Synthesis and Evaluation of P(AM-b-DADMAC) as Fixative for Dissolved and Colloidal Substances

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ABSTRACT: Acrylamide (AM) and diallyldimethyl ammonium chloride (DADMAC) block copolymer P(AM-b-DADMAC) was synthesized via reversible addition–fragmentation chain transfer (RAFT) polymerization method. The successful polymerization of controlled composition and polydispersity index of the block copolymer was confirmed by FTIR, ^{1}H-NMR, and size exclusion chromatography analyses. Differential scanning calorimetry and thermal gravimetric analysis further confirmed the interaction between the trithioester groups of RAFT agent and alkenyl groups of AM and DADMAC in the final product. With turbidity, chemical oxygen demand and focused beam reflectance measurement measurements, the block copolymer was proved to be effective at fixing dissolved and colloidal substances onto papermaking fibers, thus removing these substances from the water phase where they have a tendency to aggregate and form troublesome deposits. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 4040–4046, 2013

INTRODUCTION

The increasing utilization of recirculated white water results in high accumulation of dissolved and colloidal substances (DCS) in the wet-end of modern papermaking processes which incurs heavy pitch and sticky deposition problems, deteriorating machine runnability, product quality while increasing production cost. Polymeric chemicals called fixatives or fixing agents, characterized with high cationic charges and relatively low molecular weights, are often used to decrease the amount of DCS by neutralizing their anionicity, "fixing" them onto fibers and removing them out of the system by web-forming.[1] Polyamine, polyvinylamine, polyethyleneimine, polydiallyldimethyl ammonium chloride are the typical fixatives for this purpose.[2] Ideally, the DCS, especially the colloidal substances (CS), are expected to be attached directly onto wood fibers in a form that they retain their original single particle state (hereafter called "colloidal fixation"), however, it has been discovered that under many circumstances these highly charged polymers preferentially coagulate the colloids into bigger agglomerates.[3–7] Unfortunately, the CS macro-agglomerates can still pass through the paper web during sheet-forming, leading to significant buildup of CS within the whitewater loop. Therefore, in order to keep the size and number of the colloidal aggregates low enough in the wet-end system, it is important to fix the colloids onto wood fibers before they are agglomerated with each other. To successfully achieve this objective, the choice of fixative is critically important.[8–11]

Therefore, in this study, we intended to design a new fixing agent, the structure and functioning mechanism of which are illustrated in Figure 1. The basic idea was to synthesize a block copolymer with uncharged structural unit of acrylamide (AM) and highly charged structure unit of diallyldimethyl ammonium chloride (DADMAC). The DADMAC units are intended to fix the colloids onto fibers via "patching mechanism," while the AM units are intended to separate the CS from each other, so better control of the CS can be achieved.

The present work is therefore to use reversible addition–fragmentation chain transfer (RAFT) polymerization technique to synthesize AM-DADMAC block copolymer (P(AM-b-DADMAC)) with a well defined macro-molecular architecture and low polydispersity, and evaluating its efficiency in DCS fixation by means of turbidity, chemical oxygen demand (COD) and focused beam reflectance measurement (FBRM).
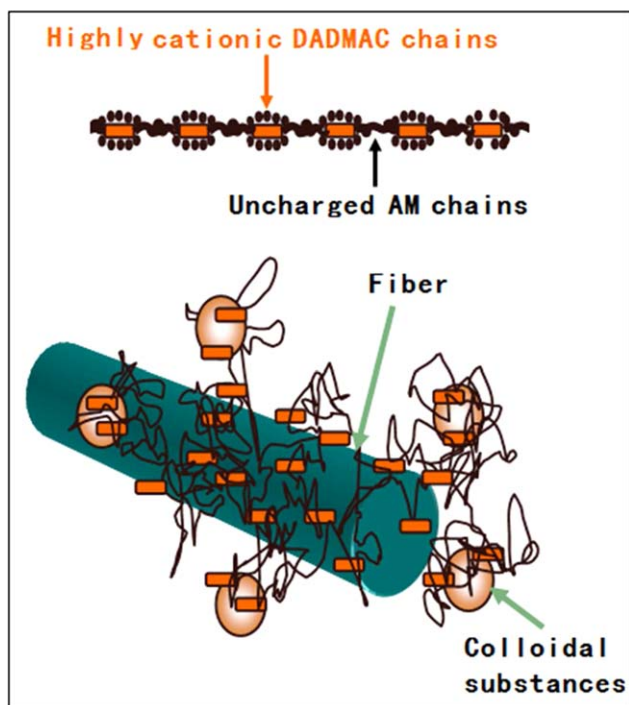
Figure 1. Illustration on the structure of P(AM-*b*-DADMAC) block copolymer and its mechanism of colloidal fixation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials

AM, 98% solid, and DADMAC, 64.2% solution, both commercial products, were obtained from local chemical market. 4,4-Azobis (4-cyanovaleric acid) (i.e., initiator V_{501}) was purchased from Sigma Aldrich Co. LLC. The other chemicals, including ammonium persulfate (A.R. Grade), sodium bisulfite (A.R. Grade), ethanol (A.R. Grade), and acetone (A.R. Grade) were purchased from Jiangtian Chemical Co. Ltd. (Tianjin, China). The nitrogen used was of high-purity grade. The thick stock sample of unbleached thermomechanical pulp (TMP) was obtained from Huatai Paper Co., Ltd. (Shandong, China). The pulp was stored at 4°C before being used to prevent deterioration.

Synthesis of P(AM-*b*-DADMAC) by Semibatch RAFT Polymerization

The synthesis of P(AM-*b*-DADMAC) was carried out by a three-step procedure (as shown in Scheme 1). Firstly, the RAFT agent of trithiocarbonate (2-(2-thiobenzoylsulfonylpropionylamino)-ethanesulfonate, I) was synthesized via the phase transfer catalyzed (PTC) reaction [Scheme 1(a)] according to the literature procedure.[12] It was then polymerized with the first monomer of AM in dimethyl sulfoxide to obtain the macro chain transfer agent of acrylamide [macroCTA-AM, Scheme 1(b), II].[13] The resulting macroCTA-AM was well-characterized with size exclusion chromatography (SEC) and ^{1}H-NMR (DMSO-d_6), and the same macroCTA-AM was used for the subsequent block copolymer syntheses. The structure of macroCTA-AM was confirmed by the appearance of a methyl signal (δ 1.59) of the

RAFT agent and the methylene and methane signal (δ 2.11 and 2.51) and an amide signal (δ 7.20) of AM in the ^{1}H-NMR.

The schematic for synthesizing P(AM-*b*-DADMAC) block copolymer is shown in Scheme 1(c). The monomer DADMAC was continuously fed into the reaction system at a constant rate during polymerization. In the beginning, 12.80 g DADMAC, 2.5 g macroCTA-AM, and 10 mL distilled water were added into a flask equipped with a mechanical stirrer. A certain amount of DADMAC (25.6 g) was dissolved in 22 mL of deionized water, and was inhaled in a syringe equipped with a micrometering pump. After nitrogen was bubbled through for at least 30 min, the polymerization system was heated to 70°C. The initiator ammonium persulfate (APS, 0.11 g) and sodium bisulfite (SBS, 0.11 g) were injected into the flask to initiate polymerization. The DADMAC solution was then fed to the system at a constant rate in 3 h. After completion of DADMAC addition, the polymerization was continued at 70°C for another 7 h, prior to termination by cooling. The resulting product was purified by directly precipitating the sample into a five times excess of ethanol and then washed with acetone. This process was repeated three times to remove homopolymers and unreacted monomers. The purified sample was then dried in vacuum oven at 40°C to constant weight. The monomer conversion was greater than 70% (determined gravimetrically).

Characterization of P(AM-*b*-DADMAC)

The FTIR spectrum of P(AM-*b*-DADMAC) in KBr pellets (1%) was recorded using a FTIR-650 (Tianjin, China) spectrometer, operating between 4000 cm^{-1} and 400 cm^{-1}. The ^{1}H-NMR (400 MHz) spectra of P(AM-*b*-DADMAC) was obtained with a Bruker plus-400 (Bruker, Germany) spectrometer at an operating temperature of 25°C using D$_2$O as a solvent. The values for the average molecular weights M_n and the weight molecular weights M_w of macroCTA-AM and P(AM-*b*-DADMAC) were determined by SEC using a DAWNEOS-Optilab rEX (Wyatt, USA) equipped with a HPLC pump (Waters, USA) and two columns OHpak SB-804 (10 μm) 8.0 × 300 mm^2 and OHpak SB-802.5 (10 μm) 8.0 × 300 mm^2 (Shodex, Japan). The eluent was 0.1M sodium nitrate solution. The flow rate was 0.5 mL/min and the operating temperature was 40°C. The thermal stability
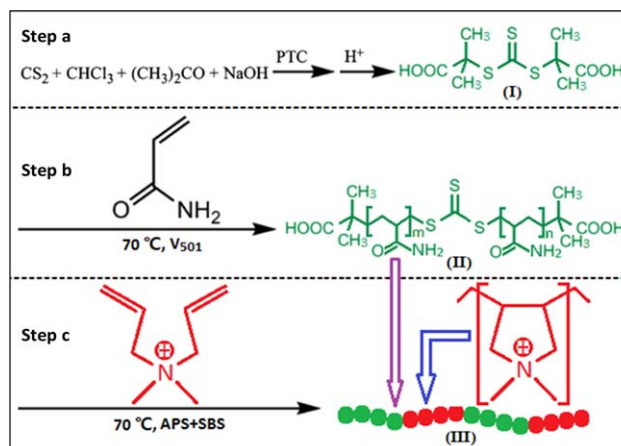
Scheme 1. Synthetic route of P(AM-*b*-DADMAC) using RAFT copolymerization of DADMAC with MacroCTA of AM.

of PAM, PDADMAC, and P(AM-b-DADMAC) were evaluated using thermogravimetric analysis (TGA, Q500, TA, USA). Samples were heated in an aluminum crucible to 600°C at a heating rate of 10°C/min while the apparatus was continually flushed with a nitrogen flow of 40 mL/min. The glass transition temperatures of these polymers were measured on a 204 F1Phoenix heat flux differential scanning calorimeter (DSC, NETZSCH, Germany). The as-prepared samples were first heated to 200°C and kept at this temperature for 5 min to erase any prior thermal history. Then the samples were cooled to −90°C to set the structure to be analyzed by subsequent heating to 200°C. The heating and cooling rates were 10°C/min. Apparent charge density of the P(AM-b-DADMAC) was determined to be 4.25 meq/g by colloidal titration with the standard sodium polyethylene sulfonate (PES-Na) solution using a particle charge detector (Mütek PCD-03, Mütek, Germany).

Wet-End Chemistry Characteristics Measurement

The hardwood TMP was beaten in a Valley beater (ZQS2-45, SUST, Shanxi, China) at 2% consistency to 35°SR (Schopper-Riegler) and diluted to 1% consistency. The fixative was dissolved in water to be 1 g/L. Then 500 mL of the pulp suspension was taken, to which pre-determined volume of the fixative solution (1.25, 2.50, 3.75, 5.00, and 7.50 mL) was added. Then the mixture was agitated for 30 s, diluted to be 0.5% consistency, and put into a dynamic drainage tester (DDJ, DSC 75, Paper Research Materials Inc., USA). The wire equipped with this DDJ was of 200 meshes, i.e., 74 μm. In the DDJ, the pulp suspension was agitated at 800 rpm for another 30 s, then dewatered and all the filtrate was collected for further analysis including, turbidity measurement by a LP2000-11 turbidity meter (Hanna Instrument, Italy), COD measurement by a COD instrument (DR 1010, HACH Co. Ltd., USA), and the number of residual colloidal contaminants and their relative particle sizes determination by a FBRM (S400A, Mettler-Toledo International Inc. USA).

FBRM, also known as scanning laser microscopy, is detailed elsewhere[14-17] and is briefly summarized here. The methodology of this technique is based on a highly focused laser beam scanning across particles in a suspension at a fixed speed. Light is backscattered into the probe whenever the focused laser beam crosses a particle or particle aggregates. The time duration of this backscattered light pulse is measured to calculate the chord length of the particles, and each measured chord length is considered a count. Each second thousands of chords are measured. As a result, a measure of the size distribution of the particles in the suspension is obtained. Statistical parameters from the chord size distribution, for example, the mean chord size and the number of total counts, are monitored. The instrument settings used for these experiments were: samples were stirred at 200 rpm; data acquisition rate was 2 s per data point.

RESULTS AND DISCUSSION

Characterization of P(AM-b-DADMAC)

The FTIR spectrum of P(AM-b-DADMAC) washed with ethanol and acetone is shown in Figure 2. The broad peaks at 3430 and 1656 cm^{-1} indicate the presence of the amide group (—NH) and carbonyl (—CO) stretching vibrations from the AM unit of the copolymer and show the presence of AM in the block copolymer.[18,19] The peaks at 2867, 2944 cm^{-1} and sharp peak at 1475 cm^{-1} could be assigned to methyl and methylene (—CH$_3$ and —CH$_2$) stretching and quaternary ammonium group (—N$^+$(CH$_3$)$_2$(CH$_2$)$_2$) bending vibration of pyrrolidinium rings from the DADMAC unit, respectively.[20,21] The peaks at 3014, 1093, 960, and 854 cm^{-1} could be assigned to methyl (—CH$_3$), sulfur/carbon double bonds (—C=S), carboxyl (—COOH), and sulfur/carbon single bond (—C—S) stretching vibrations, respectively, from the RAFT agent.[12] The FTIR data indicated that the P(AM-b-DADMAC) included the organic functional groups of AM, DADMAC, and RAFT agent.

To confirm the block cyclopolymerization of DADMAC with macroCTA-AM, ^{1}H-NMR spectrum of P(AM-b-DADMAC) was used. As shown in Figure 3, the peaks at 1.473–1.491 ppm were the methyl (①) protons of RAFT agent, demonstrating that the end groups of the resulting polymer were produced from the trithiocarbonate RAFT agent.[13] However, such peaks were not found in the spectrum of P(AM-co-DADMAC), which was polymerized by Lu et al.[22] under conditions of conventional free-radical polymerization. Peaks due to methylene groups of the main chain from PAM (②) and PDADMAC (⑨) in the ^{1}H-
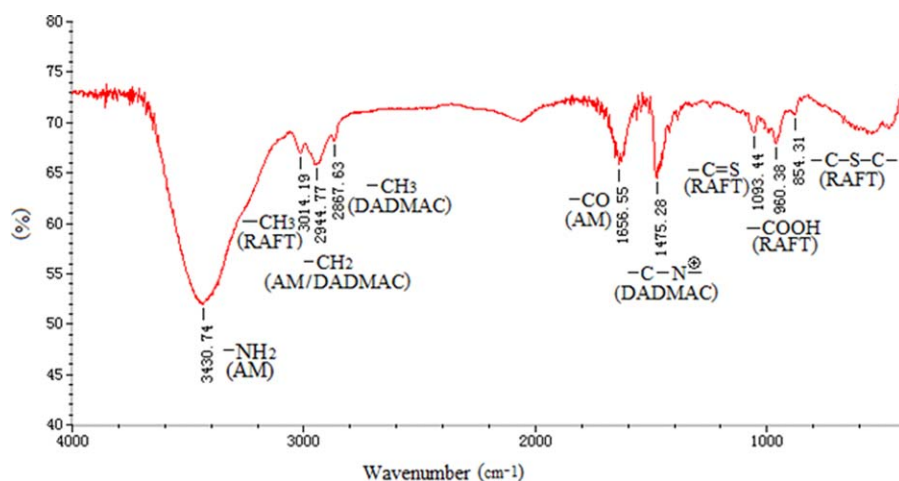

Figure 2. FTIR spectra of P(AM-b-DADMAC). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
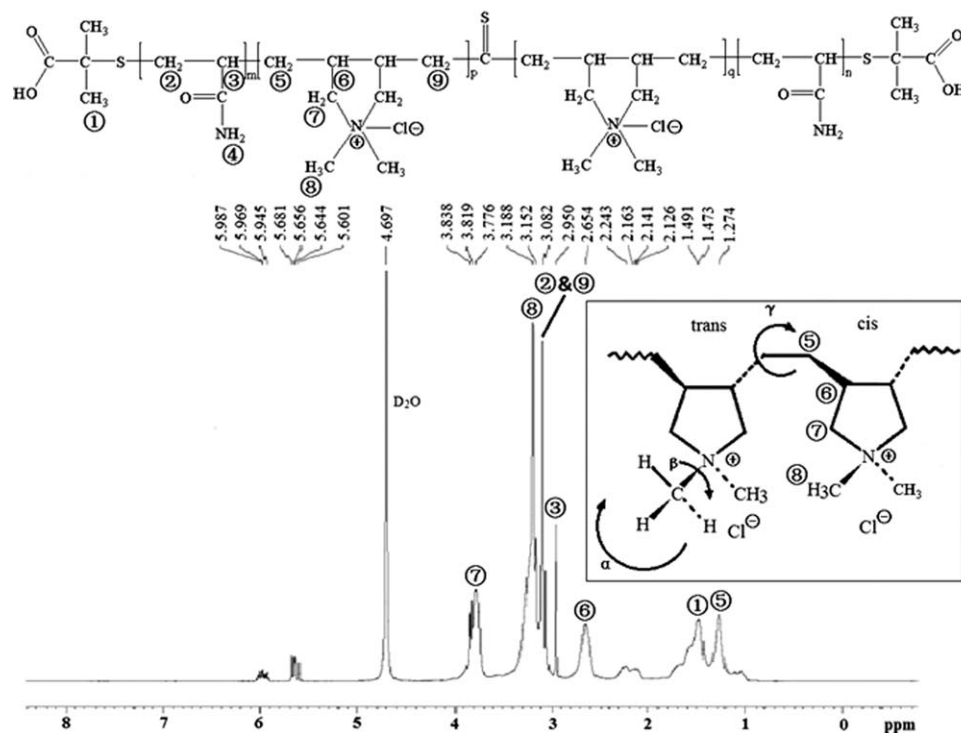
Figure 3. ^{1}H-NMR spectra of P(AM-b-DADMAC) (D$_2$O).

NMR spectrum were overlapped, and shifted from around 2.00 ppm to 3.082 ppm compared with the ^{1}H-NMR spectrum of random copolymer of AM and DADMAC,[22] suggesting that reacted RAFT agent contributed to blocking. These characteristics are in a good agreement with the results previously reported in the literature for aqueous RAFT polymerization of DADMAC with other xanthate transfer agents of AM.[23] Methyl (⑧), methylene (⑦), and methane (⑥) non-equivalent proton shifts were observed in 3.152–3.188 ppm, 3.766–3.838 ppm, and 2.243 ppm regions, respectively. Splitting of these peaks indicated the presence of *cis* and *trans* configurations from five-membered pyrrolidinium rings of the ring closing cyclopolymerization of DADMAC,[24] which was identical to what was first described by Lancaster et al.[25] and later confirmed by Assem et al.[26] by using a trithiocarbonate RAFT agent. Perhaps owing to the rapid amide hydrogen exchange with the solvent (D$_2$O), the amide group (④) signal of AM was not observed in the ^{1}H-NMR spectrum. The ^{1}H-NMR results demonstrated that the monomer DADMAC was successfully blocked with macroCTA-AM.

The values for the average molecular weights M_n and the weight molecular weights M_w of macroCTA-AM and P(AM-b-DADMAC) were determined by SEC (as shown in Figure 4). The molecular weight of macroCTA-AM was 43,400 g/mol and the polydispersity index (PDI) was 1.285. As a consequence of RAFT polymerization mediated by the trithiocarbonate CTA of AM, an controlled block copolymer, P(AM-b-DADMAC), was formed with a molecular weight of 73,780 g/mol and PDI = 1.327. Furthermore, it clearly shows that the SEC peak of the block polymer was essentially symmetrical unimodal without shoulder and tailing, which indicated that the macro-AM

enabled the controlled polymerization of DADMAC. The results of FTIR, NMR, and SEC characteristics confirmed the successful polymerization of controlled PDI and composition of P(AM-b-DADMAC) block copolymer.

Illustrated in Figure 5 are the TGA thermograms for the P(AM-b-DADMAC) block copolymer, PAM, and PDADMAC homopolymers. The P(AM-b-DADMAC) was seen to have three decomposition stages. The first weight loss was due to the residual and impurities from solvents and moisture. The second degradation started around 258.78°C and up to around 388.68°C, showing that about 44.06% of the product was degraded. The
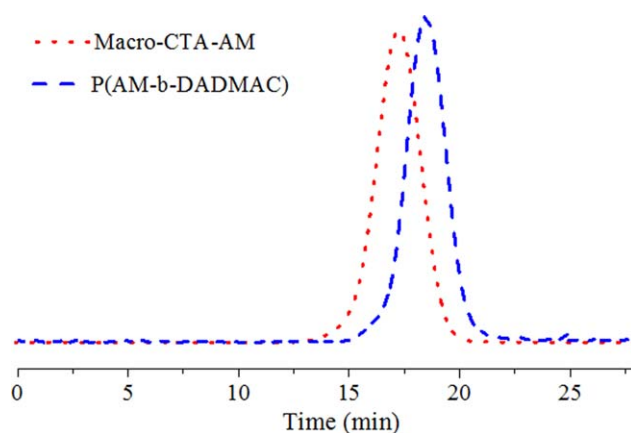

Figure 4. SEC traces of Macro-CTA of AM and P(AM-b-DADMAC). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
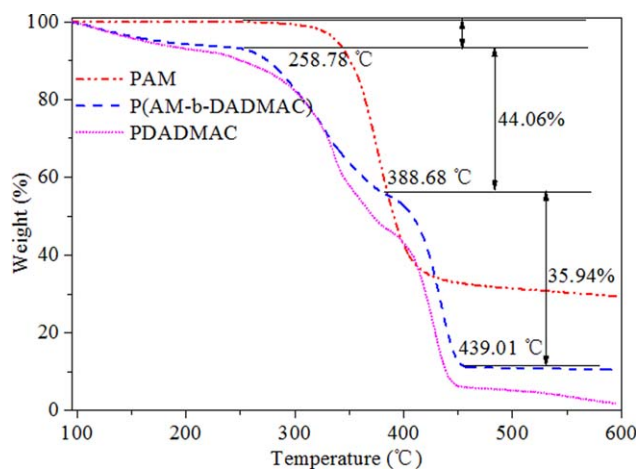
Figure 5. TGA of PAM, P(AM-*b*-DADMAC), and PDADMAC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. Turbidity and COD of DCS particles, after removing fibers by filtration, as a function of P(AM-*b*-DADMAC). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

weight loss could be attributed to the exothermic decomposition of the amide groups and the decomposition of other parts from RAFT agent associated with the elimination of carboxyl groups. The last degradation took place at about 388.68°C to 439.01°C, where about 35.94% of the product was degraded, corresponding to the slow decomposition of the rest of the polymer (main PDADMAC chain). The last degradation of P(AM-*b*-DADMAC) copolymer was higher than that of the PDADMAC homopolymer. This could be attributed to the exothermic decomposition nature of the energetic segment (trithioesters and amide groups), which could enhance the degradation of other parts from the copolymer. In addition, the TGA curve of P(AM-*b*-DADMAC) was similar to PDADMAC, which could be attributed to the higher content of DADMAC segments in the block copolymer.

The DSC thermogram of the P(AM-*b*-DADMAC) block copolymer, PAM, and PDADMAC homopolymers are shown in Figure 6. The block copolymer shows a glass transition
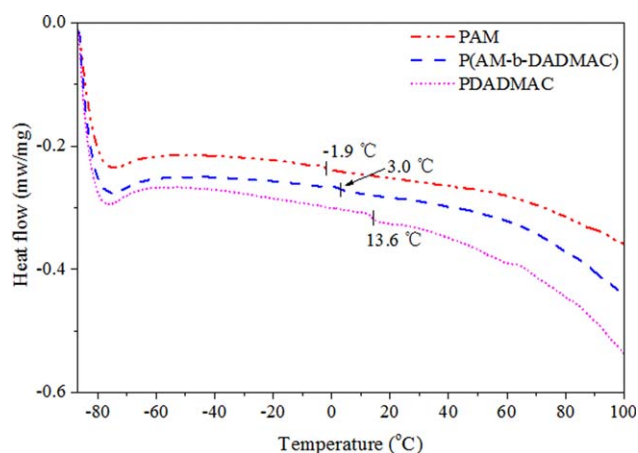

Figure 6. DSC spectrum of PAM, P(AM-*b*-DADMAC), and PDADMAC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
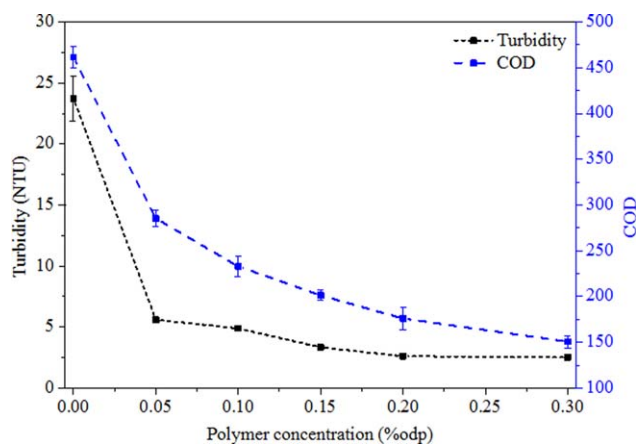
temperature (T_g) at about 3.0°C, which is between the T_g of the two homopolymers. This could be attributed to the miscibility of two different segments with each other. It indicates that there is no phase separation of the copolymer when the T_g of two constituent monomers are closer (PAM -1.9 and PDADMAC 13.6°C, respectively). Thermal analysis results of DSC and TGA provide further confirmation of the interaction between the trithioesters groups of RAFT agent and alkenyl groups of AM and DADMAC in the final product, as can be seen from the exothermic decomposition behavior.

Wet-End Characteristics of P(AM-*b*-DADMAC)

The change in the turbidity and COD of filtrates from suspensions containing a mixture of DCS and fibers were measured to evaluate the performance of the P(AM-*b*-DADMAC) regarding the removal of DCS from the papermaking system through sheet forming. It can be seen from Figure 7 that upon addition of P(AM-*b*-DADMAC), the turbidity of the filtrate significantly decreased from an initial value of 24 NTU (nephelometric turbidity unit) to about 5 NTU at the dosage of 0.05% based on oven-dried pulp (hereafter abbreviated as %odp). Further P(AM-*b*-DADMAC) addition resulted in a gradual decrease in turbidity that reached a plateau about 2 NTU. The reduction in turbidity is a sign of how well the suspended substances in the pulp slurry (including fines and CS) have been retained or fixed onto paper web.[27] In this meaning, the P(AM-*b*-DADMAC) is suitable for removing the CS from the system.

The COD value of the filtrate also decreased after the pulps were treated with the P(AM-*b*-DADMAC), and more fixatives led to lower COD value. It is known that DCS includes a lot of organic components, e. g., hemicelluloses, pectins, lignans, and lignins,[28] which are the main contributors to COD. The reduction of COD value indicated that these substances have been also removed quite well by P(AM-*b*-DADMAC). With the increasing of the concentration of P(AM-*b*-DADMAC), turbidity and COD value of the filtrate decreased significantly, indicating the block copolymer has higher efficiency for retaining both the colloidal material and soluble organic components onto the fiber.
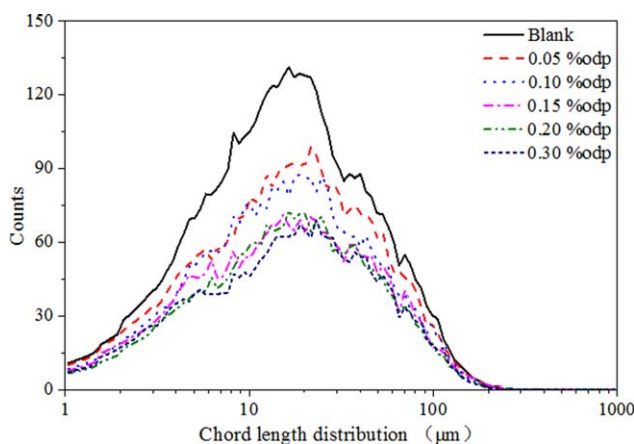
Figure 8. Chord length distribution of the pulp filtrate after treatment with P(AM-*b*-DADMAC). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of P(AM-*b*-DADMAC) on DCS Particle Size Distribution

In addition to the turbidity and COD measurement described earlier, other traditionally used analytical methods to determine the DCS load in papermaking process waters includes cationic demand, total organic carbon (TOC) measurement, and chromatography. While these methods provide additional information on the behavior of individual components in the process stream, they have difficulties in differentiating between the colloidal fixation of these colloidal species and their agglomeration.[3–7] As the agglomeration of DCS can ultimately lead to deposition, the use of traditional measurements to identify the best fixative and its optimal dose may not yield much success in removing DCS. Fortunately, the combination with the FBRM allows an unambiguous analysis, in that in the case of colloidal fixation, the total number of particles will be reduced upon addition of the polymer, and in the case of agglomeration, the larger particles will be clearly observed.[14–17]

To gain insight into the efficiency of DCS fixation with the novel block copolymer, FBRM experiments were performed on the DDJ filtrates obtained from the pulp treated with different dosages of P(AM-*b*-DADMAC), and the results are shown in Figure 8. For the blank sample without fixative treatment, it can be seen that the distribution is centered around 20 μm (Note: FBRM chord length is generally much larger than the real size of colloids.[29–31]). Upon addition of the fixative, remarkable decreases in the total number of particles were clearly seen. Interesting enough, any P(AM-*b*-DADMAC) dose caused no remarkable particle size growth, which indicated that the colloid substances were not incorporated into macroaggregates. These observations justified the high efficiency of the block copolymer in fixing DCS onto papermaking fibers.

CONCLUSIONS

Poly(AM)-poly(DADMAC) block copolymer (P(AM-*b*-DAD-MAC)) was synthesized using a semibatch RAFT cyclopolymerization of DADMAC in the presence of chain transfer agent of AM (macroCTA-AM) with continuous feeding of DADMAC. The average molecular weight (M_n) and PDIs of the resulting P(AM-*b*-DADMAC) are of 73,780 g/mol and 1.327, respectively. Thermal analysis of the block copolymer showed a single glass transition temperature in DSC, due to the miscibility of the two different segments with each other, and two clear degradation temperatures in TGA. The decrease of turbidity and COD value showed the higher efficiency of P(AM-*b*-DADMAC) in removing the DCS from the system. The FBRM results confirmed that the novel block copolymer was effective in decreasing the number of residual particles in the slurry filtrate while at the same time minimizing the potential for agglomeration among the particles.

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