Reactive & Functional Polymers 70 (2010) 972-979

Contents lists available at ScienceDirect

Reactive & Functional Polymers

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



Grafting modification of ramie fibers with poly(2,2,2-trifluoroethyl methacrylate) via reversible addition–fragmentation chain transfer (RAFT) polymerization in supercritical carbon dioxide

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ARTICLE INFO

Article history: Received 19 May 2010 Received in revised form 13 October 2010 Accepted 14 October 2010 Available online 21 October 2010

Keywords: Ramie fiber Supercritical carbon dioxide Grafting modification 2,2,2-Trifluoroethyl methacrylate RAFT

ABSTRACT

Reversible addition–fragmentation chain transfer (RAFT) polymerization was used to control the grafting of 2,2,2-trifluoroethyl methacrylate (TFEMA) with ramie fibers in supercritical carbon dioxide (scCO₂). The hydroxyl groups of the ramie fibers were converted to 2-dithiobenzoyl isobutyrate as the RAFT chain transfer agent (cellulose-CTA). Then, the subsequent grafting with TFEMA was mediated by RAFT polymerization in the presence of 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (ECPDB) as the free RAFT chain transfer agent (free CTA). The modified ramie fibers were highly hydrophobic with water contact angles of up to 149°. Size exclusion chromatography showed narrow polydispersity (PDI = 1.28) of the grafted poly(TFEMA) chains. This grafting polymerization process is a novel and environmentally friendly approach for the preparation of functional grafted copolymers utilizing ramie fiber biomass.

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1. Introduction

Reversible addition-fragmentation chain transfer (RAFT) polymerization [1,2], together with other equally important methods such as nitroxide-mediated polymerization (NMP) [3] and atom transfer radical polymerization (ATRP) [4], has revolutionized "living"/controlled radical polymerization. Compared to conventional free radical initiated polymerization [5-9], these methodologies can utilize a wider range of functional monomers using reaction conditions that are less demanding (e.g., lower reaction temperature and tolerance to oxygen). Cellulose, the most abundant and inexpensive biodegradable and renewable organic raw material in the world, has been widely studied over the past few decades. There has been increasing interest in the applications of natural cellulose, due to the decreasing reserves of fossil fuels and an increasing focus on environmental protection. Recently, growing interest in this field has been directed toward the production of new functional grafted copolymers through the modification of natural cellulose-based fibers using polymers. The resulting materials preserve the advantages of natural polymers, such as renewability, low cost and low density, ease of surface modification and recycla-

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bility [10]. For instance, grafted copolymers with antibacterial surfaces and sorption agents for the removal of heavy metals have been reported [11,12]. However, the high water absorption of hydrophilic cellulose fibers limits their large-scale applications due to the formation of weak interactions between natural fibers and polymers [13]. Thus, huge efforts have been devoted to the investigation of new processes and efficient methods to enhance compatibility with synthetic matrix polymers and to reduce the hydrophilicity of natural fibers. A popular methodology is the controlled chemical grafting modification of the cellulosic surface with hydrophobic monomers such as methyl methacrylate, styrene, acrylonitrile and butadiene [14]. Perrier's group utilized the RAFT polymerization technique to graft a variety of functional monomers onto the surface of cellulose in the form of filter paper, obtaining hydrophobic and antibacterial cellulose fiber composites [15]. Barner-Kowollik and co-workers [16] developed the RAFT technique to graft polymers onto the surface of cellulose by means of γ -radiation and mediation of free RAFT chain transfer agents, which overcame prior functionalization of the surface; the molecular weight and polydispersity were estimated from the homopolymers in the system.

Supercritical fluids are the basis for the novel "green" processes that have been developed as environmentally friendly analogs to conventional systems [17] and can be acceptable replacements for some organic solvent systems. Supercritical fluids are highly compressed gases that combine the properties of gases and liquids;



^{1381-5148/\$ -} see front matter © 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.reactfunctpolym.2010.10.007

they have the solvating power of liquids and the mass transport properties of gases. Supercritical carbon dioxide (scCO₂) has been the focus of much research because of its low critical parameters ($T_c = 31.0 \degree C$, $P_c = 7.38$ MPa) [18], lack of toxicity and non flammability, and it has been found to be an effective polymerization medium [19].

Ramie fiber, a member of the Urticaceae family, is produced mainly in China and several other Asian countries [20]. Ramie fiber is employed in many fields including clothing fabrics, twines and industrial packaging due to its excellent features and in particular, its higher cellulose content (65–75 wt%) compared with bast fibers such as hemp, flax and jute [21,22]. However, its characteristically high degree of crystallinity and chain orientation restricts the utilization and exploitation of ramie fibers. Consequently, it is very important to find a way to more efficiently utilize the abundant natural ramie resource in China and, therefore, produce more profit.

2.2.2-Trifluoroethyl methacrylate (TFEMA) is a monomer with low fluorine content (34%) and can be synthesized by the reaction of 2,2,2-trifluoroethanol and methacryloyl chloride. The homopolymer of TFEMA (PTFEMA) is a transparent and amorphous polymer that has high water repellency and stain resistance because it contains fluorine in its side chain [23]. PTFEMA is used in various coating applications because of its excellent heat and chemical resistance, low refractive index, weatherability, non-cohesiveness, water and oil repellency, and electric insulating properties [24]. Recently, TFEMA-containing homopolymers and copolymers have found applications in areas such as cladding materials for optical fibers [25]. TFEMA can be polymerized via free radical mechanisms [26]. In addition, supercritical carbon dioxide (scCO₂) can be used as a polymerization medium for TFEMA, replacing some organic solvents [27]. When PTFEMA is synthesized by the solution polymerization method, the initial monomer and final polymer must be soluble in CO₂. In that case, solution polymerization overcomes many of the disadvantages of bulk polymerization [28]. The physical properties of scCO₂ are tunable; the density can be controlled via manipulation of temperature and/or pressure. CO₂ can be removed by simple depressurization after the reaction is complete [28.29]. Lacroix-Desmazes and co-workers [30] reported a composite preparation that uses the RAFT technique in scCO₂. Zetterlund et al. [31] and Oh [32] summarized that the polymerization process in $scCO_2$ is a controlled radical polymerization (CRP), especially due to the excellent inertial property of $scCO_2$, which does not lead to chain transfer or chain termination during the polymerization.

In the present study, TFEMA was polymerized from the surface of the ramie fibers via the RAFT technique mediated by a free chain transfer agent in scCO₂, to obtain grafted copolymers with hydrophobic surface properties. Scheme 1 shows the synthesis pathway of the cellulose-based macromolecular RAFT chain transfer agent and the cellulose-g-PTFEMA copolymer, mediated by the RAFT technique in the presence of 2-(ethoxycarbonyl) prop-2-yl dithiobenzoate (ECPDB) as the free chain transfer agent.

2. Experimental

2.1. Materials

Ramie fiber, obtained from the Institute of Bast Fiber Crops at the Chinese Academy of Agriculture Sciences (CAAS), was dried for 24 h at 60 °C before use. All solvents, monomer and reagents were of the highest purity available and were used as received. 2,2'-Azobis(isobutyronitrile) (AIBN, AR grade) (Shanghai Shanpu Chemical Co. Ltd., China) was purified by recrystallization twice from ethanol, dried at room temperature in a vacuum oven, and stored in a freezer. 2-(Ethoxycarbonyl)prop-2-yl dithiobenzoate (ECPDB) was synthesized according to the reported procedure [33]. TFEMA (99+%) was provided by Weihai New Era Chemical Co. Ltd., China. It was pretreated by passage through an alumina column to remove the inhibitor (4-methoxyphenol, MEHQ), then purified by vacuum distillation before use. Carbon dioxide (99.99% purity) was purchased from Messer (China) and used as received. Bromobenzene and carbon disulfide (AR grade) were obtained from Tianjin Fuchen Chemical Co. Ltd., China and distilled with desiccant before use under reduced pressure and atmospheric pressure, respectively. 2-Bromoisobutyryl bromide (BIBB) (CP grade) (Yancheng Kelida Chemical Co. Ltd., China) was used directly and N-methyl-2-pyrrolidone (NMP) (Tianjin Fuchen Chemical Co. Ltd., China) was dried over molecular sieves (4 Å)



cellulose-g-PTFEMA

Scheme 1. Synthesis of the cellulose-g-PTFEMA copolymer mediated by the RAFT technique in scCO₂.

for at least 3 days before use. Ethyl 2-bromoisobutyrate (98+%) was purchased from Alfa Aesar. Diethyl ether, *n*-hexane, iodine plate (99.8+%) and magnesium turnings (British Drug Houses Laboratory Chemicals Group, England) were used without further purification. The scCO₂ apparatus was designed and fabricated by our group to withstand a high pressure and temperature.

2.2. Pre-treatment of ramie fiber cellulose

Ramie fiber was cut into 3.2 g segments and dried at 60 °C overnight (the chemical formula of the cellulose fiber is $(C_6H_{10}O_5)_n$. There are three hydroxyl groups in each unit of cellulose fiber. Therefore, for 3.2 g of cellulose fiber, the number of active hydroxyl groups was ((3.2 g/162 g/mol) × 3 = 0.06 mol). These were mixed in a two-neck round bottom flask with sufficient NMP to cover the ramie fiber. After ultrasonic treatment for 30 min at 25 °C, the ramie fiber was swollen for another 24 h and then used for the next step without any further pre-treatment.

2.3. Synthesis of cellulose ester (cellulose-OBIB) using 2-bromoisobutyryl bromide (BIBB)

A solution containing an excess of BIBB (22.25 mL, 0.18 mol) and 35 mL of NMP (0.36 mol) was used as the proton scavenger and was added dropwise to the swollen ramie fiber under an argon atmosphere at 0 °C (ice-water bath). The molar ratios of cellulose hydroxyl group, BIBB and NMP were 1:3:9. The mixture was heated with slow stirring at 60 °C in an oil bath for 24 h, with the flask sealed against the ingress of air. The nut-brown product was rinsed thoroughly several times with anhydrous ethanol to completely remove any unreacted BIBB and salt. The yellow final product (termed cellulose-OBIB) was vacuum dried at 60 °C overnight. The analytical data for this product were as follows: EA: Br, 20.78 wt%. Average degree of substitution (DS) at the esterification step = 1.00 (28.47% substitution).

2.4. Synthesis of cellulose-based RAFT chain transfer agent (cellulose-CTA)

Phenylmagnesium bromide was prepared from magnesium turnings (1.50 g, 0.062 mol) and bromobenzene (6.7 mL, 0.064 mol). The solution was warmed to 40 °C in a two-neck flask and an excess of a mixture of carbon disulfide (18.7 mL, 0.31 mol) and anhydrous THF (10 mL) was added dropwise over 20 min. The dark-brown mixture was allowed to react at 40 °C for 3 h. All of the above operations were carried out under an argon atmosphere. Then 2.40 g of cellulose-OBIB was added to the flask together with 30 mL of anhydrous THF. The reaction mixture was heated at 80 °C for 24 h. The solid product was washed thoroughly with dilute hydrochloric acid and THF and subjected to a Soxhlet extraction to completely remove the unreacted reagents. The resulting darkyellow sample (termed cellulose-CTA) was vacuum dried at 60 °C overnight. The analytical data for this product were as follows: EA: Br, 6.12 wt%; S, 10.86 wt%. The average degree of conversion of the OH group to cellulose-CTA in this step was 0.27 (8.97% substitution).

2.5. Synthesis of free CTA 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (ECPDB)

The synthesis of the free chain transfer agent ECPDB employed in the RAFT process was modified according to the literature [33]. A solution of phenylmagnesium bromide made from bromobenzene (6.28 g, 0.040 mol) and magnesium turnings (1.00 g, 0.041 mol) in dry THF(60 mL) was warmed to 40 °C, and carbon disulfide (3.05 g, 0.041 mol) was added dropwise over 20 min at a rate such that the reaction temperature was maintained at 40 °C; the reaction was

then carried out at 60 °C for 3 h. All of the above operations were carried out under an argon atmosphere. Ethyl 2-bromoisobutyrate (7.00 g, 0.04 mol) was added to the resultant dark-brown mixture over 15 min, after which the reaction mixture was maintained at 80 °C for 60 h. Ice-cold water (50 mL) was then added and the organic products were repeatedly extracted with diethyl ether (100 mL total). The combined ether extracts were washed with water and brine and dried over anhydrous magnesium sulfate for 24 h. After removal of the solvent using a rotary evaporator and purification by column chromatography on silica with *n*-hexane/ diethyl ether (9:1) as the eluent, ECPDB was obtained as a red oil (34.2% yield). ¹H NMR (CDCl₃) results are listed for δ (ppm): 1.21 (t, 3H, CH₂CH₃), 1.41 (a) (s, 3H, CH₃^aCCH₃^b), 1.66 (b) (s, 3H, CH₃^aCCH₃^b), 4.03 (q, 2H, OCH₂CH₃), 7.28 (dd, 2H, *m*-ArH), 7.40 (dd, 1H, *p*-ArH), 7.86 (d, 2H, *o*-ArH). ¹³C NMR (CDCl₃), δ (ppm): 13.57 (CH₃CH₂), 60.82 (CH₃CH₂), 172.41 (C=0), 54.69 (CH₃CCH₃), 24.82 (CH₃CCH₃), 221.21 (C=S), 136.2 4 (Ar-C1), 128.10 (o-ArC), 126.13 (m-ArC), 131.87 (p-ArC).

2.6. Synthesis of cellulose-g-PTFEMA via RAFT technique mediated by free CTA in $scCO_2$

Cellulose-CTA (0.18 g, 0.30 mmol), free CTA (0.0804 g, 0.30 mmol), and the initiator (AIBN) (0.005 g, 0.03 mmol) were added to a 30 mL reactor. The reactor was purged with low pressure CO₂ and alternately degassed several times with a vacuum pump to remove the air in the system. After sealing the outlet of the reaction system, TFEMA (12.6 g, 75 mmol) was added to the reactor at a constant CO₂ flow rate (approximately 1 mL min⁻¹). Pressurized CO₂ was then added to fill approximately half of the reactor, and heating of the reactor was initiated. The molar ratios of TFEMA:CTA:initiator were kept constant in all reactions at 250:1:0.1. Finally, the reaction system was pressurized to 25 MPa by feeding additional CO₂ and heated to 70 °C with stirring for the scheduled reaction time. After completion of the reaction, the reactor was cooled with ice/water and the CO₂ was released when the temperature of the reactor had decreased to room temperature. The crude product was collected and rinsed with THF to remove the unreacted monomer PTFEMA not attached to the surface of ramie fiber and residual initiator. Monomer conversion in the solution was determined by ¹H NMR spectroscopy. The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of homo-PTFEMA were measured with SEC after precipitation in *n*-hexane. The crude solid product was Soxhlet extracted with THF for 72 h to remove the soluble materials noted above. Finally, the dark-yellowish product known as cellulose-g-PTFEMA was vacuum dried at 60 °C overnight. The monomer conversion was 90% from ¹H NMR. The grafting ratio was determined using Eq. (1) as $G_{\text{cellulose-g-PTFEMA}} = 27\%$.

2.7. Grafting ratio

The grafting ratio (wt.%) of cellulose-g-PTFEMA was calculated using the formula

$$G(\mathsf{wt}\%) = (W_{\text{cellulose-g-PTFEMA}} - W_{\text{cellulose-CTA}}) \times 100/W_{\text{cellulose-CTA}}$$
(1)

where $W_{\text{cellulose-g-PTFEMA}}$ is the dry weight of the graft copolymer and $W_{\text{cellulose-CTA}}$ is the dry weight of the macromolecular RAFT chain transfer agent (cellulose-CTA).

2.8. Characterization

2.8.1. Elemental analyses (EA)

The surfaces of the samples were analyzed for Br, S and F content by energy dispersive spectrometry (EDS) (EDAX Co. Ltd., USA).

2.8.2. Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of the raw and modified ramie fibers in KBr pellets were obtained with a Nicolet 870 spectrometer. Approximately 2 mg of sample was mixed with 200 mg of spectroscopic grade KBr and the FT-IR spectra were recorded in the range of 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹ with 32 scans per sample. The baseline was autocorrected for all spectra by using the EZ OMNIC (Edi. 6.1a) spectrum software.

2.8.3. Nuclear magnetic resonance spectroscopy (NMR)

¹H NMR and ¹³C NMR spectra were recorded with a superconducting Fourier digital NMR spectrometer (Bruker, AVANCE 300 MHz). CH₂Cl₂ was used as solvent and TMS was used as a reference for the characterization of the free chain transfer agent 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (ECPDB) and for the assessment of monomer conversion.

2.8.4. X-ray diffraction (XRD)

For the X-ray diffraction (XRD) measurements, ramie fiber, cellulose-OBIB, cellulose-CTA and cellulose-g-PTFEMA were formed into small pellets with a laboratory press. XRD was carried out using a D/Max-3c diffractometer (Rigaku Co., Japan). The diffracted intensity of Cu K α radiation (wavelength 0.1542 nm, at 50 kV and 40 mA) was measured in the 2 θ range of 5–50°.

2.8.5. Thermogravimetric analysis (TGA)

Thermogravimetric analyses of the ramie fibers, cellulose-*g*-PTFEMA, and homo-PTFEMA were carried out using a thermoanalyzer system (model Q600SDT, TA Co. Ltd., USA) in a nitrogen atmosphere. Samples of approximately 5 mg were heated from room temperature to 500 °C at a rate of 10 °C min⁻¹. The onset temperature, end decomposition temperature and residual mass were calculated by the TA Instruments Universal Analysis 2000 software. All samples were vacuum dried at 60 °C for one day prior to measurements.

2.8.6. Differential scanning calorimetry (DSC)

The thermal properties of ramie fiber, cellulose-g-PTFEMA, and homo-PTFEMA were studied by DSC using a thermoanalyzer system (model Q800SDT, TA Co. Ltd., USA) with the TA Instruments Universal Analysis 2000 software. Samples of approximately 5 mg were heated in a nitrogen atmosphere from room temperature to 500 °C at a rate of 10 °C min⁻¹. All samples were vacuum dried at 60 °C for 24 h prior to measurements.

2.8.7. Contact angle measurements

A video-based contact angle measuring device, OCA 20 (Dataphysics Co., Germany), was used to determine the degree of hydrophobicity of the ramie fiber samples before and after grafting modification. A drop of water was placed on the sample surface and the contact angle was measured at 25 °C.

2.8.8. Scanning electron microscopy (SEM)

SEM photomicrographs of the ramie fibers before and after grafting were recorded at a range of magnifications with a Quanta 200 environmental scanning electron microscope (Philips-FEI Co., Holland) equipped with a secondary electron detector, at an accelerating voltage of 20 kV. The dried samples were coated with gold using a diode sputter coating unit.

2.8.9. Size exclusion chromatography (SEC)

The number-average molecular weights (M_n) and polydispersity indexes (M_w/M_n) of homopolymers formed in the graft polymerization solution were measured via SEC. This was conducted at 35 °C, with THF as the eluent and a flow rate of 1 mL min⁻¹, using a Waters 2410 instrument equipped with three Waters μ -Styragel columns (HT4, HT5 and HT6). The system was calibrated with polystyrene (PSt) standards with molecular weights in the range of 200 to 10^6 g mol⁻¹.

3. Results and discussion

3.1. Synthesis of cellulose ester (cellulose-OBIB) and cellulose-based RAFT chain transfer agent (cellulose-CTA)

The hydroxyl groups of the ramie fibers were treated with 2-bromoisobutyryl bromide (BIBB) and then converted to a cellulose-based thiocarbonyl-thio compound (cellulose-CTA) as the RAFT chain transfer agent (CTA). The formation of cellulose-OBIB and cellulose-CTA were detected by elemental analyses and FT-IR spectroscopy. From the elemental analysis results for cellulose-OBIB, the bromine content (wt.%) of the modified cellulose ester was 20.96%, which indicated that on average, 28.47% of the hydroxyl groups of raw ramie fibers were substituted by OBIB. The average sulfur content of cellulose-CTA was 10.86%, which demonstrated the successful loading of the RAFT agent attached to the surface of the ramie fibers for the subsequent copolymerization via RAFT polymerization. Additionally, the bromine content of cellulose-CTA was less than that of the precursor cellulose-OBIB, which indicates that cell-OBIB was substituted by the cellulose-based RAFT agent. Comparison of the FT-IR spectra (Fig. 1) of ramie fiber and cellulose-OBIB clearly show a very strong C=O stretching band at 1736 cm⁻¹ and weak bands at 1283 cm⁻¹ for the C–O stretch mode for cellulose-OBIB. The FT-IR spectrum of cellulose-CTA shows C=S stretching bands at 1264 and 1511 cm⁻¹, which verifies the synthesis of the cellulose-based RAFT agent.

3.2. Synthesis of cellulose-g-PTFEMA via RAFT technique mediated by free CTA in $scCO_2$

A series of graft copolymers were prepared via RAFT polymerization for different reaction times (Fig. 2). The grafting ratios were determined by gravimetric analysis and Eq. (1). The grafting ratio increased with increasing reaction times of up to 36 h and was held constant at around 26% for a longer reaction time. The reaction time-dependence of the grafting ratio is ascribed to the limited number of substitution sites of the RAFT chain transfer agent on the ramie fiber surface. It can be concluded that the seeping of the CO_2 molecules into the fibers caused the fibers to swell during the polymerization in scCO₂. The polymerization mixture was



Fig. 1. FT-IR spectra of (a) ramie fiber, (b) cellulose-OBIB, and (c) cellulose-CTA.



Fig. 2. Effect of polymerization time on the grafting ratio of cellulose-g-PTFEMA.



Fig. 3. FT-IR spectrum of cellulose-g-PTFEMA (24 h, 25% graft ratio).

heterogeneous in scCO₂ because the ramie fibers cannot dissolve in scCO₂. A majority of grafted polymers exist on the fiber surface due to the hydroxyls of the ramie fibers, which are barely exposed on the surface, allowing the grafting reaction to occur on the surface of ramie fiber. Therefore, polymerization did not occur on the inside of the ramie fibers. Soxhlet extraction was used to remove the unreacted reagents. FT-IR spectra (Fig. 3) of the cellulose-*g*-PTFEMA graft copolymer show a strong C=O stretching vibration at 1748 cm⁻¹. The bands at 1284 and 655 cm⁻¹ are attributed to stretching and bending vibrations of the C—F bonds, respectively. All of these new characteristic bands indicate successful grafting between the polymers and the ramie fibers.

3.3. XRD analysis

XRD data gave important information about the graft polymerization procedure. The XRD patterns of the ramie fiber, cellulose-OBIB, cellulose-CTA, cellulose-g-PTFEMA (24 h, 25% graft ratio) and cellulose-g-PTFEMA (36 h, 27% graft ratio) are shown in Fig. 4. The degree of crystallization decreased as the ramie fiber was converted to cellulose-OBIB and then to cellulose-CTA, which is ascribed to the transformations that destroy the hydrogen bonds in ramie fiber. Additionally, as shown in Fig. 4a–d, these samples had diffraction peaks at (2 θ) 14.8, 16.3, 22.6, and 34.0° which are



Fig. 4. X-ray wide-angle scattering curves of (a) ramie fiber, (b) cellulose-OBIB, (c) cellulose-CTA, (d) cellulose-g-PTFEMA (24 h, 25% graft ratio), and (e) cellulose-g-PTFEMA (36 h, 27% graft ratio).



Fig. 5. (1) Thermogravimetry and (2) first derivative thermogravimetry curves of (a) ramie fiber, (b) cellulose-g-PTFEMA (24 h, 25% graft ratio) and (c) homo-PTFEMA.

typical of the cellulose I crystalline form and are in agreement with a previous report [34]. However, Fig. 4e shows that the diffraction peaks at 14.8° and 16.3° were not present in the final product



Fig. 6. DSC thermograms of (a) ramie fiber, (b) cellulose-g-PTFEMA (24 h, 25% graft ratio), and (c) homo-PTFEMA.



Scheme 2. Structures of chain transfer agents ECPDB and cellulose-CTA.

because $scCO_2$ disrupts the structure of cellulose by penetrating into the ramie fiber [35]. The change of structure of the ramie fiber cellulose indicates that there is a limiting experimental condition for the preparation of highly hydrophobic ramie fiber-based graft copolymers in $scCO_2$.

3.4. Thermal analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were utilized to verify the success of the graft polymerization process and to investigate the thermal properties of ramie fiber, cellulose-g-PTFEMA, and homo-PTFEMA. TGA was performed to investigate the decomposition pattern and thermal stability of cellulose-g-PTFEMA. TGA and the first derivative thermogravimetry (DTG) curves of ramie fiber, cellulose-g-PTFEMA (24 h, 25% graft ratio), and homo-PTFEMA are shown in Fig. 5. The TGA and DTG curves show that the degradation profile of cellulose-*g*-PTFEMA includes two steps, the first due to the degradation of ramie cellulose and the latter due to the degradation of PTFEMA. The initial pyrolytic weight loss occurs at a lower temperature ($T_{\rm di}$) in cellulose-*g*-PTFEMA and homo-PTFEMA, possibly due to the presence of less thermally stable brominated chain ends and cellulose-CTA in cellulose-*g*-PTFEMA. In the DTG curve of cellulose*g*-PTFEMA, the first of two main weight loss stages corresponds to the decomposition of ramie fiber, and the second stage is attributed to the pyrolytic decomposition of the grafted polymer chains. Moreover, the residual mass of cellulose-*g*-PTFEMA was higher than that of homo-PTFEMA and lower than that of ramie fiber, which is mainly due to the formation of grafted copolymer.

3.5. Size exclusion chromatography (SEC)

In previous syntheses of cellulose-based grafting copolymers via ATRP and RAFT polymerization, the individual grafted chains were cleaved from the copolymer backbones to estimate the degree of control of the "living"/controlled radical grafting polymerization process [36–38]. However, it usually required more than three weeks for the acid hydrolysis process to occur to a significant extent, due to the highly hydrophobic character of the ramie cellulose-based graft copolymers. Moreover, in most cases, the amount of cleaved polymers was too small for SEC analysis [16]. In previous studies [15,16], the homopolymers formed in the graft polymerization in the presence of the free chain transfer agent (free CTA) with an end structure similar to that of the macromolecular chain transfer agent were isolated and analyzed by SEC. The molecular weights (M_n) and polydispersity indexes of the polymer chains attached to the surface of the ramie fibers were determined by SEC, which showed compatible results with that of DSC (Fig. 6). The formation of homopolymers and graft copolymers was expected to be well controlled. In the present study, the free CTA (ECPDB) containing a similar R group was synthesized and used to mediate the RAFT process. This free CTA can be compared with cellulose-CTA (Scheme 2), which is stable enough to form a radical and thus provides controlled polymerization of TFEMA. The PDI of homo-PTFEMA was 1.28, which illustrates the controlled radical grafting RAFT polymerization of TFEMA from the surface of ramie fibers.

3.6. Scanning electron microscopy (SEM)

SEM micrographs of the unmodified ramie fiber, cellulose-*g*-PTFEMA (24 h, 25% graft ratio), and cellulose-*g*-PTFEMA (36 h, 27% graft ratio) are shown in Fig. 7. It is apparent that the surface structure features of cellulose-*g*-PTFEMA were different from those of unmodified native ramie fibers. This result confirms that graft polymerization occurred mainly on the surface of the ramie fiber. However, Fig. 7c shows that the ramie fiber became thinner than



Fig. 7. SEM photographs of (a) ramie fiber, (b) cellulose-g-PTFEMA (24 h, 25% graft ratio), and (c) cellulose-g-PTFEMA (36 h, 27% graft ratio).



Fig. 8. Water contact angle of cellulose-g-PTFEMA polymers with characteristics (reaction time, graft ratio): (a) 6 h, 13%; (b) 12 h, 20%; (c) 24 h, 25%; and (d) 36 h, 27%.

the unmodified ramie and was split, which might be due to the change in structure of the ramie fiber after prolonged reaction in scCO₂, as discussed in Section 3.3.

3.7. Contact angle measurements

The degree of surface hydrophobicity of cellulose-g-PTFEMA was investigated by static contact angle measurements. The raw ramie fiber adsorbed water very quickly, making it impossible to measure the static contact angle. Fig. 8 shows that cellulose-g-PTFEMA became clearly hydrophobic with a contact angle of up to 149° (24 h, 25% graft ratio). As shown in Fig. 8a-c, the contact angle of cellulose-g-PTFEMA increased with the increasing grafting ratio. This trend verifies that hydrophilic raw ramie fibers can be changed to hydrophobic by graft copolymerization modification, due to the hydrophobic polymer chains covalently attached to the surface. However, Fig. 8d shows that the contact angle of cellulose-g-PTFEMA (36 h, 27% graft ratio) was 132°, which is lower than that of cellulose-g-PTFEMA (24 h, 25% graft ratio). The decrease in the contact angle might be derived from the change in structure of the ramie fibers that exposes more hydroxyl groups on the surface, which led to the decrease in the contact angle of cellulose-g-PTFEMA when the reaction time exceeded 24 h.

4. Conclusions

PTFEMA was successfully grafted from the surface of ramie fibers via controlled RAFT polymerization in scCO₂. The free RAFT chain transfer agent ECPDB was employed and the polymerization was performed in a controlled process, giving a highly hydrophobic surface according to contact angle measurements. This is a novel and environmentally friendly approach to the preparation of functional grafted copolymers that utilize the abundant ramie fiber natural resource.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (NSFC) (Grant No. 20976102) and the 973 Program of China (Program/Grant No. 2009CB226105).

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