The effect of different initiator dosages on the performance of sodium salt of MAA/St/SSS copolymer dispersant

Yanyan Zhang ¹, Yunping Chang ², Qiang Zhang ¹*

¹School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, People’s Republic of China  
²Student Service Center, Beijing Institute of Technology, Beijing 100081, People’s Republic of China  
*Corresponding author’s e-mail: zhangqiang6299@bit.edu.cn

Abstract. 500 g/L atrazine aqueous suspension concentrates (SC) were prepared by using sodium salt of methacrylic acid/styrene/ sodium p-styrene sulfonate copolymer (SMSS) synthesized with different initiator dosages as dispersants, and the performances of atrazine SC were evaluated. It is found that initiator dosages have remarkable effect on the performance of SMSS. SMSS has higher performance when the initiator dosage is 4.8 wt. %, and the suspensibility of atrazine SC could reach 98.36%, the syneresis rate is only about 0.5% and the particle size is the smallest.

1. Introduction
Polycarboxylate dispersant, as a novel type of anionic dispersant, has been widely used in ceramics, building materials, cosmetics, pesticide preparations, dyes and other fields [1-6] due to its advantages of designability of molecular structure, controllability of molecular weight and superiority of dispersion performance. Various polycarboxylate dispersants have been designed, synthesized and applied in the field of pesticide formulation.

In recent years, with the rapid development of environment-friendly pesticide agents, pesticide SC due to its environmental-friendly, low cost and high efficacy has become an important pesticide preparation, which is gradually replacing pesticide wettable powder (WP) and emulsifiable concentrate (EC). Polycarboxylate dispersant plays a significant role in pesticide SC and influences the processing and suspension stability of SC to a great extent. Sodium salt of polycarboxylate tricopolymer made of maleic anhydride, styrene and methyl methacrylate has been synthesized and used in 600 g/L imidacloprid SC [7]. Sodium salt of styrene/methacrylic acid copolymer [8] has been applied to study the effects of polymer molecular weight and solution pH on the stability of atrazine aqueous suspension.

The performances of polycarboxylate dispersant are influenced by the molecule structure, the molecular weight and side chain density [9] and so on. The molecular weight is an important factor affecting the dispersion performance of dispersants, which is generally controlled by adding different initiator dosages. The lower initiator dosage is, the higher molecular weight is, and vice versa. The dispersants synthesized with suitable initiator dosage can interact intensively with the pesticide particles and are conducive to the grinding of technical materials in SC because of its appropriate molecular weight and favourable chain length, thus maintain the suspension stability of pesticide SC.

Up till now, there are many studies [10-11] on the effect of different initiator dosages on the
performances of polymer dispersants, but there are few researches on the relationship between the initiator dosages and SC performance. Herein, atrazine SC was prepared by SMSS dispersant synthesized with different initiator dosages and the performances of SC were evaluated. Combined with laser particle size distribution technology, SC dispersant with high-performance can be controllably synthesized, which is of great significance to the development of environment-friendly pesticide preparations.

2. Experiment

2.1. Materials
Sodium p-styrene sulfonate (SSS) (≥ 98%) was purchased from Zibo Zichuan Yaodong Chemical Co., Ltd. (China). Sodium alpha-olefin sulfonate (AOS) was received from Shanghai Chuxing Chemical Co., Ltd. (China). Atrazine (≥ 97%) was purchased from Shandong Binnong Technology Co., Ltd. (China). Zirconium balls (0.8–1.0mm) were purchased from Shanghai Chile Mechanical Technology Co., Ltd. (China). Styrene (St), methacrylic acid (MAA), MgCl₂·6H₂O, CaCl₂, Na₂S₂O₈, NaOH and ethylene glycol were all analytical grade and purchased from Beijing Chemical Reagent Company (China).

2.2. Synthesis of SMSS [12]
A series of SMSS dispersants were synthesized by solution radical polymerization with MAA/St/SSS molar ratio of 4.0:1.0:0.5 and different initiator dosages. The reaction was carried out at 80 °C for 5 h. Then, the product was neutralized to pH 8.5 with 30% NaOH aqueous solutions. The SMSS was gained by drying the liquid product after the isopropanol was removed by atmospheric distillation.

2.3. Preparation and performance of 500 g/L atrazine SC

2.3.1. Preparation of 500 g/L atrazine SC. 500 g/L atrazine SC were prepared with the formula of Table 1 by wet milling with a planetary sand mill (AEXX-4-2PH11G/15P, Shanghai Beiwei Motor Co., Ltd., China). The ingredients and deionized water were mixed uniformly and added to grinding jar filled with 150ml zirconium balls with a diameter of 0.8–1.0 mm [13]. The machine ran for 3 hours with the rotation rate of 2000 rpm to obtain the desired particle size lower than 5 μm, thus, 500 g/L atrazine SC were obtained. Cooling water was used to maintain relatively stable grinding conditions throughout the process [14]. Samples prepared by SMSS synthesized with different initiator dosages are denoted as S₂.₄, S₄.₈, S₇.₂, S₉.₆ and S₁₂, respectively. For example, S₂.₄ would correspond to SMSS synthesized with 2.4 wt. % of initiator dosage.

| Components               | Mass percent (%) |
|--------------------------|------------------|
| Atrazine                 | 50               |
| SMSS                     | 4                |
| Wetting agent (AOS)      | 1.5              |
| Defoamer (organosilicone)| 0.1              |
| Antifreeze (ethylene glycol)| 4           |
| Thickener (xanthan gum)  | 0.2              |
| Deionized water          | to 100mL         |

2.3.2 Performance of 500 g/L atrazine SC. (1) Suspensibility of atrazine SC. Suspensibility of atrazine SC was determined according to Collaborative International Pesticides Analytical Council (CIPAC) Method MT161. A certain quality suspensions were transferred into 250 ml measuring cylinder with
stopper and diluted to 250 ml scale with standard hard water. Cover the stopper and invert 30 times up and down within 1 minute centering on the middle of measuring cylinder. After standing still in 30 °C thermostatic water bath for 30 minutes, the top nine-tenths were removed. The remaining tenth was assayed gravimetrically after it was dried [15]. The suspensibility w (%) is calculated by Eq. (1).

\[ w = \left( \frac{m_1 - m_3 + m_2}{m_1} \right) \times \frac{10}{9} \times 100\% \]  

(1)

Where, m₁ is the active ingredient concentration of initial sample; m₂ is the mass of evaporation dish; m₃ is the mass of evaporation dish and effective constituent of remaining tenth in the bottom of the measuring cylinder.

(2) Syneresis rate measurement. 5 mL suspensions were added into 5 mL centrifuge tube and centrifuged at 3000 rpm for 30 minutes by centrifuge (TDL-50B, Shanghai Anting Scientific Instrument Factory, China). After that, the layered state was observed and recorded to calculate the syneresis rate. The syneresis rate (%) is calculated by Eq. (2).

\[ \text{Syneresis rate} = \frac{v_1}{v} \times 100\% \]  

(2)

Where, v₁ is the volume of water separate from the upper layer; v is the volume of initial sample.

2.3.3. Particle size distribution measurements. The 15 mg/mL diluted suspensions were prepared. Before measurement, the suspensions were treated by ultrasonication for 5 minutes with ultrasonic cleaner (KQ5200B, Kunshan Ultrasonic Instrument Co., Ltd., China) and the particle size distribution was determined by laser particle analyzer (Mastersizer 3000, Malvern Instruments Co., Ltd., England).

2.3.4. Scanning electron microscope (SEM) images. The samples were prepared by dripping diluted SC suspensions on the silicon slices. The SEM images were determined via scanning electron microscope (JSM-6700F, JEOL, Japan).

3. Result and discussion

3.1. Influence of Initiator dosages on the performance of SMSS dispersant

The dispersants were synthesized by adding different initiator dosages to adjust their molecular weight, and the molecular weight of dispersants has a great influence on the performance of dispersant [8]. As shown in Figure 1 (a), with the increase of initiator dosages, the suspensibility of SC increases initially and then decreases. When the initiator dosage is 4.8 wt. %, the suspensibility achieved its maximum (about 98.36%). In addition, syneresis rate is another important index for evaluating the stability of SC suspensions, and lower syneresis rate indicates better stability. As demonstrated in Figure 1 (b), with the increase of initiator dosages, the syneresis rate increases slowly at first and then increases to 4% rapidly at 12 wt. % of initiator dosage. When the initiator dosage is 4.8 wt. %, the syneresis rates is only 0.5%, showing the best stability of atrazine SC.
Figure 1. Influence of initiator dosages on the performance of SC; (a) suspensibility; (b) syneresis rate.

3.2. Particle size distribution of atrazine SC
The particle size distribution of atrazine SC samples prepared with different dispersants is shown in Figure 2, there are significant changes of the number and shape of particle size distribution peaks. When the amount of initiator is less (2.4%), there are two overlapping peaks at about 1.1 μm and 1.9 μm, and the peak area of larger particles is larger. When the amount of initiator increased to 4.8%, the peak area of the smaller particles increased, which means that the dispersant synthesized under this condition is more conducive to the processing of SC. With the further increase of initiator dosages, the two peaks of particle size distribution change into three (S7.2 and S9.6) or even four peaks (S12), the third peak is at about 10.5 μm, and the fourth peak is a broad peak at 20~70 μm. The generation of larger particles means poor grinding efficiency, and the larger the amount of initiator is, the larger the particle size and number of larger particles become, which is obviously not conducive to SC suspension stability and spray process.
Figure 2. The particle size distribution of atrazine SC samples; (a) S₂.₄; (b) S₄.₈; (c) S₇.₂; (d) S₉.₆; (e) S₁₂.

The average particle size and uniformity of the samples are presented in Table 2. Remarkably, the particle size distribution of S₂.₄ have the best uniformity (0.502), but larger average size (2.03 μm), indicating that the presence of more large particles because of unfavorable grinding of atrazine particles during process. The particle size distribution of S₄.₈ shows better uniformity (0.622) and the smallest average particle size (1.66 μm), it is suggested that there is strong interaction between dispersant molecules and atrazine particles, which is conducive to the grinding of particles, and getting uniform and smaller particles. Compared with S₄.₈, the particle size distribution of S₇.₂, S₉.₆ and S₁₂ exhibits larger average particle size (2.29 μm, 2.68 μm and 3.09 μm respectively) and relatively worse uniformity (0.751, 1.058 and 1.481, respectively). So, it can be concluded that S₄.₈ has excellent performance, which is consistent with the performance evaluation results of dispersant.

Table 2. The average particle size and uniformity of atrazine SC samples.

| Samples | Average particle size (μm) | Uniformity |
|---------|---------------------------|------------|
| S₂.₄   | 2.03                      | 0.502      |
| S₄.₈   | 1.66                      | 0.622      |
| S₇.₂   | 2.29                      | 0.751      |
| S₉.₆   | 2.68                      | 1.058      |
| S₁₂    | 3.09                      | 1.481      |

The molecular weight is an important factor affecting the dispersion performance of dispersants, which is generally controlled by adding different initiator dosages. The dispersants synthesized with suitable initiator dosage can interact intensively with the atrazine molecules and effectively adsorb on the surface of atrazine particles, which are conducive to the grinding of technical materials in SC. The adsorption mechanism of polycarboxylate dispersant on the surface of atrazine particles has been reported that the adsorption occurs via hydrogen bonding existing between -NH- of atrazine molecules and carboxylic groups of polycarboxylate molecules [8]. If the initiator dosage is too low, the too large molecular weight and too long chain of dispersants will prevent –COO⁻ groups from attaching to -NH-, the adsorption capacity of SMSS on the surface of atrazine particles decreases. Meanwhile, polymeric dispersants with too large molecular weight have a high potential of particle-particle bridging, causing floculation. When the initiator dosage is too high, molecular weight of dispersants is too small and the SMSS dispersants possess too strong hydrophilicity, which will weaken the interactions between dispersant molecules and atrazine molecules and is not beneficial to the grinding of the pesticide particles, which would lead to an increase of larger particles and easy aggregation of in-homogeneously distributed particles [16] in SC.
3.3. The SEM images analysis

The SEM images of SC are shown in Figure 3, the atrazine grains of S$_{2.4}$ are irregular columns with the length about 1.0 μm–8.0 μm and there is less particles smaller than 1.0 μm. The particle size of S$_{4.8}$ sample is 0.5 μm ~5 μm, the distribution is more uniform and there are many particles smaller than 1.0 μm. With the further increase of initiator dosage, there are many larger particles appearing in the SC system, the irregular columnar particles become wider and thicker, and the particle size distribution become more uneven. These results are basically consistent with the change rule of particle size distribution. It is worth noting that the agglomeration of atrazine particles is not observed by SEM, so it is inferred that the change of particle size distribution is caused by different interaction strength between SMSS dispersant molecules with different molecular weight and atrazine molecules.

Figure 3. The SEM images of atrazine SC samples; (a) S$_{2.4}$, (b) S$_{4.8}$, (c) S$_{7.2}$, (d) S$_{9.6}$, (e) S$_{12}$. 
4. Conclusion
The SMSS dispersants were synthesized with different initiator dosages and used to prepare the 500 g/L atrazine SC. The evaluation results of atrazine SC show that initiator dosages have remarkable effect on the performance of SMSS dispersant. SMSS dispersant synthesized with 4.8 wt. % of initiator dosage exhibits higher performance, the suspensibility could reach 98.36%, the syneresis rate is only 0.5% and the particle size is the smallest among the as-prepared samples.

Combined with laser particle size distribution and SEM technology, it is concluded that the dispersant molecules synthesized with suitable initiator dosage can interact intensively with the atrazine molecules and effectively adsorb on the surface of atrazine particles, which are conducive to the grinding of technical materials and stability of atrazine SC. The synthesis of SC dispersant with high-performance can be precisely controlled, which is of great significance to the development of environment-friendly pesticide preparations.

Acknowledgments
This work was supported by the National Key R&D Program of China (Grant No.2018YFD0200100).

References
[1] Yoshikawa, J., Lewis, J. A., Chun, B. W. (2009) Comb Polymer Architecture, Ionic Strength, and Particle Size Effects on the BaTiO3 Suspension Stability. J. Am. Ceram. Soc., 92 [S1]: S42-S49.
[2] Gharanjig, H., Gharaajjig, K., Khosravi, A. (2019) Effects of the side chain density of polycarboxylate dispersants on dye dispersion properties. Color. Technol., 135: 160-168.
[3] Huang, Z., Yang, Y., Ran, Q.P., et al. (2018) Preparing hyperbranched polycarboxylate superplasticizers possessing excellent viscosity-reducing performance through in situ redox initialized polymerization method. Cem. Concr. Compos., 93: 323-330.
[4] Abile, R., Russo, A., Limone, C., Montagnaro, F. (2018) Impact of the charge density on the behaviour of polycarboxylate ethers as cement dispersants. Constr. Build. Mater., 180: 477-490.
[5] Wang, A.Q., Qiao, M., Xu, J., Pan, Y.M., Ran, Q.P., Wu, S.S., Chen, Q. (2016) POEGMA-b-PAA comb-like polymer dispersant for Al2O3 suspensions. J. Appl. Polym. Sci., 133: 43352-43357.
[6] Ilg, M., Plank, J. (2019) Synthesis and Properties of a Polycarboxylate Superplasticizer with a Jellyfish-Like Structure Comprising Hyperbranched Polyglycerols. Ind. Eng. Chem. Res., 58: 12913-12926.
[7] Li, Y.C., Xing, W., Zhang, B., et al. (2015) Application of polycarboxylate dispersants in 600 g/L imidacloprid aqueous suspension concentrate. Shanghai Chem. Ind., 40: 1-4.
[8] Liu, Z.Q., Yang, G.Y., Feng, Q.Q., Zhang, Q. (2016) Studies of the Atrazine Aqueous Suspension Stability in the Presence of an Anionic Polymer-Influences of Polymer Molecular Weight and Solution pH. J. Disper. Sci. Technol., 37: 1233-1240.
[9] Daroukola, M.R.R. (2018) Novel branched polymers and their structural effects on intercalation into Na-MMT and silica fume suspensions. Polym. Bull., 75: 4055-4072.
[10] Zhang, X., Hu, H.R. (2014) Synthesis and application of a polyacrylate dispersant on the preparation of ultrafine ground calcium carbonate in a laboratory stirred media mill. Powder Technol., 266: 218-227.
[11] Cui, C.C., Zhang, S.G. (2019) Synthesis, scale inhibition and dispersion performance evaluation of the environmentally benign additive IA-AMPS-APEG copolymer. Environ. Sci-Wat. Res., 5: 1736 -1747.
[12] Tian, Q.M., Zhang, Y.Y., Jia, Z.Y., Zhang, Q. (2019) Synthesis and hard water resistance mechanism of polycarboxylate dispersant for pesticide water dispersible granules. J. Disper. Sci. Technol., DOI: 10.1080/01932691.2019.1638270.
[13] Qiu, X.Q., Zeng, W.M., Yu, W., et al. (2015) Alkyl Chain Cross-Linked Sulfobutylated
Lignosulfonate: A Highly Efficient Dispersant for Carbendazim Suspension Concentrate. ACS Sustain. Chem. Eng., 3: 1551-1557.

[14] Li, B.X., Wang, W.C., Zhang, X.P., et al. (2017) Integrating uniform design and response surface methodology to optimize thiacloprid suspension. Sci. Rep., 7: 46018.

[15] Hong, N.L., Li, Y., Qiu, X.Q. (2016) A highly efficient dispersant from black liquor for carbendazim suspension concentrate: Preparation, self-assembly behavior and investigation of dispersion mechanism. J. Appl. Polym. Sci., 133: 43067.

[16] Xia, M.Q., Chen, Y.X., Ma, J., et al. (2020) Effects of low frequency magnetic field on myoglobin oxidation stability. Food Chem., 309: 125651.