# Modification of Ramie Fiber with an Amine-Containing Polymer via Atom Transfer Radical Polymerization

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**ABSTRACT:** The covalent bonding of tertiary amine 2-(dimethylamino)ethyl methacrylate to ramie fiber via atom transfer radical polymerization was obtained with a brominated initiator and the catalyst CuCl/1,10-phenanthroline. The results reveal that poly[2-(dimethylamino) ethyl methacrylate] (PDMAEMA) was successfully immobilized on the surface of the ramie fiber in a controlled polymerization. After the grafting with PDMAEMA, the crystal structure of cellulose I in the ramie fiber was still preserved, and the lateral size of the microfibrils, calculated on the basis of plane 002, was slightly increased. As a demonstration of possible applications, the modified fiber was dyed with CI Reactive Red 2. The dye uptake, which almost linearly increased with increasing molecular weight of PDMAEMA attached on the ramie fiber, was raised to be over 15 times that of the raw fiber. The reason was that the reactivity between the tertiary amines in PDMAEMA and the dichlorotriazinyl group in the dye molecules was much higher than that between the hydroxyl groups in the ramie fiber and the reactive groups in the dye molecules. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3612–3618, 2009

**Key words:** atom transfer radical polymerization (ATRP); biomaterials; fibers; renewable resources; thermogravimetric analysis (TGA)

## INTRODUCTION

Cellulose, which is the most abundant natural material in the world, has widely been studied, mainly because of its biodegradable and renewable nature.[1] Its reactive OH groups; unique structure; versatile properties, such as hydrophilicity, biocompatibility, and stereoregularity; and ability to form superstructures make cellulose very important as a starting material. Indeed, the different functional moieties tailed onto the surface of cellulosic fiber have been investigated extensively for extended application areas of the old material.[1–10]

Ramie, also called *China grass* [*Boehmeria nivea* (L.) Gaudich], is a hardy perennial herbaceous plant of the Urticaceae family, which is mainly planted in China and other Asian countries.[11,12] Ramie fiber, stripped from the stem bast of the plant, is composed primarily of cellulose. Ramie fiber has excellent characteristics, including a high Young's modulus, high intensity of the single fiber, and high water and perspiration adsorption, and good resistance to bacteria, mildew, and insect attack.[13,14] However, its poor dyeability, easy corrugation, and poor spinnability during processing prevent it from being a main textile fiber. Thus, much work has been done in this aspect.[12] Additionally, ramie fiber with the characteristics mentioned previously is potentially a good substrate of biomaterials for the design of intended properties, such as antibacterial, membrane separation, and stimulus response properties, which have not been cultivated until now.

Traditionally, most cellulose-grafted copolymers are synthesized on the basis of free-radical polymerization methods, from which generally ill-defined and poorly characterized copolymers are obtained.[5] With the emergence of controlled/living polymerization methods, well-defined grafted polymers with predetermined molecular weights and narrow polydispersities are achievable; this provides researchers with the opportunity to accurately tailor the cellulosic surface for desired properties. Being a controlled/living polymerization method, atom transfer radical polymerization (ATRP) has been widely investigated as a robust and versatile technique to synthesize polymers for grafting-from processes with accurately controlled chain lengths and

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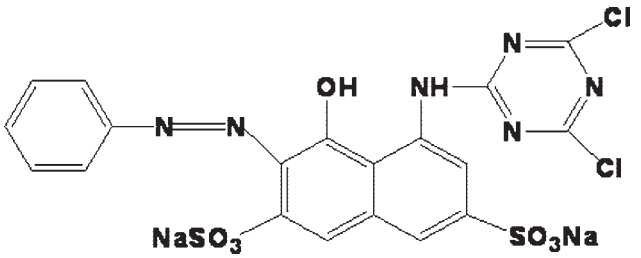



**Scheme 1** Chemical structure of CI Reactive Red 2.

polydispersities.[15–26] The particular advantages of ATRP, which are a strong bond between the substrate and a polymer grown on the surface, well-controlled chain length, and polydispersity, are of great importance for the permanent tailoring of the cellulosic surface. In earlier studies,[2,23,27,28] filter paper was examined as a substrate for the grafting of cellulose-based materials with different monomers via ATRP. Recently, cotton and jute fibers have been modified by the grafting of ethyl acrylate and/or styrene through ATRP.[7,29]

2-(Dimethylamino)ethyl methacrylate (DMAEMA) is an important monomer because the tertiary amine function allows one to fix active substances onto the resulting polymers.[30] Furthermore, being a polybase, poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) homopolymer contains pendant tertiary amines that are easily protonated below its p$K_a$ of 7.5, thus, the polymer is afforded pH tuneability for controlled-release applications.[30–32] More importantly, Matyjaszewski et al.[23] demonstrated that the quaternized ammonium groups of PDMAEMA immobilized on the surface of filter paper and glass had substantial antimicrobial capacity, in which the quaternary amines were believed to cause cell death by disrupting the cell membranes. Because of these characteristics, in this study, DMAEMA monomer was chosen to graft ramie fiber via ATRP. The PDMAEMA-grafted ramie fiber was characterized by the aspects of surface morphology, structure, and thermal behavior. As direct azo dyes have important applications in high-technology areas such as new biochemical assays,[33] for a demonstration of the applications, the modified ramie fiber was dyed with CI Reactive Red 2, and improved chromaticity was achieved.

## EXPERIMENTAL

### Materials

Ramie fiber, supplied by the Hu'nan Yuanjiang Ming-Xing Co., Ltd. (Yuanjiang, China) was cut into pieces 1 mm in length and dried in a fume hood at 60°C for 24 h. Before use, DMAEMA (Zibo Linzi Wanduofu Fine Chemical Co., Ltd., Zibo, China) was distilled over $CaH_2$ overnight. *N*-Methyl pyrrolidone (NMP), purchased from Sinopharm Chemical Reagent Co., Ltd., was first dried over $MgSO_4$ and 4-Å molecular sieves in turn. 1,10-Phenanthroline (Sinopharm Chemical Reagent Co., Shanghai, China) and 2-bromoisobutyryl bromide (Yancheng Creator Chemical Co., Ltd., China) were used without further purification. The commercial dye CI Reactive Red 2 (Qin Long Co., Yancheng, Ltd., Shenzhen, China; Scheme 1) was purified with *N*,*N*-dimethylformamide and acetone.

### Preparation of the macroinitiated ramie fiber

The dried ramie fiber (20 g) was put into a 500-mL, round-bottom flask equipped with a dropping funnel and a magnetic stirring bar. A solution of NMP was added until the ramie fiber was fully immersed in the solution. Then, the flask was cooled to 0°C in a water/ice bath. Twenty milliliters of NMP and 20 mL of 2-bromoisobutyryl bromide in the dropping funnel were transferred dropwise to the flask. After this, the temperature was raised to 80°C, and the mixture was slowly stirred for 6 h. Then, the fiber was taken out of the flask. After thorough washing with anhydrous ethanol, the initiator-modified fiber (Br fiber) was obtained after drying in a fume hood at 60°C.

### Surface-initiated ATRP of DMAEMA on the Br fiber

The surface grafting was accomplished by immersion of the Br fiber (1.0 g) in a reaction mixture containing DMAEMA, 1,10-phenanthroline (0.077 g), Cu(I)Cl (0.031 g), acetone/water (9/1 v/v), and a sacrificial initiator (0.008 g). To change the molecular weight, the mount of the DMAEMA added to the solution was changed (Table I). The flask was sealed with a rubber septum, evacuated, and back-filled with Ar gas three times. The polymerization started immediately upon degassing. All polymerizations were carried out at 30°C for 24 h. After the completion of polymerization, the fiber was subjected to intense washing with methanol, acetone, tetrahydrofuran, and water. Finally, the ramie fiber modified

**TABLE I**
**Reaction Conditions and GPC Results for the Hydrolyzed PDMAEMA Fiber**

| Sample | Fiber | Monomer (mol) | Solvent (mL) | $M_n$ | PDI |
|---|---|---|---|---|---|
| a | Raw fiber | — | — | — | — |
| b | Br fiber | — | — | — | — |
| c | PDMAEMA fiber | 0.01 | 20 | 15,752 | 1.42 |
| d | | 0.02 | 20 | 30,510 | 1.38 |
| e | | 0.05 | 20 | 44,758 | 1.55 |
| f | | 0.06 | 20 | 55,991 | 1.55 |
| g | | 0.08 | 20 | 65,654 | 1.62 |
| h | | 0.12 | 20 | 79,589 | 1.65 |

with PDMAEMA (PDMAEMA fiber) was obtained after drying at 50°C.

### Homopolymerization of DMAEMA via ATRP

The homopolymerization of DMAEMA via ATRP with the benzyl bromide initiator was as follows: benzyl bromide (0.001 mol), DMAEMA (0.1 mol), 1,10-phenanthroline (0.001 mol), and Cu(I)Cl (0.001 mol) were codissolved in acetone/water (9/1 v/v). The flask was sealed with a rubber septum, evacuated, and back-filled with Ar gas three times. The polymerization started immediately upon degassing. The polymerization was carried out at 30°C for 24 h. After completion of the polymerization, NaOH/water was added dropwise to the mixture solution until a pH of 13 was reached. Then, the mixture solution was heated to 60°C, and the PDMAEMA homopolymer was precipitated. After filtration, the PDMAEMA was put into a beaker with water; then, HCl/water was added dropwise to the solution until a pH of 4 was reached and the PDMAEMA was dissolved. Then, NaOH/water was added dropwise to the solution until a pH of 13 was reached; the solution was then heated to 60°C, and the PDMAEMA was precipitated. This process was performed three times. The final product PDMAEMA was dried in a vacuum at 50°C overnight.

### Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the raw and the modified ramie fibers were taken on a Nicolet 870 spectrometer (Madison, WI). Each spectrum was collected in the range 4000–400 $cm^{-1}$ by 32 scans at a resolution of 4 $cm^{-1}$.

### Thermogravimetric analysis (TGA) measurements

TGA measurements were performed on a Thermoanalyzer System (Q600SDT, TA Co., Ltd., New Castle, DE). About 5 mg of sample was used in each test. The sample was heated from −10 to 550°C at a heating rate of 20°C/min under a constant flow of dry nitrogen.

### Scanning electron microscopy (SEM)

SEM photomicrographs of the unmodified and modified ramie fibers were recorded on a Philips FEI model Quanta 200 field emission scanning electron microscope (Eindhoven, the Netherlands) operated at 20 kV.

### X-ray diffraction (XRD)

XRD patterns of the fibers were recorded from $2\theta = 5$ to 60° with a Rigaku D/max-1200 diffractometer (Tokyo, Japan) equipped with a graphite monochromator and Cu K$\alpha$ radiation at $\lambda = 0.154$ nm (40 kV, 40 mA).

### Gel permeation chromatography (GPC)

The number-average molecular weight ($M_n$) and polydispersity index (PDI) were analyzed by GPC. The GPC curve was recorded on a Waters (Milford, MA) 2410 instrument equipped with three Waters μ-Styragel columns. High-performance-liquid-chromatography-grade tetrahydrofuran mixed with triethylamine (2 vol %) was used as the solvent at a flow rate of 1 mL/min at 35°C.

### Dye uptake measurement

Water (about 100 mL), CI Reactive Red 2 (0.02 g), fiber (0.5 g), and NaCl (0.4 g) were placed into a 100-mL, round-bottom flask. After the mixture was maintained at 30°C for 10 min, 0.4 g of $Na_2CO_3$ was added to the flask to fix the dye molecules on the fiber. The dye uptakes of different fibers were calculated according to eq. (1) on the basis of the absorbency of the dyeing solution before and after dyeing at $\lambda = 540$ nm with a Lamda 950 spectrophotometer (PerkinElmer Co., Ltd., Waltham, MA):

$$E = (1 - A_1/A_0) \times 100\% \quad (1)$$

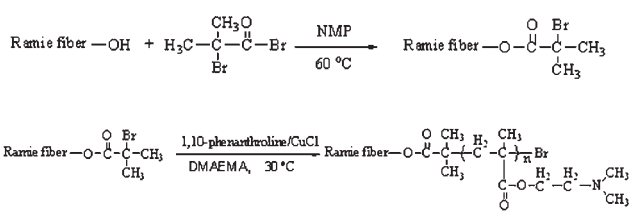
where $E$ is the dye uptake, $A_0$ is the absorbence of the original dye solution, and $A_1$ is the absorbence of the residual solution after dyeing. We measured $A_0$ by taking a fixed amount of the original dye solution before the fibers were immersed in the dye solution and then diluting the solution 25 times in water at $\lambda = 540$ nm on the Lamda 950 spectrophotometer. We measured $A_1$ by taking a fixed amount of the residual solution after dyeing and then diluting it 25 times in water at $\lambda = 540$ nm on the Lamda 950 spectrophotometer.

### Elemental analyses

The content of elemental nitrogen in the grafted fiber was determined with a Vario ELIII (Germany Elementar Analysensysteme GmbH, Hanau, Germany).

## RESULTS AND DISCUSSION

The experimental procedure for the surface-initiated ATRP of DMAEMA on the ramie fiber is depicted in Scheme 2. In the first step of the reactions, the hydroxyl groups on the ramie fiber were converted




**Scheme 2** Procedure for the preparation of PDMAEMA-grafted ramie fiber.

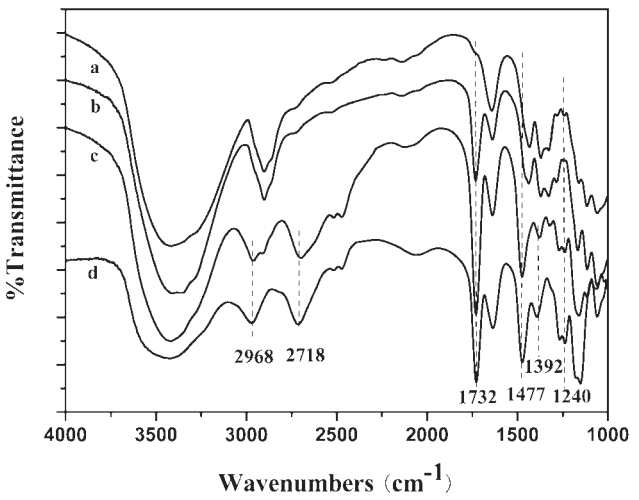



**Figure 1** FTIR spectra of (a) the raw ramie fiber, (b) the Br fiber, (c) the PDMAEMA fiber, and (d) the PDMAEMA polymer.

into surface initiators by the reaction with 2-bromoisobutyryl bromide. Then, DMAEMA was grafted onto the surface of the fiber by polymerization. To illustrate the successful immobilization and structure changes, the results from the PDMAEMA fiber prepared with 2 mL of monomer and 20 mL of solvent are discussed in the following text unless otherwise specified.

### Modification of the ramie fiber with PDMAEMA

FTIR results of different fibers are given in Figure 1. To confirm the assignment of different peaks, the FTIR spectrum of a DMAEMA polymer is also shown in Figure 1. A key difference between the raw and modified fibers was in the absence or existence of ester carbonyl groups, with the FTIR signal in the range 1730–1736 $cm^{-1}$, which corresponded to the stretching vibration of the ester carbonyl group, which was decisive for confirming the surface grafting. As expected, there was no peak for the raw ramie fiber in the range 1730–1736 $cm^{-1}$ [Fig. 1(a)], whereas a clear absorption peak at 1732 $cm^{-1}$ was observed for the Br fiber [Fig. 1(b)], which indicated that 2-bromoisobutyryl bromide was immobilized on the ramie fiber. For the PDMAEMA fiber [Fig. 1(c)], the peak intensity of the ester carbonyl group at 1732 $cm^{-1}$ was more intense than that of the Br fiber as a result of the absorption enhanced by the ester carbonyl groups in PDMAEMA. In addition, because of the long chains of the attached PDMAEMA, the absorption peaks of the C—H stretching vibrations in $—CH_2$ and $—CH_3$ groups and the bending modes of the C—H bonds in $—CH_3$ groups were clearly observed at 2718, 2968, 1477, and 1392 $cm^{-1}$, respectively. Moreover, the new absorption peak at 1240 $cm^{-1}$, which was not seen in the spectra of the raw ramie fiber or Br fiber, was assigned to the stretching vibration absorption of the —C—N bonds in amine groups. These results agreed well with the spectrum of the DMAEMA polymer [Fig. 1(d)]. The FTIR results clearly indicate that PDMAEMA was chemically bonded on the surface of the ramie fiber.

### TGA measurements

The effects of the anchored initiator and the grafted PDMAEMA on the thermal properties of the ramie fiber were investigated by TGA. Figure 2 shows the thermograms of the raw fiber, Br fiber, and PDMAEMA fiber samples. For comparison, the thermogram of a PDMAEMA polymer with a similar molecular weight to the grafted one is also provided in Figure 2. The raw fiber decomposed in the temperature range 300–410°C, and the residual amount was about 16.5 wt %. The onset temperature of decomposition for the Br fiber was remarkably decreased (180°C), and the decomposition became a two-step process as a result of the immobilization of the initiator on the ramie fiber. The declined thermal stability of the Br fiber in comparison with the raw fiber may have been due to the lower stability of the initiator. After decomposition up to 500°C, the residual amount was about 22.7 wt %, which corresponded to the Br atom, which was tailed onto the Br fiber. For the PDMAEMA fiber, the thermogram was a blend of curves for the raw ramie fiber and the PDMAEMA polymer, and a broader temperature range of decomposition than for the raw fiber was observed. Once again, the lower onset temperature (200°C) of the PDMAEMA fiber was probably due to the presence of the brominated ends with lower thermal stability, as reported in ref. 7. The TGA results indicate that the PDMAEMA was grafted

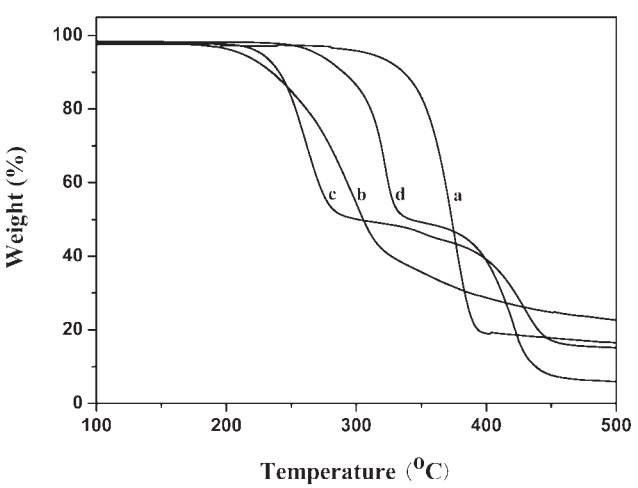



**Figure 2** TGA thermograms of (a) the raw ramie fiber, (b) the Br fiber, (c) the PDMAEMA fiber, and (d) the PDMAEMA polymer.

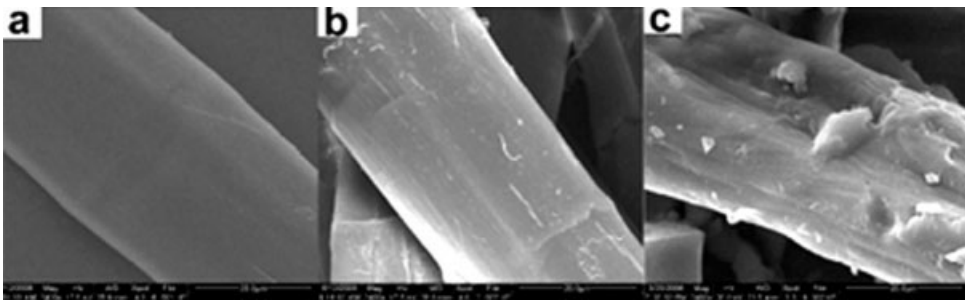



**Figure 3** SEM images of (a) the raw ramie fiber, (b) the Br fiber, and (c) the PDMAEMA fiber.

onto the ramie fiber; this was consistent with the FTIR results.

### Surface morphology and crystal structure

A previous study[34] indicated that ramie fiber with a smooth surface is composed of layered microfibrils with an *S*-helix orientation. Figure 3(a) shows that the surface of the ramie fiber was very smooth and appeared to have a layered structure.[35] After the anchoring of the initiator, a silklike material was randomly decorated on the surface [Fig. 3(b)]. When PDMAEMA was grafted, a very rough surface with partly covered polymer-like granules was observable [Fig. 3(c)], which suggested that PDMAEMA was grafted onto the surface of the ramie fiber. This was consistent with previous reports[7,28] on the modification of the cellulose-based fibers.

XRD patterns of different fibers at 2θ of 5.0–30.0° are shown in Figure 4. The raw ramie fiber with diffraction peaks at 14.8, 16.4, and 22.6° showed the characteristic crystalline form of cellulose I, as reported in our previous article.[12] After the ramie fiber was grafted with the initiator or the PDMAEMA, the cellulose I structure of the ramie fiber was still preserved, as reflected from the quite similar peak positions and patterns of the XRD diffractions. Thus, the reaction between hydroxyl groups in the ramie fiber and the initiator and the following grafting of PDMAEMA did not change the crystalline form, that is, cellulose I, of the ramie fiber.[36] This was understandable because the grafting took place on the crystalline surface and/or amorphous region of the ramie fiber, as is also shown in the SEM patterns in Figure 2. However, the peak intensity of the grafted fibers decreased obviously and was in the decreasing sequence of the raw fiber, Br fiber, and PDMAEMA fiber; this indicated that the degree of crystallinity declined apparently when the hydroxyl groups in the ramie fiber reacted with the initiator and the PDMAEMA was grafted. To quantify this, the lateral dimension of the microfibrils in different fibers was estimated on the basis of the full width at half maximum (FWHM) of the most intensive peak from the crystalline plane 002 and the Debye–Scherrer equation. The lateral dimensions of the microfibrils in the raw fiber, Br fiber, and PDMAEMA fiber were estimated to be 8.64, 8.93, and 9.05 nm, respectively. Thus, the increase in the lateral size of the microfibrils from the raw fiber to the PDMAEMA fiber suggested that the PDMAEMA was successfully grafted onto ramie fiber. The FTIR signal in the range 1730–1736 $cm^{-1}$ (see Fig. 1), which corresponded to the stretching vibration of the ester carbonyl group, also confirmed that PDMAEMA was successfully grafted onto the surface of the ramie fiber. As the attached initiator or PDMAEMA on the ramie fiber was randomly distributed in a noncrystal form, the amorphous quantity in the ramie fiber should have increased for the Br fiber and PDMAEMA fiber and led to a decrease in the XRD peak intensity, that is, the degree of crystallinity.

### Molecular weight analyses

To quantify the molecular weight and PDI of the PDMAEMA that attached to the ramie fiber, each sample was hydrolyzed with a solution of 1*M* HCl

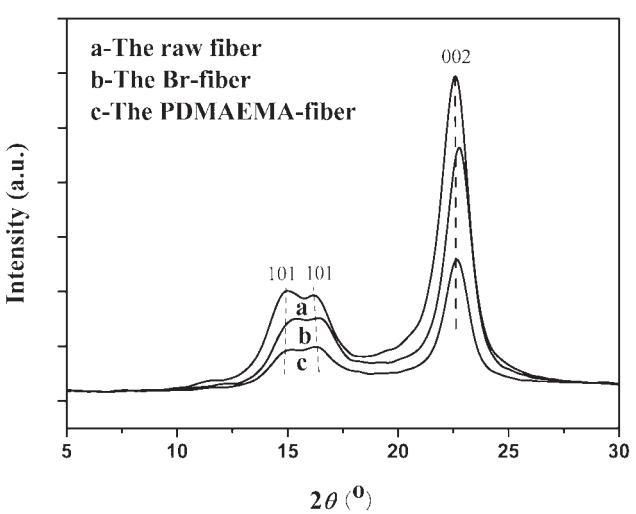



**Figure 4** XRD patterns of (a) the raw ramie fiber, (b) the Br fiber, and (c) the PDMAEMA fiber.

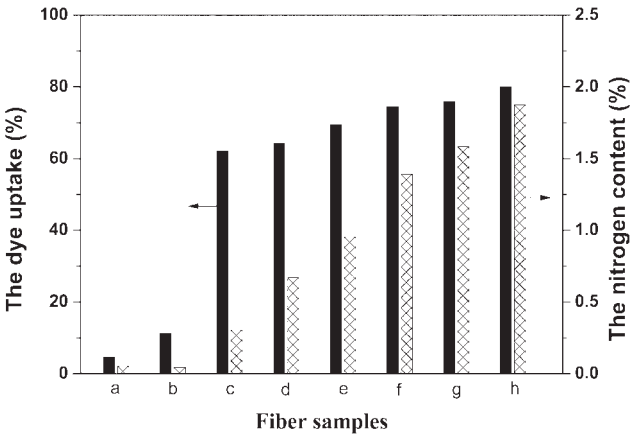



**Figure 5** Dye uptake and nitrogen contents for different fibers (for the designations of the different samples, see Table I).

at 70°C for 24 h. Then, the fiber after the cleavage of PDMAEMA was filtered off, and a NaOH solution was added dropwise until a pH of 13 was reached. After the solution was heated to 60°C, the cleaved PDMAEMA was precipitated. Finally, the product was dried *in vacuo* at 50°C. The $M_n$ and PDI values are shown in Table I. $M_n$ increased almost linearly with increasing amount of monomer used. Furthermore, a narrow and relatively lower PDI from 1.38 to 1.62 was obtained throughout the polymerization. Under the conditions investigated, the results indicate that the grafting polymerization of DMAEMA on the ramie fiber catalyzed by 1,10-phenanthroline/CuCl was a controlled process.

### Dye uptake of the fibers

Figure 5 shows the dye uptakes of different fibers. The dye uptake of the Br fiber was slightly higher than that of the raw fiber. This may have been because the immobilization of the initiator on the ramie fiber was favorable to the diffusion of dye molecules onto the fiber surface; this led to a higher dye uptake. However, the dye uptakes of the PDMAEMA grafted fibers were much higher than those of the Br fiber and the raw fiber. By examining the data shown in Figure 5 and Table I, one can see that the dye uptake increased continuously with increasing molecular weight of the PDMAEMA grafted onto the ramie fiber. To determine the reasons for this, we analyzed the nitrogen content of different fibers, and the results are given in Figure 5. As there was no nitrogen in the initiator and the nitrogen in the ramie fiber was considered to be an impurity, within experimental error, the nitrogen content in the raw fiber and the Br fiber was basically the same and very low. However, as a result of the amine groups in DMAEMA, the nitrogen content increased continuously with increasing molecular weight of the PDMAEMA grafted onto the fiber, which supported the FTIR results on the successful grafting of PDMAEMA. It is believed that a covalent bond can be easily formed between the halogenation *s*-triazine groups in CI Reactive Red 2 and the tertiary amine groups in PDMAEMA through a nucleophilic substitution reaction.[37,38] Thus, the dye molecule could be easily fixed onto the surface of the PDMAEMA-grafted fiber with a greatly improved dye uptake. The higher molecular weight of the PDMAEMA grafted onto the fiber implied a higher content of tertiary amines; thus, a higher dye uptake was obtained.

## CONCLUSIONS

In this study, PDMAEMA was covalently bonded onto the surface of ramie fiber via ATRP in a system with a brominated initiator and a catalyst of CuCl/1,10-phenanthroline. The FTIR results confirmed that PDMAEMA was successfully immobilized on the surface of the ramie fiber; these results were also supported by XRD, TGA, and elemental analysis. The GPC results revealed that the surface-initiated ATRP of DMAEMA on the surface of the ramie fiber under the conditions investigated was a controlled process. The properties of the PDMAEMA fiber were quit different from the raw ramie, as indicated by the SEM photomicrograph and TGA. The dye uptake for the PDMAEMA fiber (ca. 80%) was improved compared with the raw fiber (ca. 5%) because the reactivity between the tertiary amines in PDMAEMA and the dichlorotriazinyl group in the dye molecules was much higher than that between the hydroxyl groups in the ramie fiber and the reactive groups in the dye molecules.

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