

Research Article

Dispersion Performance of Polycarboxylate Terpolymers with Different Alkyl Side-Chain Lengths in Pesticide Suspension Concentrate

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A versatile dispersant plays a critical role in the suspension stability of pesticide suspension concentrate (SC) systems. Herein, a series of novel acrylate ester-based polycarboxylate terpolymers (PTs) were designed as dispersant for pesticide suspension concentrate and successfully synthesized in aqueous solutions from the copolymerization of α -methacrylic acid, allyl polyoxyethylene ether, and acrylate (methyl acrylate, ethyl acrylate, and *n*-butyl acrylate). Terpolymers were characterized by FT-IR and ¹H-NMR to confirm their structure. The surface activities of PTs were evaluated according to critical micelle concentration (CMC) and the surface tension at CMC (γ_{CMC}). PT-3 with the longest alkyl side-chain length displayed the most superior surface activity due to its lowest CMC value compared with that of the other PTs. Additionally, the dispersion properties of PTs as dispersants in a 600 g/L imidacloprid SC were evaluated. Results showed that compared to the other two PTs, PT-3 contributes to the excellent dispersion properties on imidacloprid SC. Meanwhile, the obtained SC system exhibited shear thinning behavior under high-speed shearing showing typical features of pseudo-plastic non-Newtonian fluids, which conforms to the Herschel-Buckley model. Our results revealed that the effect of the alkyl side-chain length of dispersants could be considered the primary modulator of dispersion performance of SCs.

1. Introduction

Pesticide aqueous SC, as an eco-friendly water-based formulation, exhibits excellent advantages, such as high suspension and bioefficacy, low cost, and safety for operators [1, 2]. However, SC belongs to a thermodynamic and unstable dispersed system and easily encounters physical stability obstacles, such as Ostwald ripening and the flocculation or agglomeration of particles [3], which encloses lots of water and results in increasing the viscosity and decreasing the fluidity of SC. This is especially true for high-concentration SC. Ionic polymeric surfactants, which adsorbed onto solid particles and prevent the particles from

aggregation because of electrostatic or steric repulsion, were often served as dispersants to address the above problems [4, 5]. Among these polymers, polyacrylic acid (PAA) is most widely used as a dispersant. Compared to PAA, the molecular structure of polycarboxylate copolymers is easy to be modified, which can meet specific properties for various applications.

Especially, polycarboxylate copolymers such as terpolymers are considered as a versatile dispersant because of their numerous branched chain groups, including carboxyl group, sulfonic acid group, amino group, and polyoxyethylene group side chains, which is widely used in concrete, ceramics, paints, and dye to obviously

improve suspension stability of the aqueous suspension system [6–9]. This is due to the fact that the carboxylate groups of the admixtures act as anchors to adsorb on the surface of the particles and show electrostatic effect. Meanwhile, the polyethylene oxide side chains also prevent the steric effect and prevent agglomeration of the particles [10–13]. For example, Wang et al. and Bai et al. found that the particular molecular structure of polycarboxylate-based terpolymers guaranteed their good dispersibility for CaCO₃ suspensions and had strong anti-redispersion power [14, 15]. Hence, it has great significance in designing suitable polycarboxylate terpolymers as dispersants for efficiently improving the stability of pesticide SC.

Imidacloprid is a chloro-nicotinyl insecticide which specifically blocks the microtubular neuronal pathway, which is commonly used in rice, soybean, maize, potatoes, vegetables, sugar beets, fruit, cotton, hops, and turf and is especially systemic when used as the seed or soil treatment [16]. Herein, three kinds of polycarboxylate terpolymers with different carbon side-chain lengths as an anchoring unit were designed and successfully synthesized. Moreover, the obtained PTs were selected as dispersants to prepare 600 g/L imidacloprid SC to verify its effect on the suspension stability of SC.

2. Experimental Section

2.1. Materials. Technical-grade imidacloprid (98.5% purity) was kindly supplied by Jiangsu Jiannong Agrochemical and Chemical Co. Ltd. (China). Allyl polyoxyethylene ether (APEG), α -methacrylic acid (MAA), methyl acrylate (MA), ethyl acrylate (EA), and *n*-butyl acrylate (BA) were obtained from Sinopharm Chemical Reagent Co. (China). Xanthan gum was of food reagent grade and obtained from the Shanghai Ji Hu Chemical Co., Ltd of China. The SR-08 wetting agent was purchased from the Shanghai ShiDa Micromolecular Materials Co., Ltd. The ethylene glycol antifreeze agent was obtained from Shanghai Titan Technology Co., Ltd. Double distilled water was used in the experiment. All chemicals were of analytic grade and were used without further purification.

2.2. Synthesis of Polycarboxylate Terpolymers (PTs). Scheme 1 illustrates the synthesis of PTs by free-radical polymerization of APEG and MAA with MA, EA, and BA, which are denoted as PT-1, PT-2, and PT-3, respectively. The mole ratio of APEG: MAA: MA/EA/BA was 4:1:1. Specifically, 0.5 wt.% of initiator and 1 wt.% chain transfer agent were added to the monomers. Appropriate amounts of distilled water and sodium bisulfite (a certain amount of chain transfer agent, water, and methanol) were added into a 250 mL four-mouth flask and stirred at 80°C. APEG, MAA, and MA/EA/BA were dissolved in methanol and added dropwise into the reactor. Then, the mixture was allowed to react at 80°C for 3.5 h. Next, the mixture was cooled to room temperature and its pH was adjusted to 7–8 with 30 wt.% NaOH. Finally, the PTs were obtained.

2.3. Structural Characterization of PTs. The PTs were purified with a dialysis bag and the powder was obtained by freeze-drying. Infrared spectroscopy was analyzed by potassium bromide pellet method. Using deuterium instead of water as the solvent, the structure was characterized by ¹H NMR spectroscopy.

2.4. Measurement of Critical Micelle Concentration (CMC) Values of PTs. Surface tension of PT aqueous solutions was measured at 25°C with a JYW-2008 tensiometer (CDTM Ltd., China) by the Wilhelmy plate method. Prior to each experiment, the instrument was calibrated and checked by measuring the surface tension of distilled water. The CMC value was obtained from the breakpoint of the plot of surface tension (γ) versus $\ln c$ [17].

According to Gibbs law, the maximum surface excess concentration (Γ_{CMC}) and the minimum surface area per surfactant molecule (A_{CMC}) were calculated by the Gibbs adsorption isotherm equations (equations (1) and (2)). And, the Gibbs free energy of micellization, ΔG_{mic}^{\ominus} , and the Gibbs free energy of adsorption ΔG_{ad}^{\ominus} were calculated using equations (3) and (4) [4].

$$\Gamma_{CMC} = \frac{-1}{2.303nTR} \left(\frac{\partial \gamma}{\partial \lg C} \right)_T, \quad (1)$$

$$A_{cmc} = \frac{1}{N_A \Gamma_{cmc}}, \quad (2)$$

$$\Delta G_{mic}^{\ominus} = nRT \ln CMC, \quad (3)$$

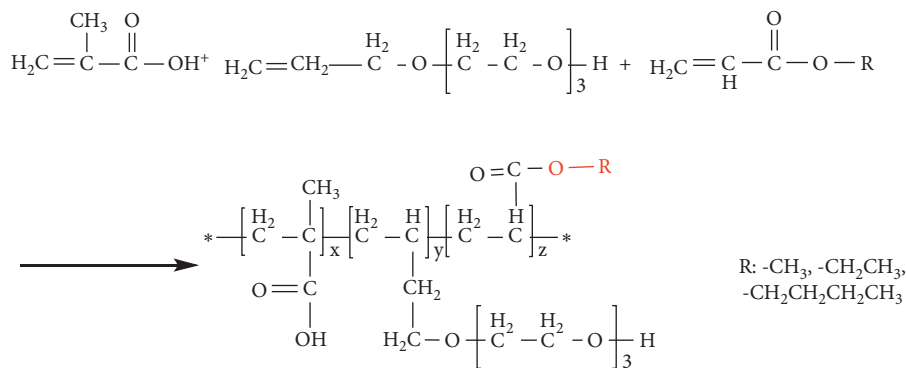
$$\Delta G_{ad}^{\ominus} = nRT \ln CMC - 0.6023(\gamma_0 - \gamma_{cmc})A_{cmc}, \quad (4)$$

where γ_0 , N_A , and γ_{CMC} are the PTs of pure water, Avogadro's number, and the surfactant solutions at CMC, respectively. Here, n is the number of species at the interface whose concentration changes with surfactant concentration ($n=1$ for a gemini surfactant and $n=2$ for an anionic surfactant). R and T take their usual meanings.

2.5. Preparation of 600 g/L Imidacloprid SC. 600 g/L imidacloprid SCs were prepared by wet sand grinding technology. The optimum formulation of SCs was determined by pre-experiment. Typically, 50 g imidacloprid, 2 g PTs, 1 g wetting agent SR-08, 4 g xanthan gum, and 4 g ethylene glycol were mixed together with the rest of the water. Then, the mixture was obtained after grinding under room temperature until the particle size distribution of less than 3 μ m.

2.6. Characterization of the 600 g/L Imidacloprid SC

2.6.1. Zeta Potential of 600 g/L Imidacloprid SC. A small amount of 600 g/L imidacloprid SC was weighed in a 250 mL beaker using an analytical balance. After diluting the imidacloprid to a given concentration by adding deionized water, the solution was transferred to a 50 mL centrifuge tube and centrifuged at 3000 r/min for 5 min. The zeta



SCHEME 1: Synthesis process of PTs.

potential of the supernatant of the centrifugation was measured on a Malvern Nano ZS90. Each sample was measured three times, and the average was used.

2.7. Measurement of Suspensibility of 600 g/L Imidacloprid SC

2.7.1. Suspensibility of 600 g/L Imidacloprid SC. The suspensibility of SC was measured according to GB/T 14825-2006.

2.7.2. Determination of SC Viscosity and Rheological Properties. The viscosity and rheological properties of the SC were measured using an Anton Par MCR 102 rotational rheometer. The shear viscosity of SC samples was studied at 25°C with a shear rate of 0–1000 s⁻¹.

Viscosity recovery as a critical factor of SC was measured in three stages. That is, the sample was subjected to a constant low-speed shear (0.25 s⁻¹) in the initial 25 s, high-speed shear (1000 s⁻¹) in the next 10 s, and then constant low-speed shear (0.25 s⁻¹) for recovery.

3. Results and Discussion

The chemical structures of PTs were analyzed by FT-IR and ¹H-NMR (Figure 1). Taking the case of PT-3, as presented in Figure 1(a), the wide stretching vibration peak of –OH is at 3394 cm⁻¹, the stretching vibration peaks of methyl and methylene appear at 2922 cm⁻¹ and 2871 cm⁻¹, and the characteristic peak of C=O locates at 1735 cm⁻¹. A value of 1453 cm⁻¹ is the bending vibration of methyl and methylene, 1109 cm⁻¹ is the stretching vibration peak of C–O–C, and the characteristic peaks of double bond at 2500–2000 cm⁻¹ disappear after copolymerization.

Figure 1(b) shows ¹H-NMR spectrum of PT-3. Among them, δ = 4.70 is the solvent peak and δ = 3.8–3.47 is the oxyethylene structural unit (CH₂CH₂O) in the polyether. The proton peak of H on the main carbon chain is at δ = 1.36–1.58, and the proton peaks of –CH₃ and –CH₂ are near δ = 0.9. After δ = 5.7, there is no double bond proton peak, indicating that it disappears and participates in the reaction polymerization.

Furthermore, the GPC analysis was utilized to obtain the molecular weight of various PTs and their distributions. The

M_n and M_w/M_n of PTs are listed in Table 1. The M_n and M_w/M_n of PT-1, PT-2, and PT-3 are 2160, 2310, and 2287, and 2.47, 2.83, and 2.28, respectively. The results indicate that the various dispersants are randomly copolymerized by free-radical copolymerization.

3.1. CMC and Thermodynamic Properties. CMC and surface tension at this concentration (γ_{CMC}) are important factors to measure the surface activity of surfactant aqueous solutions. Figure 2 and Table 2 show the surface tension of PTs, from which we realize that the aqueous solution exhibited a continuous decrease of surface tension and remained unchanged with the concentration increasing to CMCs. Compared with other PTs, the CMC and γ_{CMC} values of PT-3 are minimum, which indicated that PT-3 has the most superior surface activity. The hydrophobic monomer BA makes PT-3 more hydrophobic, resulting in its lower CMC and γ_{CMC} [18].

The adsorption data of PTs are listed in Table 2. PT-3 has a largest Γ_{max} and smallest A_{min} , conferring its superior surface activity. Meanwhile, the negative values of ΔG_{mic} show the micellization process, and it is a thermodynamic spontaneous process. The order of absolute value of ΔG_{mic} is PT-3 > PT-2 > PT-1, which suggests that PT-3 has the strongest driving force for micellization or adsorption at the air-liquid interface [19]. This could be attributed to the greatest hydrophobic performances of PT-3, leading to an easier formation of micelles [20].

3.2. Impacts of Dispersant Dosage on Zeta Potential and Viscosity of 600 g/L Imidacloprid SC. Zeta potential is one of the key parameters usually utilized to estimate suspension stability, which reflects the effective adsorption of dispersants on the surface of particles. Figure 3(a) shows the effects of PTs on the zeta potential of 600 g/L imidacloprid SC. It was found that the amount of PTs dramatically affected the zeta potential. The zeta potential decreases sharply with increasing PTs from 0 to 2 wt.%. Moreover, the continued increase of the dispersant beyond 2 wt.% up to 6 wt.% decreases a little zeta potential, suggesting that the dispersants gradually reached saturation adsorption on the surface of pesticide particles at the concentration of 6 wt.%. Surprisingly, the zeta potential decreases with further increase in PT

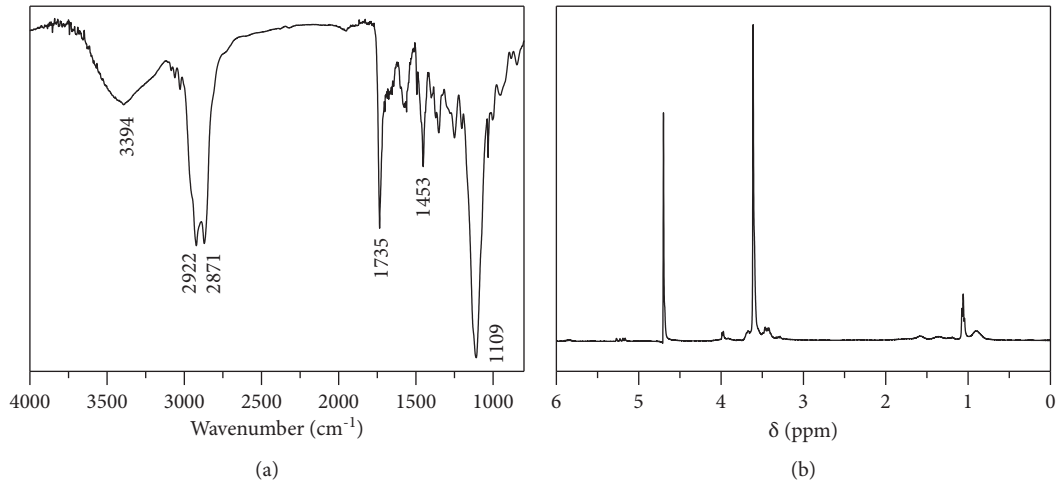
FIGURE 1: FTIR spectrum and $^1\text{H-NMR}$ spectra of PT-3.

TABLE 1: Monomer combination and GPC results for the various PTs.

Sample	Monomer			Ratio		M_n (g/mol)	M_w/M_n
	MAA	APEG	MA	EA	BA		
PT-1	1	4	1			2160	2.47
PT-2	1	4		1		2310	2.83
PT-3	1	4			1	2287	2.28

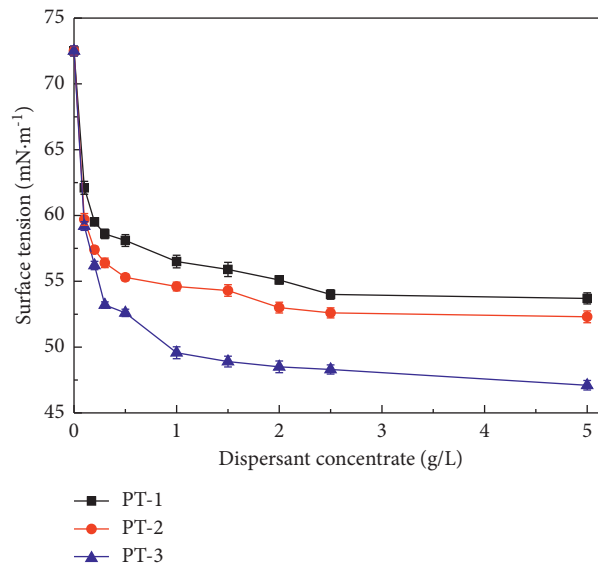


FIGURE 2: Evaluation of the CMC values of PTs by means of the Wilhelmy plate method.

TABLE 2: Surface properties of PTs.

Dispersants	γ_{CMC} (mN/m)	CMC (g/L)	Γ_{max} ($\times 10^{-6}$ mol/m 2)	A_{CMC} (nm 2 /molecule)	ΔG_{mic} (kJ/mol)
PT-1	53.70	2.50	4.66	0.354	-20.728
PT-2	52.30	2.15	5.36	0.310	-22.854
PT-3	47.10	1.33	6.58	0.252	-24.498

dosage. This is because that excessive counterions of dispersants enter into the diffusion layer in the double electrical layer, resulting in the slight decrease in zeta potential values

[21]. Additionally, the absolute of zeta potential of 600 g/L imidacloprid SC obtained from PT-3 is minimum, indicating that PT-3 could provide stronger electrostatic

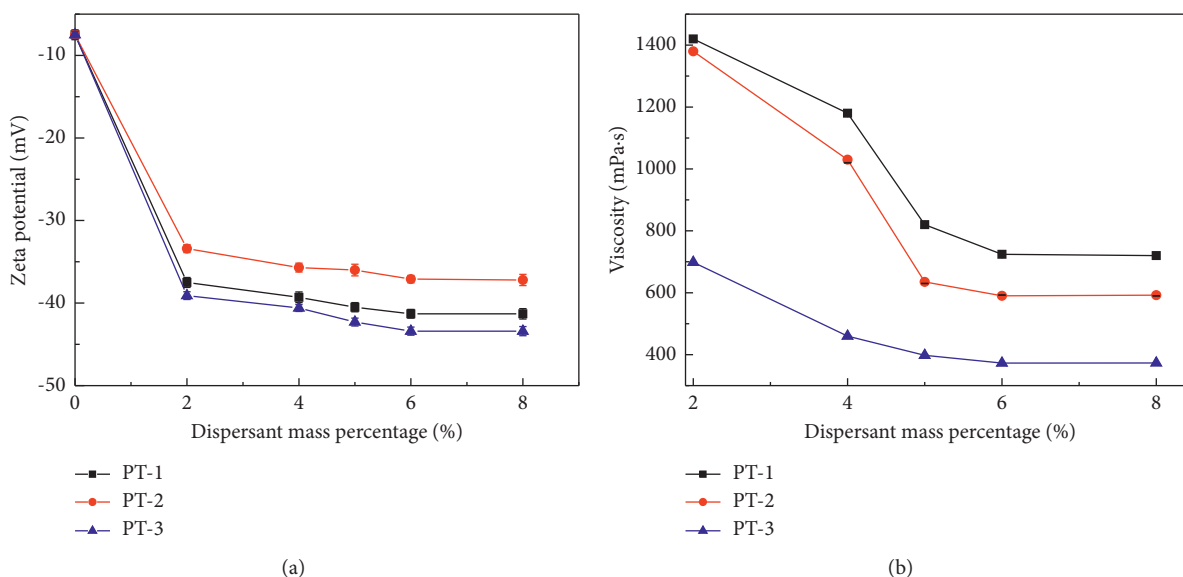


FIGURE 3: Impacts of PTs on zeta potential and viscosity of 600 g/L imidacloprid SC.

repulsion than PT-1 and PT-2. Hence, the optimal dispersant and additive amount are PT-3 and 6%, respectively.

The dispersant can effectively improve the viscosity of suspension systems and further effect on suspension stability. Subsequently, we investigated the effect of PT amounts on the viscosity of 600 g/L imidacloprid SC. As illustrated in Figure 3(b), it was found that the viscosity of imidacloprid SC sharply decreased and then slightly increased with increasing amounts of the PTs. When the dispersant dosage reached 6%, the viscosity of the SC is minimum, which agrees with the results of zeta potential (Figure 3(a)). However, when the amount of dispersants is above 6%, it leads to a slight increase in viscosity, which could be because that the excess dispersant causes counterions to enter the diffusion layer and the electrostatic repulsion decreases. Therefore, the combined bridging and depletion effects result in increased viscosity of the suspension system [19]. Notably, PT-3 reveals a greater influence on the viscosity of the SC, indicating that PT-3 exhibits superior dispersion capacity for SC.

We further investigated the thermal stability and rheological properties of 600 g/L imidacloprid SC made of PTs in 6 wt.% dosage.

3.3. Analysis of Thermal Stability of 600 g/L Imidacloprid SC. The physical stability of pesticide SC systems is of great significance for its long-term storage. The long-term storage stability is very important for pesticide formulations for practical usage in agriculture since delamination, caking, and degradation of the active pesticide may occur during storage. To study storage stability, the optimum SC samples made of PTs in 6 wt.% dosage were kept under $54 \pm 2^\circ\text{C}$ for 14 days to determine their thermal stability (Table 3).

The changes of suspension rate and particle size distribution are important quality indexes and often used to

characterize the physical stability of SC. As listed in Table 3, the suspension rate of the SC sample made of PT-3 is still greater than 95%, while the average diameter of particles is about 2.24 and $5.86 \mu\text{m}$, respectively, before and after thermal storage, indicating PT-3 can effectively improve the physical stability of 600 g/L imidacloprid SC. Moreover, the SC prepared from PT-3 has suitable viscosity and viscosity change after thermal storage. Accordingly, the PT-3 is a promising dispersant for improving the thermal stability of 600 g/L imidacloprid SC.

3.4. Analysis of Rheological Properties of 600 g/L Imidacloprid SC. The suspension stability of SC systems was investigated by the rheological method. Apparent viscosity and thixotropy can obviously reflect the suspension stability of the SC system [22, 23]. Figure 4 shows the rheological curves of the PTs with 600 g/L imidacloprid SC in 6 wt.% dosage. The apparent viscosity of SC systems decreases with increasing shear rate, suggesting that the SC systems exhibited shear thinning behavior. Thus, three SCs had the characteristics of typical non-Newtonian pseudo-plastic fluid.

The three-stage thixotropy was used to verify the viscosity recovery of SC systems and can reflect the relationship between the viscosity and the change of network structure of the SC system. The results of the three-step thixotropy test are shown in the illustration of Figure 4(b). At low-speed shear, the spatial network structure of the SCs is stable and the systems exhibit high viscosity. Moreover, when the shear rate reached 1000 s^{-1} , the structures of SC systems were damaged, resulting in a rapid decline in viscosity. In the third stage (0.25 s^{-1} after 35 s), the structure of the SC system was restored. Notably, SC obtained from PT-3 had a higher structural recovery than SCs made of PT-1 and PT-2, indicating that SC made of PT-3 had higher stability, which is in accordance with the results of thermal stability (Table 3).

TABLE 3: The performances of 600 g/L imidacloprid SC before (A) and after (B) thermal storage.

Sample	Viscosity (MPa·s)		Suspension rate (%)		Particles size (μm)	
	A	B	A	B	A	B
PT-1	724	1265	92.8 ± 0.3	89.4 ± 0.1	2.13	8.33
PT-2	590	972	94.6 ± 0.5	90.2 ± 0.2	2.17	7.36
PT-3	373.4	525	96.3 ± 0.5	95.6 ± 0.3	2.24	5.86

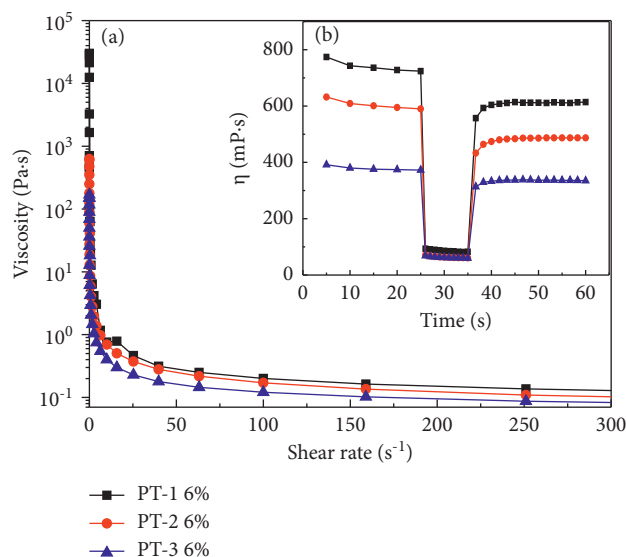


FIGURE 4: Rheological properties (a) and three-stage shearing curve (b) of 600 g/L imidacloprid SC.

3.5. *The Proposed Stability Mechanism of Imidacloprid SC Prepared from PTs.* When the pesticide particles were dispersed into aqueous solution, the particles were first wetted by water, and by increasing the wettability of the pesticide surface, dispersants reduce the frequently observed tendency of hydrophobic pesticide particles to spontaneously aggregate in aqueous suspensions; thus, the lower the surface tension of the dispersant aqueous solutions is, the easier the wetting of pesticide particles will be so as to contribute to the dispersion of pesticide particles more readily into aqueous solution [4, 24]. Compared with PT-1 and PT-2, PT-3 had the lowest CMC (Table 2). Therefore, PT-3 exhibits much better strong adsorption and wetting ability at the pesticide surface.

Remarkably, PT-3 has carboxylate groups and the longest hydrophobic alkyl side chain, as the anchoring points, which make it steadily be adsorbed on the surface imidacloprid particles. Meanwhile, PTs contain neutral EO pendants, which provide steric hindrance among imidacloprid particles. For the above reasons, PT-3 is endowed with a superior ability to stabilize and disperse imidacloprid particles and maintained the suspension stability of imidacloprid SC.

4. Conclusion

Three polycarboxylate terpolymers containing different carbon side-chain lengths were successfully synthesized by free-radical polymerization. PT-3 serves as an effective dispersant to stabilize the 600 g/L imidacloprid SC. When PT-3 dosage

reached 6%, the SC had the minimum viscosity and the maximum zeta potential, which are very beneficial for improving its suspension stability. Meanwhile, rheological properties showed further evidence that the SC made of PT-3 exhibits excellent suspension stability compared to other PTs.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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