Chemosphere 167 (2017) 71–81

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

UV-initiated template copolymerization of AM and MAPTAC: Microblock structure, copolymerization mechanism, and flocculation performance

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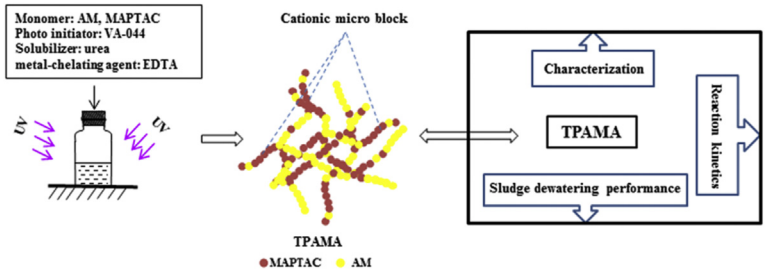
HIGHLIGHTS

- A cationic polyacrylamide (CPAM) with microblock structure was synthesized through UV-initiated template copolymerization.
- All of the instrumental analysis results confirmed the micro block structure of the template CPAM.
- Reaction kinetics revealed I (ZIP) template polymerization mechanism of this reaction.
- The template copolymer showed excellent sludge dewatering performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 July 2016
Received in revised form
2 August 2016
Accepted 12 September 2016
Available online 4 October 2016

Handling Editor: W Mitch

Keywords:
Cationic polyacrylamide
Sludge dewatering
Polymer flocculant
Microblock structure
Copolymerization mechanism

ABSTRACT

Flocculation as the core technology of sludge pretreatment can improve the dewatering performance of sludge that enables to reduce the cost of sludge transportation and the subsequent disposal costs. Therefore, synthesis of high-efficiency and economic flocculant is remarkably desired in this field. This study presents a cationic polyacrylamide (CPAM) flocculant with microblock structure synthesized through ultraviolet (UV)-initiated template copolymerization by using acrylamide (AM) and methacrylamido propyl trimethyl ammonium chloride (MAPTAC) as monomers, sodium polyacrylate (PAAS) as template, and 2,2'-azobis [2-(2-imidazolin-2-yl) propane] dihydrochloride (VA-044) as photoinitiator. The microblock structure of the CPAM was observed through nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM) analyses. Furthermore, thermogravimetric/differential scanning calorimetry (TG/DSC) analysis was used to evaluate its thermal decomposition property. The copolymerization mechanism was investigated through the determination of the binding constant M_K and study on polymerization kinetics. Results showed that the copolymerization was conducted in accordance with the I (ZIP) template polymerization mechanism, and revealed the coexistence of bimolecular termination free-radical

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http://dx.doi.org/10.1016/j.chemosphere.2016.09.046

reaction and mono-radical termination in the polymerization process. Results of sludge dewatering tests indicated the superior flocculation performance of microblock flocculant than random distributed CPAM. The residual turbidity, filter cake moisture content, and specific resistance to filtration reached 9.37 NTU, 68.01%, and 6.24 (10^{12} m kg^{-1}), respectively, at 40 mg L^{-1} of template poly(AM-MAPTAC) and pH 6.0. Furthermore, all flocculant except commercial CPAM showed a wide scope of pH application.

1. Introduction

With the development of industry, urbanization, and increasingly stringent environmental protection requirements, both sewage discharge and its treatment depth have increased. Consequently, large amounts of excess sludge generated in the process of wastewater treatment are now being increasingly taken seriously. Therefore, the research and development of a high-efficiency sludge dewatering agent is very crucial.

Cationic acrylamide (CPAM) is the most commonly used sludge dewatering agent. This polymer usually features high positive charge density, water solubility, and high intrinsic viscosity (Chang et al., 2005; Zhao et al., 2013; Lee et al., 2014)_ENREF_1. Nevertheless, this polymer synthesized by traditional methods such as thermally induced solution polymerization usually features smooth and regular surface area and random distribution of acrylamide (AM) and cationic monomers in polymer chain (Guan et al., 2014). In general, polymers with irregular, uneven, and porous surface area would have a larger specific surface area and thus enhance the probability of contact with colloidal particles; polymers with regular microblock structure can make full use of the cationic units in the polymer chain and thus enhance their charge neutralization effect (Chen et al., 2016). Therefore, the use of a suitable synthesis method to prepare AM polymers with a large specific surface area and regular microblock structure will significantly improve the flocculation and dewatering performance.

Ultraviolet (UV) radiation can induce the activation of carbon fiber surface and generation of free radicals. The free radicals react with monomer radicals to form chemical bonds, thereby increasing the surface energy and surface roughness (which is usually shown by the increase in surface porosity) of carbon fiber. (Deng et al., 2009; Akkaya, 2012; Kordoghli et al., 2012). Our previous studies have also proved the surface modification effect of UV light in the synthesis of polyacrylamide polymer (Liao et al., 2014; Zheng et al., 2014). As one of the main technologies for surface modification of polymeric materials, UV-induced polymer surface modification has been widely recognized for its simplicity, effectiveness, and versatility. Besides, UV initiation presents the advantages of low reaction temperature, short reaction time, less photoinitiator, and higher monomer conversion rates, thereby attracting increased attention.

Template polymerization is a new method for the synthesis of polymers with specific sequence structure (Saito, 2008; Saito and Saito, 2011). In the process of template polymerization, the preassemble of reaction monomer on the template polymer molecular chain will improve the ordered nature of the reaction system, and chain growth progresses along the template polymer chain, which has an important effect on the polymerization kinetics and the structure of the product (Połowiński, 2002). Thus far, most of the research on template polymerization is limited to homopolymerization, and less research has been conducted on template copolymerization. In our previous studies, template copolymerization technology has been used for the synthesis of conventional CPAM (poly (acrylamide-acryloyloxyethyltrimethylammonium chloride) and poly (acrylamide-diallyl dimethyl ammonium chloride)). Characterization results showed the regular microblock structure of CPAM, which proved the feasibility for the use of template copolymerization in the synthesis of CPAM with regular microblock structure. (Guan et al., 2015; Chen et al., 2016). However, the polymerization mechanism remains to be further studied to meet the needs of the development of the reaction process and the reactor design in practical engineering application. Furthermore, this template copolymerization technology should also be applied to the synthesis of CPAM or other polymer flocculant with high efficiency and wide serviceability in view of processing diverse sludge materials and stricter environmental protection policy.

In this study, we report the preparation of CPAM with irregular, uneven, and porous surface area and regular microblock structure through UV-initiated template copolymerization. Nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and thermogravimetric/differential scanning calorimetry (TG/DSC) analyses were used for comparative analysis of template copolymer and copolymer obtained by non-template copolymerization. Furthermore, the polymerization mechanism was investigated through the determination of the binding constant M_K and study on polymerization kinetics. Finally, the sludge dewatering efficiency of template copolymer was evaluated in terms of residual turbidity (RT), filter cake moisture content (FCMC), specific resistance to filtration (SRF), and floc properties.

2. Material and methods

2.1. Raw materials

AM, methacrylamido propyl trimethyl ammonium chloride (MAPTAC), and commercial CPAM (synthesized through copolymerization of AM and acryloyloxyethyltrimethylammonium chloride (DAC)) used in this study were of technical grade, whereas the other reagents were of analytical reagent grade. The details of reagents used in this study are as follows: AM and commercial CPAM (Chongqing Lanjie Tap Water Company, Chongqing, China); PAAS (M_W = 3000, Shandong Xintai Water Treatment Company, Zaozhuang, China); VA-044 (Ruihong Biological Technology, Shanghai, China); MAPTAC (50 wt% in water; Nanjing Jingruijiuan Biotechnology Co., Ltd. Nanjing, China); PAM, ethylenediaminetetraacetic acid (EDTA), urea, and other analytical reagents (Chongqing Chuandong Chemical Group Co., Ltd., Chongqing, China). PAMA (poly(AM-MAPTAC)) was synthesized by UV-initiated copolymerization without adding template PAAS. All reagents were used in the experiment without further purification.

2.2. Synthesis of template copolymers

Template polymerization in combination with UV-initiated technology was adopted to synthesize template copolymers (template poly(AM-MAPTAC): TPAMA). Predetermined amounts of AM, MAPTAC, PAAS, distilled water, EDTA, and urea were added into a 10 ml Pyrex glass vessel (details of the feed ratio are listed in