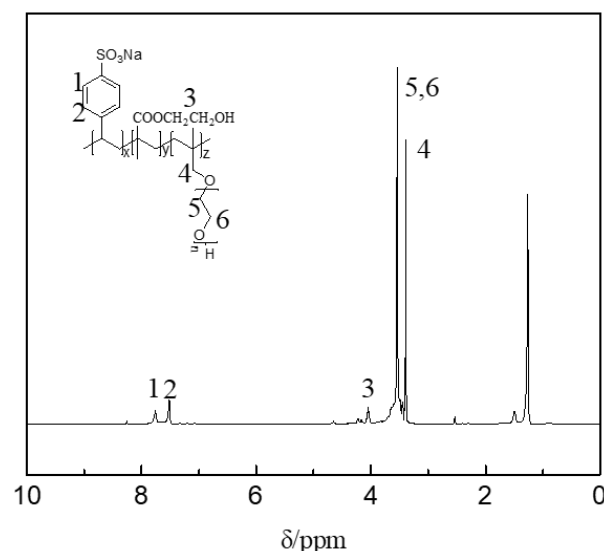


Figure 4. ¹H nuclear magnetic resonance (NMR) spectrum of the polysulfonate dispersant.

3.2.3. Gel Permeation Chromatography (GPC) Analysis

The molecular weight of terpolymers was determined by GPC. Calibration was carried out with polystyrene standards. The molecular weight and its distribution of polysulfonate dispersant are shown in Table 3 and Figure 5. Isopropyl alcohol and ethanol have the heat transfer and chain transfer function to synthesize low molecular weight polyacrylamide [17]. Therefore, in this work ethanol is a heat transfer solvent and a precipitant of a polysulfonate copolymer. Changing the solvent ratio can affect the solubility parameter

between the copolymer and the solvent, then affects the molecular weight of the polysulfonate dispersant. The GPC results show that the molecular weight distribution of the polysulfonate dispersant is narrow.

Table 3. Molecular weight distribution of the polysulfonate dispersants.

Retention Time (min)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	M_{z+1} (g/mol)	Polydispersity Index
14.12	10617	13404	13982	15277	1.26

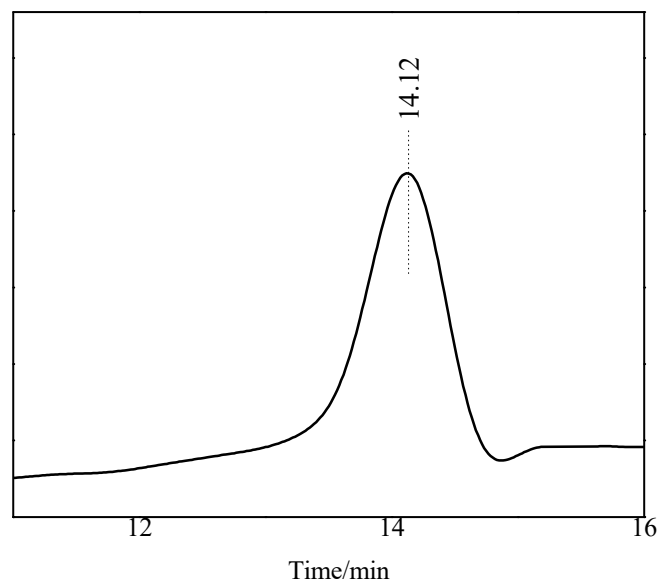


Figure 5. Gel permeation chromatography (GPC) results of the polysulfonate dispersant.

3.2.4. Suspension Performance

Figure 6 shows the difference in the suspension rate and flow point of the polysulfonate dispersant and APEG. It can be seen from Figure 6 that after adding the same amount of polysulfonate dispersant or APEG, the polysulfonate dispersant can make the suspension rate of pendimethalin solid particles higher and the flow point lower, which indicates that the polysulfonate dispersant has good dispersing performance for pendimethalin.

3.2.5. Surface Tension Analysis

Figure 7 shows the surface tension of the dispersant solution with different concentrations. The results indicate that the surface tension of the solution is rapidly reduced after adding the surfactant, finally gradually becomes gentle, and an obvious turning point is observed. At the turning point concentration, the solution begins to form micelles [18]. The CMC is determined by the intersection of two straight lines on Figure 7. The surface tension at CMC is 46.43 mN/m. The results support the conclusion that the polysulfonate dispersant has a strong ability to lower the surface tension [19].

3.2.6. Zeta Potential Analysis

Zeta potential analysis is employed to explore the impact of the polysulfonate comb-like polymers on the surface charge of pendimethalin particles. Figure 8 shows the zeta potential of pendimethalin particles as the function of the dispersant concentration. The more dispersant that is added, the more the negative potential on the surface of the particles increases, indicating that more dispersant is adsorbed on the surface of the particles. Based on the electric double layer theory and the adsorption behavior, the dispersant is adsorbed on the surface of pendimethalin particles and the hydrophilic APEG side chains extend into the solution to form the adsorbed layer [19].

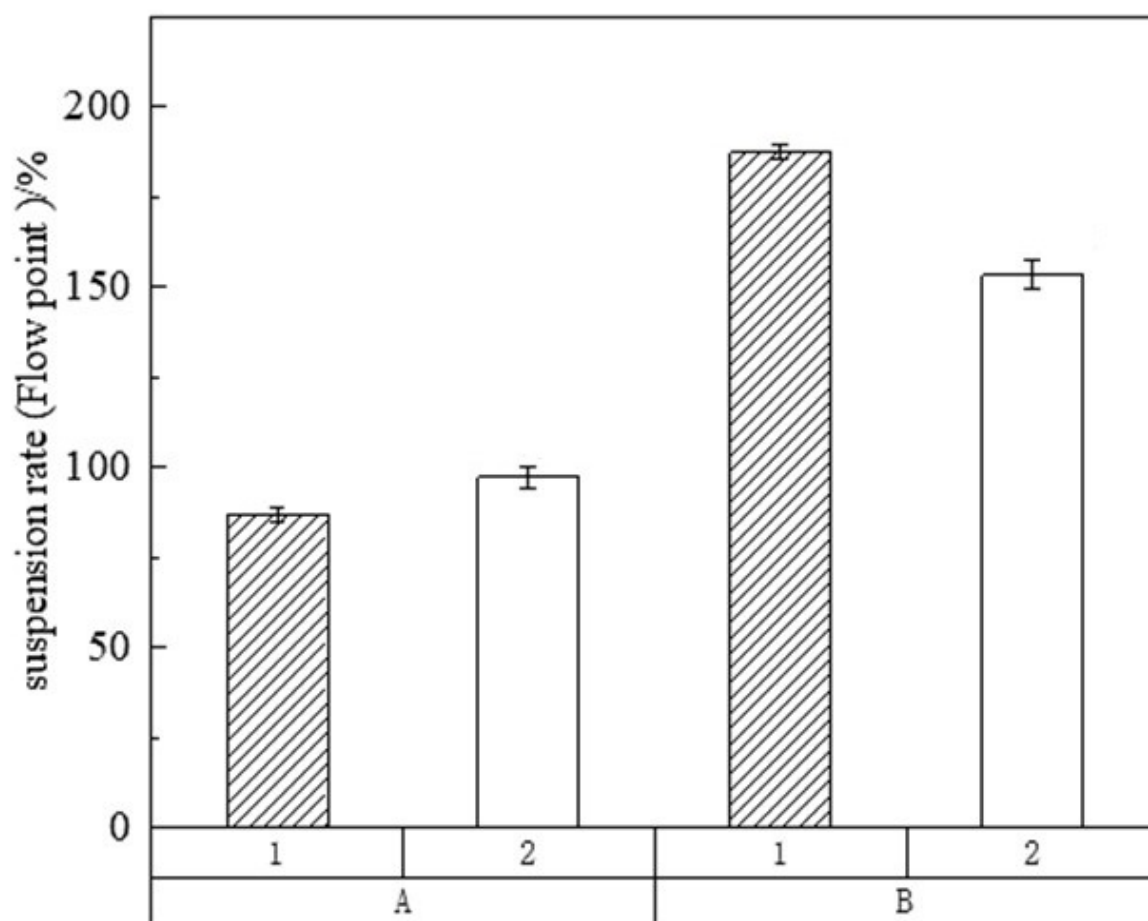


Figure 6. Suspension rate and flow point of APEG and the polysulfonate dispersant (A1 and B1 are suspension rate and flow point value of APEG; A2 and B2 are suspension rate and flow point value of the polysulfonate dispersant).

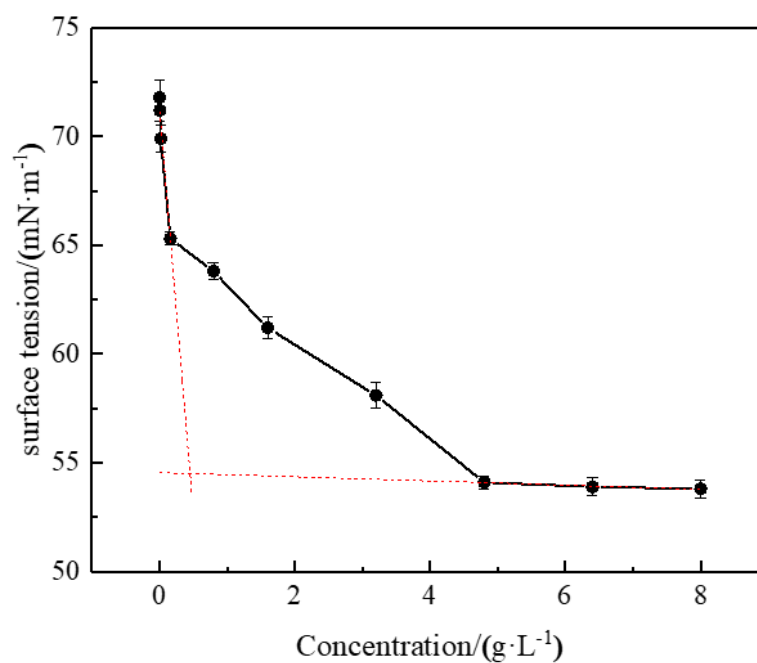


Figure 7. The surface tension of the dispersant solution with different concentrations.

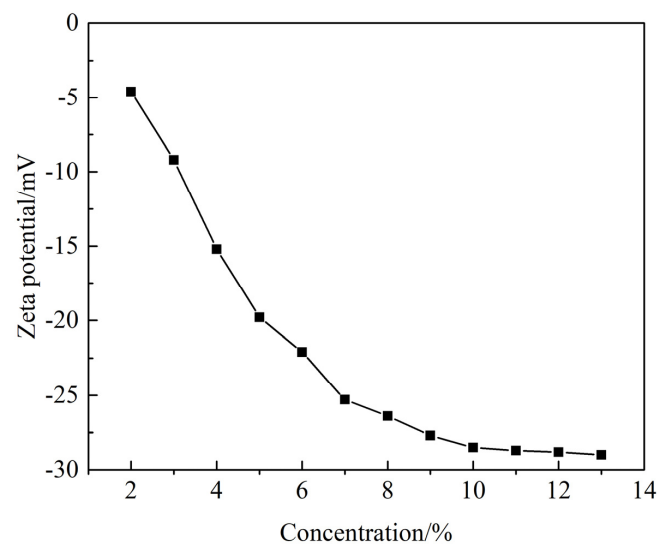


Figure 8. The zeta potential of the pendimethalin suspensions with different concentrations.

3.2.7. Particle Size Analysis

In order to further evaluate the dispersibility of the polysulfonate dispersant, the particle size analysis of pendimethalin suspensions with different dispersant contents was carried out, as shown in Figure 9. The results show that when the amount of dispersant is between 10% and 12%, pendimethalin suspension with a narrow particle size distribution can be obtained. The side chains of polysulfonate dispersant can provide steric repulsion and sulfonic acid groups provide an electrostatic effect, which is the main reason for the dispersion performance of polymer dispersant [19,20]. Increasing the amount of polysulfonate dispersant within a certain range is beneficial to the improvement of dispersion efficiency. However, if the concentration of the dispersant is too high, it will cause entanglement and flocculation between the polymer chains and the pendimethalin particles to aggregate.

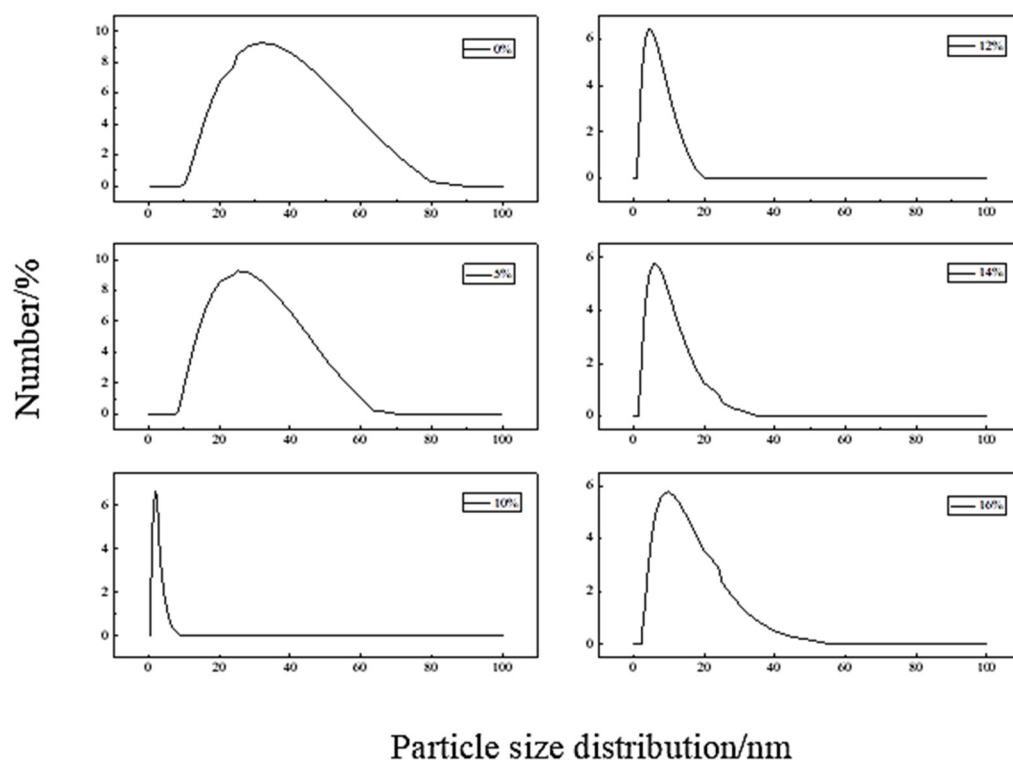


Figure 9. The effect of dispersant dosage on pendimethalin suspension particle size.

Pendimethalin has a melting point of 54~58 °C and is easily crystallized by heat at continuous storage over 14 days in (54 ± 2.0) °C. A variety of conventional agricultural dispersants, such as lignin sulfonate, sodium naphthalene sulfonate formaldehyde condensate, alkylphenol ethoxy ether phosphate, etc., have been used in formula screening, but have not solved the problem of thermal storage crystallization. Figure 10 shows that the average particle size after adding 10% polysulfonate dispersant is 1.152 μm , and the average particle size after the heat storage is 1.7469 μm . The effect of heat storage on pendimethalin particle size indicates that there is no obvious growth of crystals during the heat storage process, and the polysulfonate dispersant has a good dispersing effect on pendimethalin particles and effectively prevents the agglomeration of pendimethalin particles.

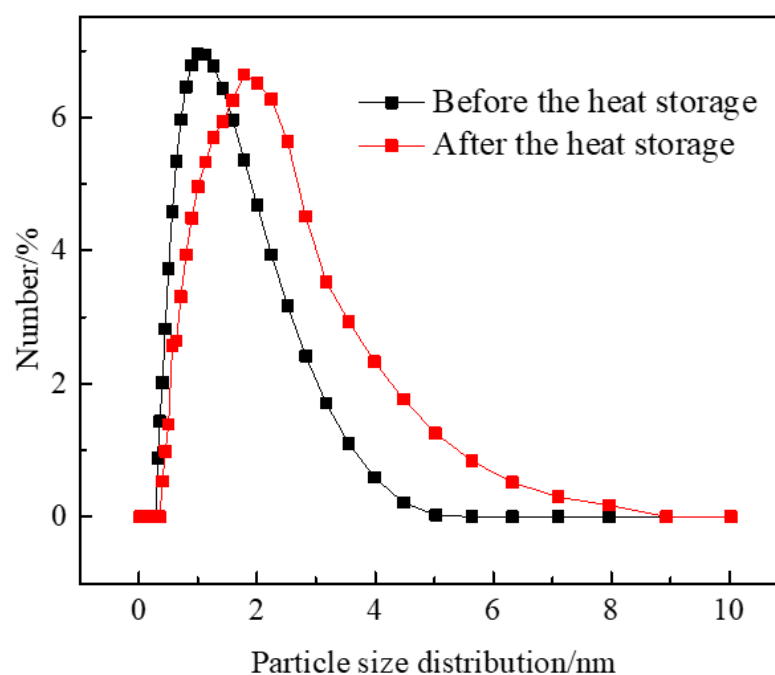


Figure 10. The effect of heat storage on pendimethalin particle size.

4. Conclusions

In this work, APEG, HEMA and SSS were used as monomers, and the polysulfonate dispersant was obtained by optimizing the synthesis reaction conditions. The results show that the dispersion performance of polysulfonate dispersant is closely related to the molecular structure and the amount of dispersant. When the anchor group content and the solvated chain content are balanced and the polysulfonate dispersant on the surface of the pendimethalin particles has a better adsorption density and a better adsorption layer thickness, the dispersant has a better dispersion performance. The sulfonic acid group of the polysulfonate provides an electrostatic effect for dispersion, and the side chain of PEO forms a hydrophilic solvent layer to provide a steric hindrance effect. This research provides basic theoretical and experimental support for the development of suspensions, especially the development and use of high-efficiency dispersants.

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