

Adjustable Wettability of Methyl Methacrylate Modified Ramie Fiber

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ABSTRACT: The surface hydrophobicity/hydrophilicity of ramie fiber was regulated through the atom transfer radical polymerization of methyl methacrylate from initiators immobilized on the fiber. The optimal reaction conditions for preparing the macroinitiated ramie fiber were determined to be a temperature of 60°C and a reaction time of 24 h. The grafted copolymers were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, energy-dispersive analysis of X-rays, gel permeation chromatography, and thermogravimetric analysis. The results indicate that poly(methyl methacrylate) was covalently bonded onto the

surface of the ramie fiber, and the polymerization of methyl methacrylate was a living/controlled process under the investigated conditions. The results of the contact angle measurements indicate that the wettability of the ramie fiber could be widely regulated by control of the grafted ratios of poly(methyl methacrylate) from 26 to 33 wt %. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2888–2894, 2008

Key words: atom transfer radical polymerization (ATRP); differential scanning calorimetry (DSC); fibers; graft copolymers; modification

INTRODUCTION

Natural fibrous materials have held a key role in the worldwide chemical and textile industries.¹ Ramie fiber (also called China grass), which is composed mainly of cellulose, is one of the oldest textile fibers with unique striking properties, such as high air perviousness and good antibacterial ability.² However, in some aspects, the properties of ramie fiber are inferior to those of synthetic polymers. Thus, the modification of ramie fiber has attracted great attention and has continuously been pursued for the improvement of its desired properties.³ Because of its high crystallinity and high degree of orientation, currently, it is still a challenge to modify ramie fiber. Since the invention of atom transfer radical polymerization (ATRP) in 1995,^{4,5} it has been extensively investigated as a robust and versatile technique for the synthesis of polymers for grafting-from processes

with accurately controlled chain lengths and polydispersities.^{6–13} Several works on grafting polymers to natural cellulose substrates by ATRP have been reported, and filter paper as a substrate was exclusively used for a demonstration purpose.^{14,15} Recently, natural cellulosic fibers, such as jute fiber, were grafted with polystyrene through ATRP.¹⁶ To the best of our knowledge, there has been no report on the grafting of polymers to ramie fiber. Moreover, it is a fact that surface properties play an increasingly important role for polymers with tailored properties, and this has stimulated a desire to control properties, such as the wettability and hydrophobicity, of cellulose fibers.^{17–19}

In this study, the grafting of methyl methacrylate (MMA) onto the surface of ramie fiber through the ATRP method in a living/controlled manner was investigated under mild conditions. The grafted fiber was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM)/energy-dispersive analysis of X-rays (EDAX), Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), gel permeation chromatography (GPC), and contact angle measurements. The covalently bonded poly(methyl methacrylate) (PMMA) on the ramie fiber significantly modified the hydrophobicity/hydrophilicity of the fiber, which could be easily regulated by control of the grafted ratios of PMMA, that is, the polymerization degree of PMMA on the initiator-modified fiber.

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EXPERIMENTAL

Materials

Ramie fiber, supplied by Hu'nan Yuanjiang Mingxing Co., Ltd. (Yiyang, China), was cut into samples approximately 1 mm in length for the experiments. MMA (analytical reagent, 99%, Aldrich, Milwaukee, WI) was distilled over CaH₂ at a room temperature overnight. *N*-methyl pyrrolidone (NMP; chemically pure, 98%), purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), was sequentially dried over MgSO₄ and 4 Å molecular sieves. *N,N,N',N''*-pentamethyldiethylene triamine (PMDETA; chemically pure, 98%), 2-bromoisobutyryl bromide (chemically pure, 98%), and 4-(dimethylamino)pyridine (DMAP, chemically pure, 98%) were all commercial products and were used without further purification.

Preparation of the fiber macroinitiator

The ramie fiber (0.366 g) was dried at 60°C for 24 h and then placed with DMAP in a 50-mL, round-bottom flask equipped with a dropping funnel and a magnetic stirring bar. A solution of NMP was added until all of the ramie fiber was covered. The flask was cooled to 0°C with a water/ice bath. The dropping funnel was filled with 2 mL of NMP and 2 mL of 2-bromoisobutyryl bromide, and the solution was then added dropwise to the flask. After that, the temperature of the flask was increased to 60°C. The flask was shaken and slowly stirred for 24 h. The initiator-modified ramie fiber was removed from the flask and washed thoroughly with anhydrous ethanol. The treated fiber was dried at 60°C. The reaction was carried out at 30, 40, 50, 60, and 70°C for 24 h and at 60°C for 6, 12, 18, and 24 h, respectively.

Surface-initiated ATRP of MMA

The grafting of MMA was accomplished by the immersion of the initiator-modified fiber into reaction mixtures containing MMA, Cu(I)Br (56 mg), PMDETA (85 µL), sacrificial initiator (ethyl 2-bromopropionate, 5 mol % of the monomer), and tetrahydrofuran (THF). The flask was sealed with a rubber septum, evacuated, and then back-filled with Ar three times. The polymerization started immediately upon degassing. All of the polymerizations were carried out at 30°C for 24 h. The PMMA-grafted fiber was subjected to intense washing with ethanol, acetone, and THF and then dried *in vacuo* at 50°C.

Characterization

FTIR spectra of the unmodified and modified ramie fibers were collected with a Nicolet 870 spectrometer

(Madison, WI). Spectra were recorded in the range 4000–400 cm⁻¹ with 32 scans at a resolution of 4 cm⁻¹.

SEM photomicrographs of the unmodified and modified ramie fibers were recorded on a Philips FEI Quanta 200 field emission scanning electron microscope (Eindhoven, The Netherlands), which was operated at 20 kV. The surface content of Br on the modified fiber was determined by EDAX.

XRD patterns of the fibers were recorded from 2θ = 5 to 60° with a Rigakav D/max-1200 diffractometer with a graphite monochromator and Cu Kα radiation at λ = 0.154 nm (40 kV, 40 mA).

The TGA measurements were performed on a thermoanalyzer system (model Q600SDT, TA Co., Ltd., New Castle, DE). Samples of about 5 mg, placed in a DSC pan, were heated from -10 to 550°C at a temperature ramp of 20°C/min under a constant flow of dry nitrogen.

To accomplish GPC analysis, the PMMA-grafted fiber was extracted in KOH/MeOH to cleave the covalently bounded PMMA from the ramie fiber. The fiber was then filtered off and rinsed in THF. The THF solution of the extracted material was analyzed by GPC. The GPC curve was recorded with a Waters 2410 instrument equipped with three Waters µ-Styragel columns (Milford, MA). High-performance-liquid-chromatography-grade THF, mixed with triethylamine (2 vol %), was used as a solvent at a flow rate of 1 mL/min at 35°C. The number-average molecular weight (*M_n*) and polydispersity index (PDI) values of the samples were calibrated with polystyrene provided by the GPC supplier.

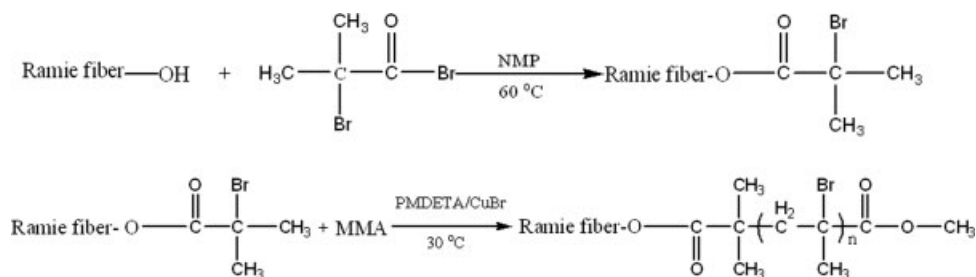
The contact angles of water for the modified and unmodified ramie fibers were measured with a JY-82 tensiometer and contact angle meter (±0.5°, Chengde Precision Testing Machine Co., Ltd., Chengdu, China).

RESULTS AND DISCUSSION

The experimental procedure for the surface modification of the ramie fiber is schematically outlined in Scheme 1. The hydroxyl groups on the ramie fiber were converted into tertiary bromoester groups as initiators, and then, MMA was polymerized on the surface of the fiber.

Surface grafting of ramie fiber

For the reaction between the hydroxyl groups in the ramie fiber and 2-bromoisobutyrylbromide, the FTIR spectra (Fig. 1) clearly showed the absorption peak of the ester carbonyl group (1732 cm⁻¹) for the initiator-modified fibers, even at a temperature as low as 30°C, whereas this peak did not exist in the raw fiber, which suggested that 2-bromoisobutyrylbromide was immobilized on the fiber surface. More-



Scheme 1 Procedure for the preparation of the PMMA-grafted ramie fiber.

over, the peak intensity of the ester carbonyl group increased with an increase in reaction temperature. The reaction mixtures became solid, and the products could not be separated after the reaction at 70°C for 24 h.

The effect of time on the reaction between the hydroxyl groups in the ramie fiber and the initiator was investigated at 60°C, and the FTIR spectra of the initiator-modified fibers are provided in Figure 2. The peak intensity of the ester carbonyl group (1732 cm^{-1}) was very low for a reaction of 6 h. The peak intensity of the ester carbonyl group increased gradually from 6 to 18 h. However, from 18 to 24 h, the peak intensity of the ester carbonyl group increased greatly.

To further confirm the successful immobilization of the initiator on the fiber, EDAX analysis was carried out to determine the content of Br on the fibers. From the results listed in Table I, the amount of Br increased continuously with an increase in temperature and time. Moreover, there was a sharp increase in Br content on the surface of the ramie fiber for the cases in which the reaction temperature was increased from 50 to 60°C or the reaction time was prolonged from 18 to 24 h. These results were consistent with those of the FTIR observations.

The FTIR and EDAX results indicate that the initiator was successfully immobilized on the surface of the ramie fiber, and the optimal conditions for a higher degree of substitution of the ramie fiber were a temperature of 60°C and a reaction time of 24 h.

The fiber initiator-modified under the conditions of 60°C and 24 h was applied to graft PMMA, and the FTIR spectra of the PMMA-grafted fiber are provided in Figure 3. For comparison purposes, the FTIR spectra of the ramie fiber and the initiator-modified fiber are also shown in Figure 3. The PMMA-grafted fiber showed a double peak at the wave-number range 2950–3000 cm^{-1} , which corresponded to the characteristic peaks of the methyl group in the pure PMMA polymer and was not found in the spectra of the initiator-modified fiber and the raw fiber. Moreover, the peak intensity of the ester carbonyl group at 1732 cm^{-1} in the PMMA-grafted fiber was higher than that in the initiator-modified fiber. This was from the contribution of the ester carbonyl groups in the initiator-modified fiber and in the PMMA polymer, which resulted in an increase in the peak intensity at 1732 cm^{-1} . These results indicate that PMMA was polymerized on the initiator-modified fiber.

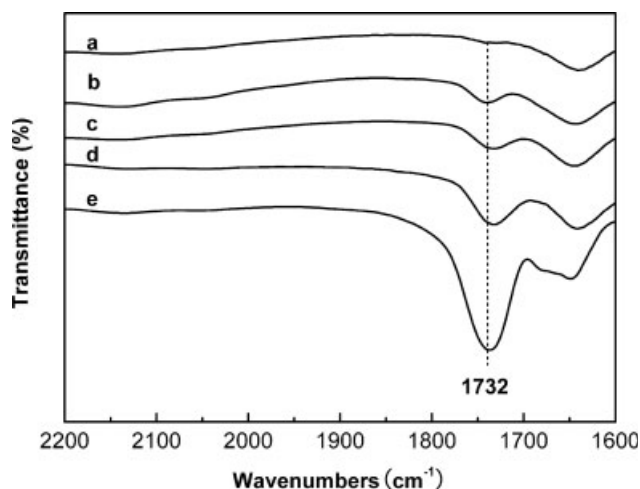


Figure 1 FTIR spectra of (a) ramie fiber and fibers initiator-modified at (b) 30, (c) 40, (d) 50, and (e) 60°C for 24 h.

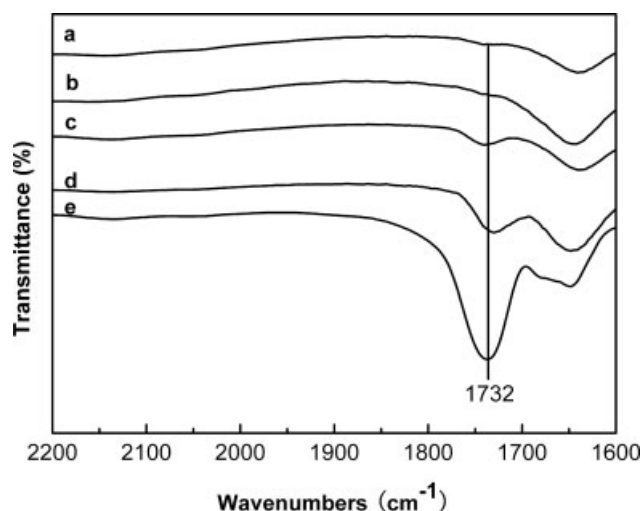


Figure 2 FTIR spectra of (a) ramie fiber and fibers initiator-modified at 60°C for (b) 6, (c) 12, (d) 18, and (e) 24 h.

TABLE I
Br Content on the Ramie Fibers Modified by the Initiator Under Different Conditions

Temperature (°C)	Reaction time (h)	Br (wt %)
30	24	1.02
40	24	1.66
50	24	4.02
60	6	0.54
	12	1.25
	18	3.55
	24	12.44

Characteristics of the surface and structure of ramie fiber

SEM photomicrographs of the raw and modified ramie fibers are shown in Figure 4. The surface of the raw ramie fiber [Fig. 4(a)] was very smooth. However, some small grains or pellets on the slightly accidented surface were clearly seen in the case of the initiator-modified fiber [Fig. 4(b)], which suggested that the 2-bromoisobutyryl bromide reacted with the ramie fiber. The surface of the PMMA-grafted fiber [Fig. 4(c)] became obviously accidented and seemed covered with some small patches. The surface properties strongly correlated with its topology and morphology in addition to its chemical composition. Thus, the surface properties of the ramie fiber were changed after it was grafted with the initiator or PMMA, which is confirmed in a later part of the article that discusses the contact angle measurements.

Figure 5 shows the XRD patterns of the raw and modified ramie fibers. As shown in Figure 5, the crystal structure of the ramie fiber was still preserved after initiator modification and PMMA grafting. With the peak positions under consideration, both the modified and unmodified fibers showed the characteristic diffractions of the cellulose I phase, that is, a sharp peak at 2θ of about 23° and two overlapped weaker diffractions at 2θ values of 15° and 16° .³ However, when the peak intensity of the different fibers was considered, a clear changing trend was found; that is, the modified fiber showed a lower peak intensity than the raw fiber. Moreover, it is interesting that the peak intensity was almost the same for the initiator-modified fiber and the PMMA-grafted fibers with different grafting ratios, which suggests that the initiator-modified and the PMMA-grafted polymerization were mainly carried on the surface of the ramie fiber.

Ramie fiber is composed of a crystalline region and an amorphous zone. As there was no pretreatment of the ramie fiber before grafting, the initiator could not penetrate into the crystalline regions for the reaction with hydroxyl groups. Thus, it is rational to propose that the reactions of 2-bromoisobutyryl bromide with hydroxyl groups in the fiber took place on the crystalline surface and/or the amorphous region of the fiber. Furthermore, MMA reacted with the initiator immobilized on the fiber rather than with the hydroxyl groups on the fiber (see Scheme 1). Therefore, the XRD diffraction positions of the raw and modified fibers were similar; that is, there was no change in the crystallite structure of the raw fiber, the initiator-modified fiber, and the PMMA-grafted fiber.

Under the reaction conditions investigated, the 2-bromoisobutyryl bromide immobilized on the fiber was quite limited [see Fig. 4(b)], and the PMMA on the fiber was randomly oriented. Thus, the decrease in the XRD peak intensity may be explained as an increase in the amorphous region after the noncrystalline immobilization of the initiator and/or the grafting of PMMA, which led to the decrease in the peak intensity of the XRD diffractions.

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TGA

TGA was used to probe the decomposition pattern and the thermal stability of the ramie fibers. The thermal decomposition of the raw ramie fiber started at about 300°C and quickly finished at about 410°C [Fig. 6(a)]. The amount of residual mass was about 13.4 wt % after decomposition to a temperature of 500°C . In the case of the initiator-modified fiber [Fig. 6(b)], the decomposition became a two-step process and proceeded in the temperature range $180\text{--}500^\circ\text{C}$. As a result of the incorporation of the Br atom, the amount of residual mass accounted for about 22.7 wt %, which was obviously higher than that of the raw fiber (13.4 wt %), after decomposition to a temperature of 500°C .

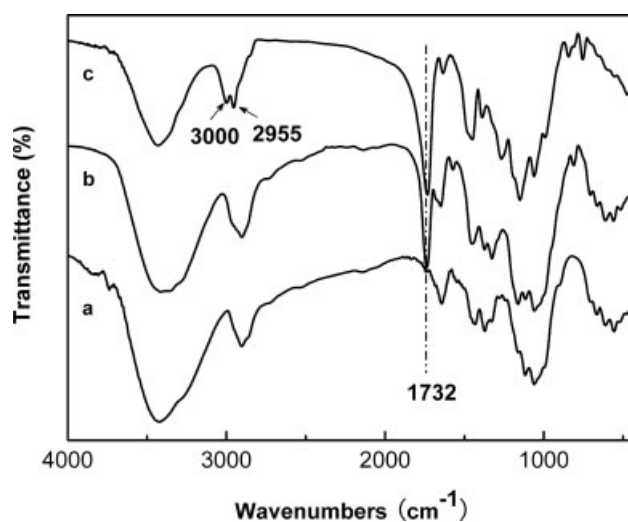


Figure 3 FTIR spectra of (a) ramie fiber, (b) initiator-modified ramie fiber, and (c) PMMA-grafted fiber (reaction conditions: temperature = 60°C and time = 24 h).

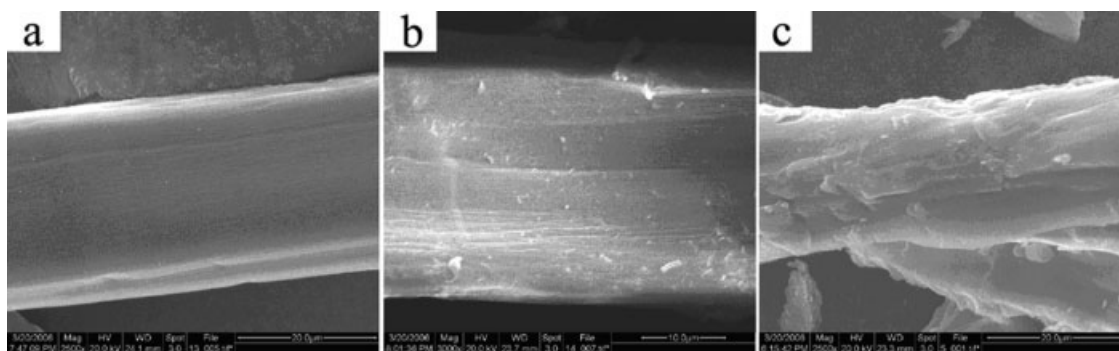


Figure 4 SEM photomicrographs of (a) ramie fiber, (b) initiator-modified fiber, and (c) PMMA-grafted fiber (reaction conditions: temperature = 60°C and time = 24 h).

The PMMA-grafted samples [Fig. 6(c–e)] showed a transitional degradation profile, in which the ramie fiber degraded first and this triggered the degradation of PMMA. Regardless of the grafting ratios, the TGA patterns of the PMMA-grafted fibers were quite similar, and only a slight modification in the weight loss versus temperature was observed. When the residual mass after the decomposition was taken into account, the PMMA-grafted fiber with a higher grafting ratio always produced a lower residual mass. Moreover, all of the PMMA-grafted fiber gave an obviously lower amount of residual mass than the initiator-modified fiber. With the fiber with 26% grafting ratio as an example, the residual mass was about 17.3 wt %, which was obviously lower than 22.7 wt % of the initiator-modified fiber. This could reasonably be ascribed to the relatively decreased amount of the Br with the increase in the grafting ratios of PMMA. Thus, the thermal behavior of the ramie fibers with the immobilization of the initiator and the grafting of PMMA was apparently altered.

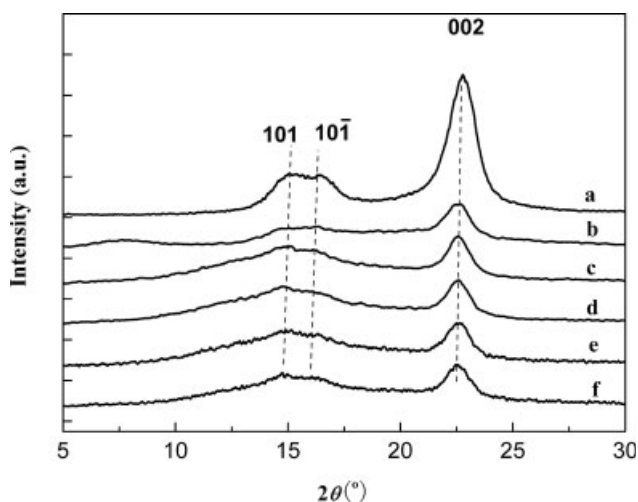


Figure 5 XRD patterns of (a) raw ramie fiber, (b) initiator-modified fiber, and (c–f) PMMA-grafted fibers with 26, 28, 31, and 33% grafting ratios, respectively.

Molecular weight analyses

To quantify the molecular weights and PDIs of the PMMA chains that attached to the initiator-modified fiber substrates, the samples were hydrolyzed in a solution of KOH/MeOH at 70°C for 1 week. The solution was filtered, evaporated with a rotary evaporator, dissolved in dichloromethane, and then washed with a small amount of distilled water. Finally, the solution of PMMA was precipitated into water/MeOH and dried *in vacuo* at 50°C for 24 h. Figure 7 shows the M_n and PDI values of the PMMA. The GPC curves of PMMA shown in Figure 7 are sharp peaks, and PDI values from 1.17 to 1.55 were obtained throughout the polymerization.

The M_n of PMMA grafted on the initiator-modified fiber increased linearly with an increase in the MMA amount added, as shown in Figure 8, which indicated that this was a controlled polymerization. All of these data convincingly revealed that the polymerization of MMA catalyzed by PMDETA/CuBr under the investigated conditions was a living/controlled process.

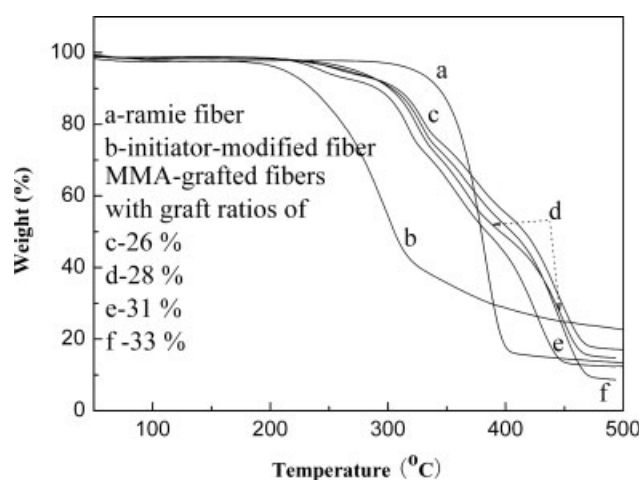


Figure 6 TGA thermograms of the raw and modified ramie fibers.

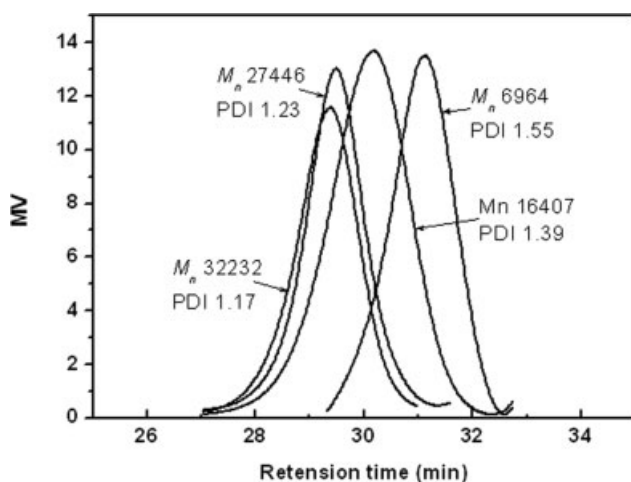


Figure 7 GPC curves for different conversions of MMA (MW = molecular weight).

Therefore, the living/controlled polymerization of MMA on the macroinitiated ramie fiber by ATRP was successfully achieved. With the relatively lower crystallinities of other natural fibers such as cotton, wood, and wool in comparison with ramie fiber, we can reasonably expect that the demonstrated method can be extended to the modification of the aforementioned fibers, and therefore, their properties can be adjusted.

Surface wettability evaluation

The wettability of fibers were characterized by changes in the contact angle. The contact angles of water for the raw fiber, the initiator-modified fiber, and the MMA-grafted fiber are shown in Table II.

The raw fiber, with a contact angle of 75.9°, was essentially hydrophobic; however, when a drop of water was dipped on its surface, the water was

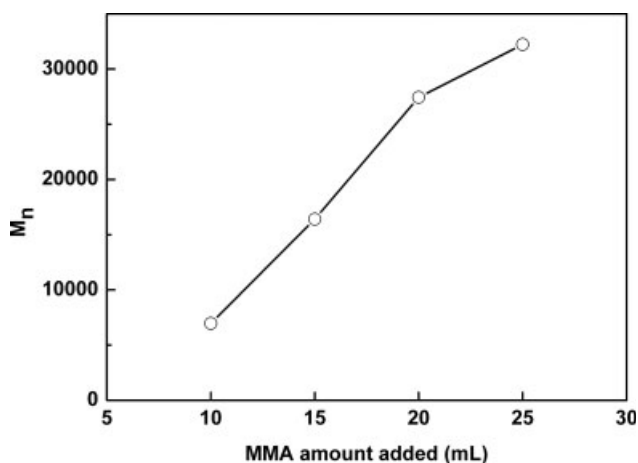


Figure 8 M_n of PMMA grafted onto the fiber versus the amount of MMA added to the reaction mixture.

TABLE II
Contact Angles of Water for the Raw Ramie Fiber, Initiator-Modified Fiber, and PMMA-Grafted Fibers

Sample	PMMA grafting ratio (wt %)	Contact angle (°)
Ramie fiber	—	75.91
Initiator-modified fiber	—	92.17
MMA-grafted fiber	26	105.17
	28	106.37
	31	109.62
	33	114.42

adsorbed quickly. The initiator-modified fiber, with a contact angle of 92.2°, became more hydrophobic than the raw fiber and adsorbed water slowly. There was no water adsorption observed for the PMMA-grafted fiber, and the contact angles continuously increased with the increase in the PMMA grafting ratios. This indicated that the hydrophobicity of the ramie fiber was easily adjusted via the surface grafting of PMMA. Therefore, it is straightforward that the hydrophobicity of the PMMA-grafted fiber was regulated by control of the grafted ratios of PMMA, that is, the polymerization degree of MMA on the initiator-modified fiber.

CONCLUSIONS

The living/controlled polymerization of MMA on the macroinitiated ramie fiber by ATRP was successfully achieved, as revealed from the FTIR, EDAX, and GPC analyses. The optimal reaction conditions for the preparation of the macroinitiated fiber were determined to be a temperature of 60°C and a reaction time of 24 h. The XRD results indicate that the crystal structure of the ramie fiber was still preserved after initiator modification and PMMA grafting, although the diffraction intensities of the modified fibers decreased obviously. The contact angle measurements indicated that this modification of the ramie fiber changed the surface hydrophobic/hydrophilic properties significantly. The wettability of the PMMA-grafted fiber could be easily regulated by control of the polymerization degree of PMMA on the initiator-modified fiber.

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