

Preparation and performance of cationic flocculant for papermaking based on the graft polymerization of cationic chains from colloidal silica particles



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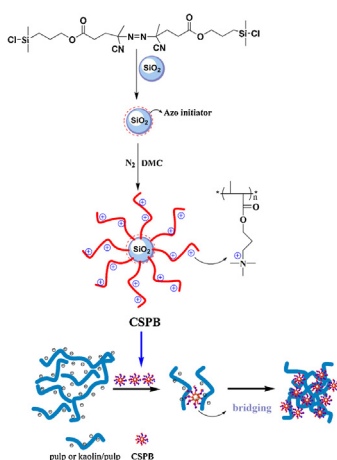
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HIGHLIGHTS

- Cationic spherical polyelectrolyte brushes (CSPB) were synthesized by “grafting from” polymerization.
- CSPB acted as flocculants or retention-aids for bleached eucalyptus kraft pulp and kaolin/pulp particles.
- Bridging flocculation model may be the mainly mechanism for CSPB on flocculation of pulp.
- The CSPB achieved a better flocculation and retention-aid efficiency than PDMC.

GRAPHICAL ABSTRACT



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ABSTRACT

The cationic spherical polyelectrolyte brushes (CSPB), with poly(2-(acryloyloxy) ethyltrimethylammonium chloride) chains grafted from the surfaces of colloidal silica particles were prepared and evaluated. The CSPB was characterized by Fourier-transform infrared spectrometry, thermo gravimetric analysis, colloid titration, gel permeation chromatography, transmission electron microscopy and X-ray photoelectron spectroscopy. The results show that CSPB with 1.8×10^{-3} mmol/g surface grafting density was successfully fabricated. The CSPB was investigated as flocculation and retention-aids for bleached eucalyptus kraft pulp and kaolin/pulp particles using relative turbidity, zeta potential, Focused beam reflectance measurement (FBRM), dynamic drainage jar and field emission scanning electron microscopy methods. The results showed that the zeta potential of pulp suspension gradually changed from negative to zero and then to positive, maximum flocculation occurred when the zeta potential was still negative. The data also suggested that the efficiency of both flocculation and retention-aid were increased and then demonstrated a gradual downward trend as the concentration of the CSPB increased. FBRM showed that

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flocs of CSPB had low re-flocculate ability. Bridging flocculation model may be the mainly mechanism for CSPB on flocculation of pulp.

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1. Introduction

In the papermaking industry, flocculation is a key issue. Flocculants are often used to fix fine particles onto fibers, to bring about agglomeration of fines and fillers [1,2]. Typical flocculants include inorganic and organic flocculants. The major drawbacks of using inorganic flocculants such as alum, ferrite flocculants or polyaluminum chloride, are basically the inorganic coagulants have limited ability to withstand hydrodynamic shear [3,4]. For organic flocculants are extensively used, due to their high tailorability and reduced sludge production [5]. Organic flocculants like natural polymers and synthetic polymers can be adsorbed onto anionic cellulosic fibers. Aggregation of the particles can occur by charge neutralization, bridging or patching mechanism [6]. Natural polymers like cationic starch was usually employed, but the efficiency of flocculation and retention-aid still need to enhance. While synthetic polymers have attracted considerable research interest for many advantages, such as their controllable structure, molecular weight and cationic charge densities [7].

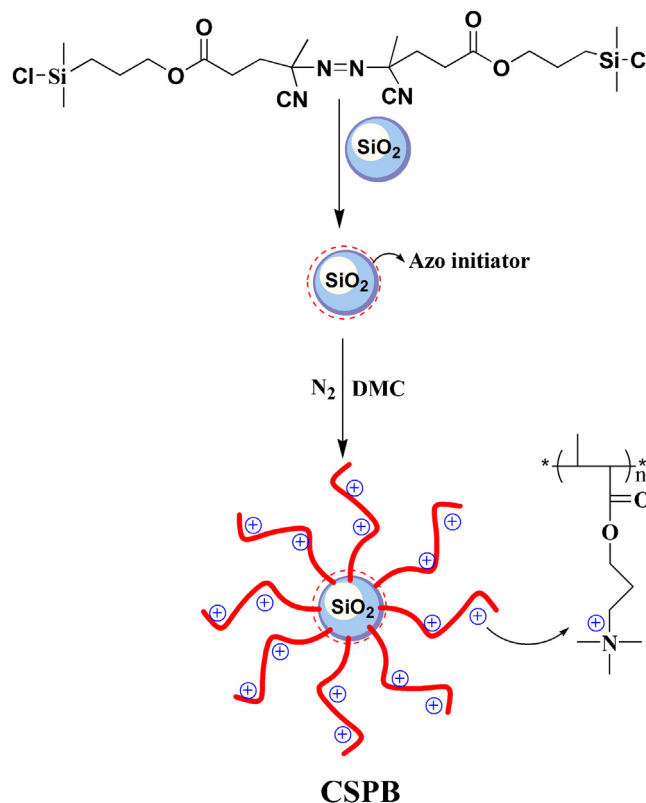
Recently, researchers observed that flocs induced by branched polyacrylamides (PAMs) were smaller and stronger [8], and flocculation efficiency was higher than by linear ones in presence of high hydrodynamic forces [6]. In addition, it was found out that bridging flocculation by particles is more effective and less concentration dependent compared with neutralization or patching flocculation caused by polyelectrolyte [9]. Then particles modified with appropriate dense polyelectrolyte may act an attractive flocculants for the papermaking industry. Polyelectrolyte brushes, consist of polyelectrolyte chains densely attached to a planar or curved surface, have received increasing interest for its unique properties and applications, such as adhesion, flocculate agent, nanoreactors and so on [10–12]. Cationic spherical polyelectrolyte brushes (CSPB) take unique highly degree of branching and cationic charged density. And the structure similar to both branched polymers and the cationic charged particles, ensure the fibers with high effective of flocculation and retention-aid during the papermaking [13,14].

Here in, CSPB, with poly(2-(acryloyloxy) ethyltrimethylammonium chloride) chains grafted from the surfaces of colloidal silica particles was prepared by “grafting from” approach, because the approach offers the formation of polymer brushes with tunable grafting density and brushes thickness in a controllable fashion. Then the effect of various dosages of CSPB concentration on flocculation and retention-aid of both for bleached eucalyptus kraft pulp and kaolin/pulp particles were investigated. For comparison, the flocculation and retention-aid performance of PDMC was also evaluated on the same situations.

2. Experimental

2.1. Materials

Toluene was refluxed over a sodium/potassium alloy and distilled under nitrogen atmosphere [15]. Dichloromethane and *n*-hexane were refluxed over calcium hydride and distilled under nitrogen. 2-(Acryloyloxy) ethyltrimethylammonium chloride (DMC) and distilled under reduced pressure before use. All the other reagents used in these experiments were of analytical grade and used without further purification. Nanosilica modified by



Scheme 1. Synthetic process of CSPB.

organic silicon toluene with particle size of 70 nm were purchased from Zhang Jiagang Chosen New Material Co., Ltd., which were synthesized by the method described as previous report [16]. Bleached eucalyptus kraft pulp (35°SR) was stored under refrigeration (4 °C).

2.2. Synthesis of CSPB

The synthetic process of CSPB are schematically described in Scheme 1, which mainly contained three steps. First, the azo initiator 4,4'-azobis(4-cyanopentanoic acid-(3'-hydridodiethylsilyl) propyl ester) was prepared based on the literature [17,18]. Second, azo initiator was attached to the surface of the SiO₂. Lastly, DMC grafted from these surface-attached initiators in situ by free radical polymerization. In typical synthesis, approximately 0.2 g of azo initiator was placed in a flask, into which 50 ml of toluene was added. 0.5 g of SiO₂ and 1 ml pyridine were added into the toluene solution and stirred overnight. The modified SiO₂ was washed with toluene and ethanol three times alternately with repeated centrifugation, and the remaining solids were dried in a vacuum overnight, the product after dried named SiO₂@Azo. Surface-initiated polymerization of DMC was carried out in bulk at 60 °C using the surface-attached initiator SiO₂@Azo in water. After the desired polymerization time, the product was subjected to repeated centrifugation and washed with distilled water [17] until PDMC was no longer detected in the supernatant by Fourier transform infrared spectroscopy. PDMC was taken from the solution of supernatant for the use of flocculation and retention-aid.

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