# Grafting of Polystyrene and Poly(p-chlorostyrene) from the Surface of Ramie Fiber via RAFT Polymerization

Jie Yi,[1] Jing Chen,[1] Zhao-Tie Liu,[1,2] Zhong-Wen Liu[1,2]

[1]School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, People's Republic of China
[2]Key Laboratory of Applied Surface and Colloid Chemistry, Shaanxi Normal University, Ministry of Education, Xi'an 710062, People's Republic of China

**ABSTRACT:** Reversible addition-fragmentation chain transfer (RAFT) radical polymerization was used for controlled grafting of styrene and p-chlorostyrene from the surface of ramie fiber. The hydroxyl groups in ramie fiber were first converted to thiocarbonylthio groups as the RAFT chain transfer agent then used to mediate the RAFT polymerization of styrene, and p-chlorostyrene in tetrahydrofuran using azobis (isobutyronitrile) as initiator at 60°C. The grafted copolymers were analyzed by Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetry, and contact angle measurements. The results confirmed that grafting occurred on the surface of the ramie fiber, substantially increasing the water contact angle from 75.31° to 147° for polystyrene grafted ramie fiber (cell-PS) and 135° for poly(p-chlorostyrene) (cell-PSCl), and improving the hydrophobicity of the grafted fiber. The homopolymers formed in the polymerization were analyzed by size exclusion chromatography to estimate the molecular weights and polydispersity indices (PDIs) of chains grafted from the surface of the ramie fiber, as well as showed narrow chain length distributions with a PDI of 1.32–1.70. These materials possess potential applications in many advanced technologies. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3551–3557, 2010

**Key words:** RAFT; polystyrene; poly(p-chlorostyrene); ramie fiber; grafting-from

## INTRODUCTION

Cellulosic grafted copolymers are receiving increasing attention due to their wide range of applications. They can be used as membrane materials,[1] thermoplastic elastomers, antibacterial surfaces,[2] sorption agents for the removal of heavy metals,[3] ion-exchange materials,[4] controlled drug delivery vehicles,[5] and other applications. Using natural cellulose fiber in composites is of great interest because cellulose is the most abundant natural resource with low cost, low density, and high toughness. They can be easily modified into composites with reproducible properties.

In the present work, we used ramie fiber, also called China grass, which is one of the most valuable natural fibers grown in temperate and tropical areas, especially in China. Ramie produces one of the strongest and longest plant fibers. These fibers are lustrous with an almost silky appearance.[6] It is superior to cotton and silk in their length and strength. The specific strength of ramie is almost the same as for E-glass fiber, and it shows higher elongation.[7] Ramie fibers are widely used in the textile industry due to their softness, bleachability, and superior dyeability.

The water contact angle of natural ramie fiber is 75.31°, as demonstrates that ramie fiber is sufficiently hydrophilic. There are only weak interfacial interactions between ramie fibers and hydrophobic nonpolar polymer matrices. Ramie fiber and hydrophobic polymers are consequently incompatible. This is the principal obstacle to forming their polymeric composites. Reducing the hydrophilicity of cellulose fiber is the most efficient way to improve its compatibility. Existing method is modifying the cellulose surface through the controlled grafting of hydrophobic monomers.[8]

It is well known that monomers such as methyl methacrylate, styrene, butadiene, and vinyl acetate can be grafted onto the surface of cellulose fibers to improve their compatibility with hydrophobic polymer matrices, and enhance the adhesion between the fiber and polymeric substrates. Controlled grafting of isobutyl vinyl ether onto cellulose, for example, was found to significantly reduce the hydrophilicity of the cellulose surface.[9] Roy et al.[10] successfully grafted polystyrene (PS) from the surface of filter paper, which is made from cotton fiber, and obtained well-defined cellulose-PS grafted copolymers with a super-hydrophobic cellulose surface. The water contact angle of this modified surface reached to 130°.

Synthesis of cellulosic grafted copolymers has been carried out primarily by free radical polymerization, which has developed into a mature technology. Free radical polymerization has the advantages of versatility, synthetic ease, and compatibility with a wide variety of functional groups, and it is utilized to produce millions of tons of vinyl-based homopolymers and copolymers. However, for preparation of well-defined macromolecules conventional free radical procedures have deficiencies such as a propensity to give a variety of termination reactions. In the context of grafted copolymers, the polymeric chain grows from the radical site produced by irradiation or chemical means via a "grafting-from" approach.[11] Hence, the grafting process, molecular weight, molecular weight distribution, and yields are difficult to control. Moreover, large amounts of homopolymer may be formed in the grafting-from process, and degradation of cellulose backbone chains may occur in the formation of the graft sites.

Living polymerization is becoming more and more attractive due to its ability to circumvent drawbacks of conventional free radical polymerization. The living techniques utilize initiation by anions or cations and can give a high level of control in producing well-defined polymers with low polydispersity and precise molecular architectures. Controlled grafting of cellulose using anionic or cationic polymerization methods by the "grafting-to" technique has been reported.[12–14] However, ionic polymerization is limited to a few functionalized monomers in comparison with radical polymerization. The stringent experimental conditions for ionic polymerization are usually demanding. These include high-purity reagents, low temperature, and inert atmosphere.[15]

The advantage of living/controlled radical polymerization (LCRP) is that it offers the control and precision of living ionic polymerization, together with the versatility of free radical polymerization. Widely used LCRP methods are nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer polymerization (RAFT). NMP and ATRP have been used for modification of cellulose with synthetic polymer side chains. Although both methods provide well-defined grafted copolymers, they have, in general, the drawbacks of high-reaction temperatures. Moreover, there is a limited range of monomers for NMP and contamination problem due to the residuals from catalyst and ligands in ATRP.[16]

RAFT polymerization can also be used for the synthesis of well-defined grafted copolymers. The RAFT process has several advantages in comparison with other LRCP methods: (1) It gives precise control of the polymerization, (2) a large range of functional monomers including styrene, methyl methacrylate, and butadiene can be used, and (3) relatively straightforward reaction conditions such as moderate temperature and pressure are used. RAFT has been recently applied to grafting various monomers onto solid substrates such as silicon wafers and carbon nanotubes. Moad and coworkers have reported grafting of vinyl monomers onto cotton fabric surfaces using the RAFT technique.[17] Rizzardo and coworkers[18] reported grafting of PS, poly(methyl acrylate) (PMA), and poly(methyl methacrylate) (PMMA) from cotton via RAFT. To create high-hydrophobic surface of modified ramie fiber, we selected styrene and *p*-chlorostyrene as monomers to improve the hydrophobic property of modified ramie fiber. In this study, hydrophobic PS and poly(*p*-chlorostyrene) (PSCl) have been covalently grafted from the backbone of ramie fiber, to change the hydrophilic surface of the fiber to a hydrophobic surface. The pathway for the preparation of the PS and PSCl grafted ramie fiber, and the synthesis of the cellulose-based RAFT agent is similar to our previous paper.[19]

## EXPERIMENTAL

### Materials

All solvents, monomers, and reagents with the highest available purity were used as received except as otherwise stated. Carbon disulfide ($CS_2$) and bromobenzene (AR grade) were purchased from Tianjing Fuchen Chemical Co. (Tianjing, China), and purified by vacuum and atmospheric pressure distillation, respectively. 2,2′-Azobis(isobutyronitrile) (AIBN), AR grade (Shanghai Shanpu Chemical Co., China), was recrystallized twice from ethanol, dried at ambient temperature in a vacuum oven, and stored in a freezer. The 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (ECPDB) RAFT agent was prepared according to the reported method.[20] *N*-methyl-2-pyrrolidone was dried with $MgSO_4$, then filtered and dried over molecular sieves (4 Å) for at least 3 days before use. 2-Bromoisobutyryl bromide (BIBB), CP grade, was supplied by Yancheng Kelida Chemical Co., China, and used as received. Tetrahydrofuran (THF) from Shanghai Sinopharm Group Chemical Reagent Co., China, was distilled from Na/diphenylketone under argon. 2-(Dimethylamino)pyridine (DMAP) (AR grade; Xi'an Chemical Co., China), magnesium cell chips (British Drug Houses Laboratory Chemicals Group, England), ethyl 2-bromoisobutyrate (Alfa Aesar, Tianjing, China), diethyl ether, *n*-hexane, and iodine were all used as received. Styrene and *p*-chlorostyrene (Fujian Chuangxing Chemical Co., China) were both distilled from desiccant under reduced pressure. Ramie fiber obtained from the

Institute of Bast Fiber Crops, Chinese Academy of Agriculture Sciences (CAAS, Changsha, China), was dried for 24 h at 60°C before use.

### Water contact angle measurement (WCAM)

The hydrophobicity of cellulose-*g*-PS and cellulose-*g*-PSCl copolymers was evaluated using a video-based water contact angle measuring device (OCA 20, Dataphysics Co., Germany). A drop of water (1 μL) was placed on the surface via the sessile and pendant drop method. The measurements of water contact angle were made at 23°C.

### Scanning electron microscopy (SEM)

The surface morphology of the raw and modified ramie fibers was observed using an environmental scanning electron microscope (ESEM, Quanta 200, Philips-FEI Co., Netherlands). The samples were gold coated before ESEM observation. Electron micrographs of each sample were obtained at magnifications of 1200 or 2400.

### Fourier transform infrared spectrometry

Fourier transform infrared spectroscopy (FT-IR) spectra of the raw and modified ramie fibers were obtained using a Nicolet 870 spectrometer (Madison, WI), with 32 scans averaged for each sample. About 1 mg of fibers was ground and dispersed in about 150 mg of potassium bromide (KBr) in a mortar. The fibers/KBr mixture was pressed into circular disks for scanning. Each spectrum was collected in the range 4000–400 cm$^{-1}$ with scan speed 0.5 cm$^{-1}$ s$^{-1}$.

### Nuclear magnetic resonance spectroscopy

$^1$H-NMR (nuclear magnetic resonance spectroscopy) and $^{13}$C-NMR spectra of the free chain transfer agent (CTA) ECPDB were recorded using a superconducting Fourier digital NMR spectrometer (Bruker, AVANCF 300 MHz). Tetramethylsilane was used as reference material.

### Thermogravimetry

Thermogravimetric analysis (TG) of the raw ramie fiber, cell-OBIB, cell-CTA, cell-*g*-PS (PSCl) copolymers, and homopolymers (all predried at 40°C under vacuum) was carried with a model Q600SDT (TA Instruments Co., USA) thermoanalyzer system, under a nitrogen atmosphere. The samples (5 mg) were heated from room temperature to 500°C at 10°C min$^{-1}$. The TA Instruments Universal Analysis 2000 software was used to calculate the onset temperature, end decomposition temperature, and residual mass.

### Size exclusion chromatography (SEC)

The number average molecular weight ($M_n$) and polydispersity indices ($M_w/M_n$) of homopolymers formed in the graft polymerization reaction mixture were measured with a Waters 2410 instrument equipped with three Waters μ-Styragel columns (HT4, HT5, and HT6) (Milford, MA) using THF as the eluent at 1 mL min$^{-1}$ flow rate at 35°C. The system was calibrated with PS standards with molecular weights 200 to 10$^6$ g/mol.

### Grafting ratio

The grafting ratio of cell-*g*-PS and cell-*g*-PSCl copolymers was calculated using the following formula.

$$G(\text{wt \%}) = (W_{\text{graft copolymer}} - W_{\text{cell-CTA}}) \times 100/W_{\text{cell-CTA}} \quad (1)$$

where $W_{\text{graft copolymer}}$ and $W_{\text{cell-CTA}}$ are the mass of grafted copolymer formed and the mass of cell-CTA used in the grafting reaction, respectively.

### Elemental analysis (EA)

The surface contents of Br and S of samples were analyzed by an energy dispersive spectrometer (EDS) (EDAX Co., Mahwah, NJ).

### Pretreatment of ramie fiber

Ramie fibers that had been oven dried at 60°C for 24 h were cut into pieces 1–2 mm in length. The fiber pieces (3 g, number of moles of active hydroxyl group = 3.20/162 × 3 = 0.06 mol) were immersed in NMP (about 15 mL) in a two-neck round-bottom flask (250 mL) for about 12 h at ambient temperature, to swell the fibers. The mixture was used without any further treatment for the next step of process.

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

The two-neck round-bottom flask with the pretreated ramie fiber sample was cooled in an ice bath, and the air in the flask replaced by argon via the exhaustion method. DMAP (0.18 g, 0.009 mol) used as catalyst was dissolved in NMP (5 mL), and the solution added to the mixture in the flask through a constant pressure funnel (150 mL) under argon atmosphere. A solution containing 35 mL BIBB in

NMP (0.36 mol), used as a proton scavenger, and an excess amount of BIBB (22.5 mL, 0.18 mol) was then added dropwise to the reaction flask. The approximate molar ratio NMP : BIBB : cellulose hydroxyl group was 9 : 3 : 1. The flask was then sealed and heated for 24 h at 60°C with slow stirring in an oil bath. The deep yellow reaction product was thoroughly washed with anhydrous ethanol to remove unreacted BIBB and salt, and vacuum dried at 40°C overnight. The cellulose ester product is referred to henceforth as cell-OBIB. The analytical data for this product were as follows:

Gravimetry

Weight of dry cell-OBIB = 6.13 g; percent mass increase = 104.33%.

Elemental analysis

Br, 24.19 wt %. Average degree of substitution (DS), the average number of reacted hydroxyl groups per repeating unit of cellulose, in the esterification step = 0.99 (32.99% substitution).

## Synthesis of cellulose-based raft chain transfer agent (cell-CTA)

Cell-CTA was synthesized from cell-OBIB. First, magnesium turnings (1.50 g, 0.062 mol) and bromobenzene (7 mL, 0.067 mol) were mixed, then the solution was warmed to 40°C and an excess of carbon disulfide (19.2 mL, 0.32 mol) mixed with anhydrous THF (10 mL) was added dropwise into the two-neck flask over 30 min. The color of the solution changed from dark green to red black over about 4 h at 40°C. All of these operations were carried out under an argon atmosphere. Cell-OBIB (2.00 g) was added to the reaction mixture, followed by anhydrous THF (35 mL), and the mixture was heated at 80°C for 24 h. After reaction, the products were rinsed with THF and dilute hydrochloric acid, and unreacted reagents were removed by Soxhlet extraction. The deep yellow resulting product, referred to as cell-CTA, was vacuum dried at 40°C overnight. The analytical data for this product were as follows.

Gravimetry

Weight of dry cell-CTA = 2.98 g; percent mass increase = 49.00%.

EA

Br, 4.73 wt %; S, 7.12 wt %. Average degree of conversion of OH group in cellulose to cell-CTA in this step = 0.42 (13.29%).

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

The free chain transfer agent ECPDB used in the RAFT process was synthesized as previously reported.[20] The steps of the synthesis of ECPDB were very similar to those used for cell-CTA, except for the reagent dosage, types of reagents, and product treatment. The detailed synthesis procedure and ^{1}H-NMR results are given in our previous paper.[19]

## Synthesis of cellulose-g-PS and cellulose-g-PSCl grafted copolymers (cell-g-PS and cell-g-PSCl) via RAFT technique mediated by free-CTA and cell-CTA

Cell-CTA (0.5 g, 1.36 mmol of RAFT agent loading) was immersed in anhydrous THF (35 mL) in a two-neck flask for about 12 h. Monomer (9 mL of styrene or 9.37 mL of p-chlorostyrene), initiator (AIBN) (0.005 g, 0.03 mmol, dissolved in 10 mL of dry THF), free-CTA (0.0804 g, 0.3 mmol, dissolved in 5 mL of dry THF), and 15 mL of anhydrous THF were added to the flask. The initial molar ratios monomer : cell CTA : free-CTA : AIBN were 500 : 1 : 1 : 0.1. The mixture was degassed with argon for at least 30 min and heated in a preheated oil bath at 60°C for 72 h under argon. The flask was then opened to the air and cooled in an ice-water bath. The raw products were washed with THF to remove unreacted monomer, homopolymer (PS or PSCl), and residual initiator. The average molecular weights ($M_n$) and polydispersity indices ($M_w/M_n$) of free homopolymers were measured by SEC after the process of water setting out. The solid graft copolymer products were washed with THF using Soxhlet extraction for about 72 h to completely remove the THF-soluble material referred to above. Finally, the deep yellow cellulose-g-PS or cellulose-gPSCl were vacuum dried at 40°C overnight. The grafting ratios calculated using eq. (1) were: Gravimetry, $G_{cell-PS}$ = 17.52%; $G_{cell-PSCl}$ = 33.96%.

## RESULTS AND DISCUSSION

### Synthesis of cellulose ester (cell-OBIB) and cellulose-based RAFT chain transfer agent (cell-CTA)

Naturally occurring ramie fiber is made up of D-anhydroglucose units joined by β-1,4-linkages. It exhibits a high degree of crystallinity in its native state due to strong intermolecular hydrogen bonding. Consequently, most of the OH groups of the cellulose are not accessible for reaction. Only the OH groups in the amorphous regions and on the surface of the crystalline regions can react, because the reagent molecules are not able to penetrate the highly ordered crystalline regions. It was necessary to pretreat the cellulose fibers using ultrasonic and
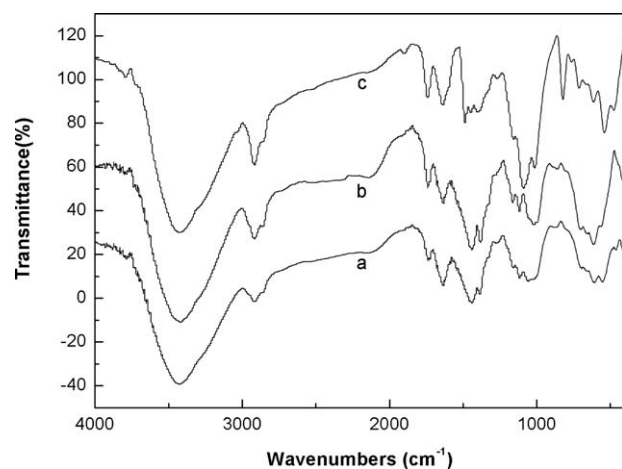
**Figure 1** FT-IR spectra of (a) cellulose-based RAFT chain transfer agent (cell-CTA), (b) ramie cellulose-based graft copolymer cell-g-polystyrene, and (c) cell-g-poly(p-chlorostyrene).

swelling treatment in solvent for a sufficient time to break hydrogen bonds and open up the more ordered regions. By doing so, a higher degree of substitution in the esterification step and a higher loading of RAFT agent in the subsequent step were achieved than would otherwise have been possible.

The hydroxy groups of the ramie fibers were treated with 2-bromoisobutyryl bromide (BIBB) and converted to the corresponding cellulose-based thiocarbonylthio compound (cell-CTA), which was used as the RAFT agent. A large excess of BIBB was required in the first step to improve the reaction efficiency and to obtain a sufficiently high degree of substitution. The structures of cellulose 2-bromoisobutyryl bromide (cellulose-OBIB) and cellulose-based RAFT reagent (cellulose-CTA) were confirmed by FT-IR spectroscopy and elemental analyses. From the elemental analyses, average of 23.83 wt % bromine was found in cellulose-OBIB samples and on average 31.96% of the hydroxy groups of raw ramie fiber were successfully substituted by OBIB in the first step to form the cellulose ester. An average of 7.12 wt % of sulfur was detected by elemental analyses of cellulose-CTA, indicating successful loading of RAFT agent onto the cellulose surface. Furthermore, smaller bromine content in the cellulose-CTA compared with cellulose-OBIB showed that cell-OBIB was substituted by cellulose-based RAFT agent.

The FT-IR results of ramie fiber before, and after the esterification process is reported in our previous paper.[19] A very strong stretching band for the C=O group at 1739 $cm^{-1}$ and weak bands at 1277 $cm^{-1}$ for the C—O stretch mode confirm that formation of cellulose-OBIB was successful. The C=S stretching bands at 1273 and 1581 $cm^{-1}$ in the FT-IR spectra of cell-CTA confirmed that the cellulose-based RAFT agent was successfully prepared.

## Graft copolymerization via RAFT technique mediated by free-CTA and cell-CTA

Cellulose-g-PS and cellulose-g-PSCl copolymers were prepared using RAFT polymerization. The FT-IR spectra of the copolymers [Fig. 1(b)] showed new bands at 3020, 1619, 1449, 759, and 798 $cm^{-1}$, which are characteristic bands of PS. Roy et al.[10] used the absorption band at about 698 $cm^{-1}$ as the main evidence of grafting, and for quantitative determination of PS in cotton cellulose-PS copolymers. The C—Cl stretching vibration at 820 $cm^{-1}$ [Fig. 1(c)] confirmed successful preparation of cellulose-g-PSCl copolymer.

## Purification procedure for cell-CTA and cell-polymers

Soxhlet extraction was used to remove unreacted reagents from cell-CTA or cell-polymers. The crude solid products were extracted in THF for 72 h. First cell-CTA was synthesized from cell-OBIB in THF, and then cell-polymer was synthesized from PS or PSCl. Although cell-OBIB is insoluble in THF, the reactant $C_6H_5CS_2MgBr$ can dissolve in THF. The reactions occurred on the surface of cell-OBIB in heterogeneous conditions. Because of the insolubility of cell-CTA in THF, PS, or PSCl homopolymers on the surface of cell-PS or cell-PSCl were removed via Soxhlet extraction because THF is a good solvent for the homopolymers. The final cell-polymer products were pure cell-PS or cell-PSCl copolymers surface grafted through covalent bonds.

### Size exclusion chromatography (SEC)

In most cases, the grafted chains of cellulose-based grafted copolymer synthesized via ATRP and RAFT techniques must be cleaved from the copolymer substrate to determine the degree of control of the LCRP graft polymerization process.[9,10,12,14] However, the process of cleaving can take more than 3 weeks due to the highly hydrophobic character of the ramie cellulose-based grafted copolymers, and the amount of cleaved polymers was too small for characterization by SEC analysis. Using a previously reported method, the homopolymers formed in the graft polymerization in the presence of free chain transfer agent (CTA) containing a similar end structure to that of the macromolecular chain transfer agent were isolated and analyzed by SEC to provide an estimate

**TABLE I**
**Estimated Molecular Weight Data for Cell-PS and Cell-PSCl Grafted Chains**

| Sample | $M_n$ (g mol$^{-1}$) | PDI |
|---|---|---|
| Cell-PS | 18,464 | 1.32 |
| Cell-PSCl | 13,269 | 1.70 |
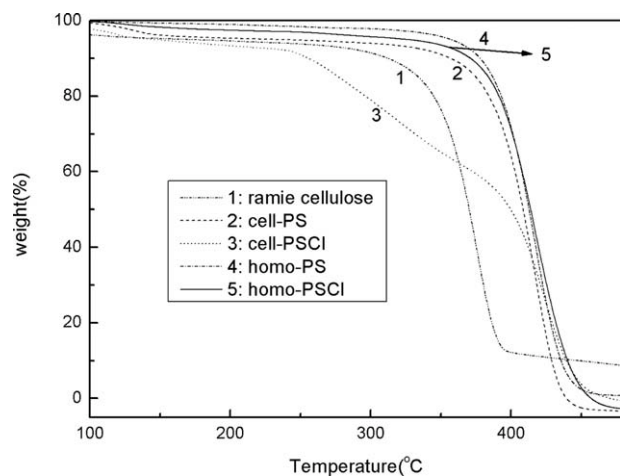
**Figure 2** TGA thermograms of (1) raw ramie cellulose, (2) cell-PS, (3) cell-PSCl, (4) homo-PS, and (5) homo-PSCl.

of the molecular weights ($M_n$) and polydispersity index of polymer chains attached to the surface of cellulose. We found that the free-CTA containing a similar R group[19] to the cell-CTA was sufficiently stable to form a radical and give controlled polymerization of styrene, but not *p*-chlorostyrene. As can be seen from Table I, the PDI of PS was 1.32 illustrating well-controlled radical RAFT polymerization of styrene. In the case of PSCl, polymerization was less well controlled (PDI = 1.70).

Thermal analysis

Thermogravimetric analysis (TGA) was used to prove the success of the graft polymerization process and to quantify the thermal properties of the cellulose-based copolymers and the corresponding homopolymers (PS and PSCl). The decomposition patterns and thermal stabilities of the grafted copolymers are shown in Figure 2. For comparison, the TGA thermograms of raw ramie cellulose and the homopolymers (homo-PS and homo-PSCl) have been measured as well (Fig. 2). TG curves in Figure 2 show that the degradation of the ramie cellulose-based copolymers includes two stages: the first is due to the degradation of raw ramie cellulose, whereas the

**TABLE II**
**Thermal Stability of Raw Ramie Cellulose, Cell-PMMA, Cell-PMA, Homo-PMMA, and Homo-PMA**

| Sample | $T_{di}/°C$ |
|---|---|
| Raw ramie cellulose | 265 |
| Cell-PS | 120 |
| Cell-PSCl | 248 |
| Homo-PS | 318 |
| Homo-PSCl | 326 |

latter is of the degradation of polymer (PS or PSCl). The initial weight loss occurs at a lower temperature ($T_{di}$) for cell-PS and cell-PSCl, which may resulting from the presence of the less thermally stable brominated chain ends and cell-CTA in the macroinitiators. The data are summarized in Table II. The residual masses of the grafted copolymers were lower than those of raw ramie cellulose and higher than those of homopolymers, because of the formation of composite grafted copolymers.

Scanning electron microscopy (SEM)

SEM micrographs of raw ramie fibers and grafted copolymers (cell-PS and cell-PSCl) are shown in Figure 3. It is apparent that the grafted celluloses had structural features different from those of the unmodified cellulose and that graft polymerization occurred mainly on the surface of the fibers.

Contact angle measurements

The surface hydrophobicities of cell-PS and cell-PSCl were investigated via static water contact angle measurements. The raw ramie cellulose adsorbed water rapidly to measure the water contact angle by the static method. However, the grafted copolymers showed favorable hydrophobicity with water contact angles 147° for cell-PS and 135° for cell-PSCl, respectively. The results showed that the hydrophilic surface of raw ramie fiber was modified to be hydrophobic by covalently bonding hydrophobic grafts to the surface of the fibers.
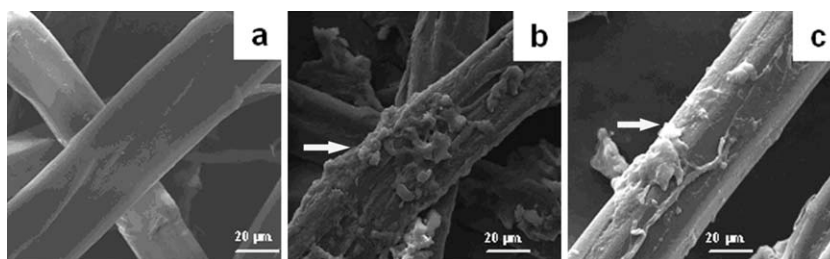


**Figure 3** SEM photographs of (a) raw ramie fibers, (b) cell-PS, and (c) cell-PSCl.

## CONCLUSIONS

Cell-g-PS and cell-*g*-PSCl copolymers were successfully synthesized via RAFT polymerization in which the RAFT chain transfer agent ECPDB was used. The polymerization was well controlled, particularly for cell-*g*-PS, giving highly hydrophobic surfaces. This methodology is a novel and feasible approach to preparation of functional composite materials utilizing the abundant ramie fiber natural resource.

## References

1. Nishioka, N.; Yamaguchi, H.; Kosai, K. J Appl Polym Sci 1990, 40, 2007.
2. Lee, S. B.; Koepsel, R. R.; Morley, S. W.; Matyjaszewski, K.; Sun, Y.; Russell, A. Biomacromolecules 2004, 5, 877.
3. Waly, A.; Abdel-Mohdy, F. A.; Aly, A. S.; Hebeish, A. J Appl Polym Sci 1998, 68, 2151.
4. Chauhan, G. S.; Guleria, L.; Sharma, R. Cellulose 2005, 12, 97.
5. Goni, I.; Ferrero, M. C.; Jimenez-Castellanos, R. M.; Gurruchaga, M. Drug Dev Ind Pharm 2002, 28, 1101.
6. Liu, Z. T.; Yang, Y. N.; Zhang, L. L.; Liu, Z. W.; Xiong, H. P. Cellulose 2007, 14, 337.
7. Herrmann, A. S.; Nickel, J.; Riedel, U. Polym Degrad Stab 1998, 59, 251.
8. Mohanty, A. K.; Misra, M.; Drzal, L. T. Compos Interface 2001, 8, 313.
9. Tsubokawa, N.; Iida, T.; Takayama, T. J Appl Polym Sci 2000, 75, 515.
10. Roy, D.; Guthrie, J. T.; Perrier, S. Macromolecules 2005, 38, 10363.
11. McDowall, D. J.; Gupta, B. S.; Stannett, V. T. Prog Polym Sci 1984, 10, 1.
12. Roy, D.; Knapp, J. S.; Guthrie, J. T.; Perrier, S. Biomacromolecules 2008, 9, 91.
13. Månsson, P.; Westfelt, L. J J Polym Sci Part A: Polym Chem 1981, 19, 1509.
14. Biermann, C. J.; Chung, J. B.; Narayan, R. Macromolecule 1987, 20, 954.
15. Gupta, K. C.; Sahoo, S. Cellulose 2001, 8, 233.
16. Carlmark, A.; Malmström, E. J Am Chem Soc 2002, 124, 900.
17. Moad, G.; Rizzardo, E.; Thang, S. H. Aust J Chem 2006, 59, 669.
18. Moad, G.; Rizzardo, E.; Thang, S. H. Aust J Chem 2005, 58, 379.
19. Chen, J.; Yi, J.; Sun, P.; Liu, Z.-T.; Liu, Z.-W. Cellulose 2009, 16, 1133.
20. Chong, Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. Macromolecules 2003, 36, 2256.