Synthesis of polyacetone acrylamide and detection of amine benzene

Wenting Song*, Nanjie Mei

School of chemistry and chemical engineering, Beijing Institute of technology, Beijing 102488, PR China
*Corresponding author’s e-mail: 756554580@qq.com

Abstract. A single homogeneous spherical polyacetone acrylamide particles was synthesized by inverse suspension polymerization. By adjusting the conditions of initiator, cross-linking agent, dispersant, water-oil ratio, reaction time and reaction temperature, the adsorbent material with large specific surface area and pore structure was obtained. Polyacetone acrylamide particles can effectively detect aniline by ultraviolet absorption spectroscopy, the adsorption rate reaches 41.95% within 2 hours, and the adsorption reaches equilibrium within 5 hours, and the adsorption rate reaches 51.30%.

1. Introduction
DAAM is a versatile chemical and chemical raw material. The polymer obtained by simple polymerization can be applied in various fields such as biochemical sensors and drug delivery systems.[1-3] At present, there are few studies on the polymerization of DAAM, and the polymerization of acrylamide has been relatively mature. Therefore, we mainly refer to the polymerization method of acrylamide during the polymerization process. Generally, the larger the polymer particles, the better the adsorption effect. In order to prepare larger particles, a suspension polymerization process must be employed.[4] However, the premise of successful suspension polymerization is that the dispersed droplet phase has a lower solubility in the dispersion medium in order to maintain the dispersed emulsion droplets. The solubility of DAAM in water is high, so it is necessary to use inverse suspension polymerization. Inverse suspension polymerization refers to dispersing a water-soluble monomer in a continuous phase of an organic solvent under the action of a stirring and dispersing agent to form a water-in-oil suspension, further obtaining a spherical polymer.[5-7]

Aniline is an important chemical raw material for industrial production, but it also remains in industrial wastewater, causing serious damage to the environment and ecosystem[8-10]. Traditionally, various analytical techniques, including photolysis, electrolysis, adsorption, oxidation, biodegradation have been utilized to treat aniline.[11-13] However, some problems remain unresolved, such as lower adsorption capacity, high cost, and low recycling. In recent years, functional polymers have been used more in the adsorption of aniline in sewage, through the strong attraction of aniline or other aromatic compounds with polymers.[14-16] Therefore, it is essential to develop effective method for detecting and adsorbing aniline. In this work, spherical particles of polyacetone acrylamide were designed and synthesized to realize the detection and adsorption of aniline.
2. Synthesis

As shown in Scheme 1, Cyclohexane and paraffin are used as the oil phase, N-N-methylenebisacrylamide is used as the crosslinking agent, the initiator is potassium sulfate and a reducing agent anhydrous sodium sulfite, and Span 80 is a dispersing agent. Diacetone acrylamide is heated in a water bath of the above system and mechanically stirred with a stirring paddle to form a stable dispersion. In order to obtain the best polymer particles, we studied the effects of initiators, crosslinkers and dispersants on the reaction.

2.1. Effects of initiator

The initiator potassium persulfate has the main function of initiating polymerization of the monomer at the initial stage of the reaction. If the amount of the initiator is too large, the polymerization rate is too fast, the molecular weight is low, and finally a paste polymer is formed. If the amount of the initiator is insufficient, the polymerization reaction hardly occurs, and finally the polymerization fails. As shown in table 1, diacetone acrylamide polymerizes in different initiator levels. When the amount of the initiator is less than 0.4%, the product obtained by polymerization is in the form of a white emulsion. When the amount of the initiator is more than 0.4%, the product obtained by polymerization is in the form of a block, and the optimum ratio of the initiator is 0.4%, the monomer is a stable spherical particle that best meets our requirements. A picture of the first group, the third group, and the fourth group of products is shown in Figure 1, from left to right are white emulsion material, the spherical particles and bulk polymer.

| group | initiator (%) | Polymer form       |
|-------|--------------|--------------------|
| 1     | 0.2%         | white emulsion     |
| 2     | 0.3%         | white emulsion     |
| 3     | 0.4%         | spherical particle |
| 4     | 0.5%         | adhesive solid     |
| 5     | 0.6%         | adhesive solid     |

Table 1. Effect of initiator content on polymerization

a Reaction conditions: The molar ratio of the reducing agent to the initiator is 1:0.8, the crosslinker is 33% of the mass of the monomer, the water-oil ratio is 1:3, the stirring speed is 300 rpm, the temperature is 40 °C, and the reaction time is 4 hours. b Initiator to monomer percentage.
2.2. Effects of crosslinkers
The crosslinkers agent is capable of attaching the polymerized segment to increase the degree of crosslinking. The hardness of the polymer increases to form a spherical shape and the shape is more stable. However, in order to obtain a spherical polymer having a uniform size, it is necessary to adjust the amount of the crosslinkers. As shown in table 2, diacetone acrylamide polymerizes in different crosslinkers levels. When the amount of crosslinkers is 24%, the product obtained by the polymerization is a white paste. When the amount of the initiator reach 28%, the product obtained by the polymerization formed a pellet shape but the hardness is low, and the optimum ratio of the initiator is 33%, forming stable spherical particles. As shown in Figure 1, the polymerization product with a crosslinkers content of 28% and 33%, respectively.

Table 2. Effect of crosslinkers content on polymerization

| group | crosslinkers (%) | Polymer form               |
|-------|------------------|----------------------------|
| 1     | 21               | Paste                      |
| 2     | 24               | Paste                      |
| 3     | 28               | Spherical particles, low hardness |
| 4     | 33               | Stable spherical           |

*a* Reaction conditions: The molar ratio of the reducing agent to the initiator is 1:0.8, the initiator is 0.4% of the mass of the monomer, the water-oil ratio is 1:3, the stirring speed is 300 rpm, the temperature is 40 °C, and the reaction time is 4 hours. *b* Crosslinkers to monomer percentage.

2.3. Effects of dispersants
The dispersant directly determines the size of the spherical particles. The more the dispersing agent, the smaller the droplets formed by the water-in-oil, but they are easily bonded at the later stage of the reaction to form irregular spherical particles. If the dispersant is insufficient, droplets cannot be
formed, and the water and oil phases are stratified, and the reverse phase suspension polymerization cannot be performed. As shown in table 3, diacetone acrylamide polymerizes in different dispersant levels. When the amount of dispersant is 0.2 mL, the product obtained by the polymerization is a white paste. When the amount of the dispersant reach 0.3 mL, the product obtained by the polymerization formed spherical particle, and the optimum ratio of the initiator is 0.5 mL, forming adhesive solid.

Table 3. Effect of dispersant content on polymerization

| group | Span 80 (mL) | Polymer form     |
|-------|--------------|------------------|
| 1     | 0.1          | Paste            |
| 2     | 0.2          | Paste            |
| 3     | 0.3          | spherical particle|
| 4     | 0.4          | adhesive solid   |
| 5     | 0.5          | adhesive solid   |

*Reaction conditions: The molar ratio of the reducing agent to the initiator is 1:0.8, the initiator is 0.4% of the mass of the monomer, the crosslinker is 33% of the mass of the monomer, the water-oil ratio is 1:3, the stirring speed is 300 rpm, the temperature is 40 °C, and the reaction time is 4 hours.*

3. Result and discussion

3.1. Infrared spectroscopy
Infrared spectroscopy shows that pure polymer is obtained.

3.2. Adsorption of aniline by polydiacetone acrylamide
The polydiacetone acrylamide obtained by inverse suspension polymerization has a large specific surface area, and the ketone carbonyl can form a hydrogen bond with aniline, thereby achieving the purpose of adsorbing aniline. We measured the change of aniline concentration by UV-visible spectrophotometer. In the ultraviolet absorption spectrum, the absorption peak of aniline appeared at 230 nm and 280 nm. Here, we use the absorption peak of 230 nm to characterize the concentration of aniline.

3.3. Effect of adsorption time on adsorption performance
Add 0.2g of poly-diacetone acrylamide to 50mL of 100mg/L aniline solution, and stir the reaction for 1 hour, 2 hours, 3 hours, 4 hours, 5 hours, 8 hours, then dilute 50 times separately, and measure the UV spectrum of diluted aniline solution. The relationship between adsorption rate and time is shown in Figure 4. In the first two hours, the adsorption amount quickly reached 41.95% from 0%. The
subsequent few hours of change was very slow, almost reached equilibrium at 5 hours, and the adsorption rate reached 51.30%. Because the concentration of aniline is large at the beginning of the reaction, the adsorption rate of aniline by the polymer spherical particles is large under strong hydrogen bonding and surface adsorption. When the adsorption time was 5 hours, the surface of the polymer was completely adsorbed, so that the adsorption rate gradually became equilibrium and no longer increased. Since the adsorption reached equilibrium in 5 hours, we took 5 hours as the adsorption time of the reaction.

Figure 4. The relationship between adsorption rate and time.

4. Conclusion
In summary, Polydiacetone acrylamide was synthesized by reverse suspension polymerization, and stable spherical diacetone acrylamide (DAAM) particles were finally obtained by screening conditions such as initiator, crosslinkers agent and dispersant. The UV-Vis spectra of aniline aqueous solution were studied to verify the adsorption capacity of polymer beads to aniline aqueous solution. The present work not only enriches the polymerization mode of DAAM, but also provides a feasible way to adsorb industrial pollutants such as aniline.

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