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RAFT Synthesis of Cellulose-*g*-Polymethylmethacrylate Copolymer in an Ionic Liquid

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ABSTRACT: We demonstrate for the first time the feasibility in conducting the graft copolymerization of methylmethacrylate (MMA) with cellulose by the means of the reversible addition-fragmentation chain transfer (RAFT) polymerization in an ionic liquid [1-*N*-butyl-3-methylimidazolium chloride] (BMIMCl). Cellulose was first converted to a macromolecular chain transfer agent to which MMA was grafted by RAFT in BMIMCl. The success of the occurrence of different reactions was validated by elemental analyses, Fourier transform infrared and nuclear magnetic resonance spectroscopies. The results demonstrate that the MMA polymer chains were grafted onto the cellulose while the use of the ionic liquid as a reaction medium enhanced the polymerization rate to a moderate extent. Gel permeation chromatography analysis of poly(MMA) chains cleaved from the cellulose by acidic hydrolysis indicated low polydispersity indices (ca. 1.3) that were consistent with the "living" nature of the RAFT. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000000, 2012

KEYWORDS: cellulose; copolymerization; graft copolymers; living polymerization; reversible addition fragmentation chain transfer (RAFT)

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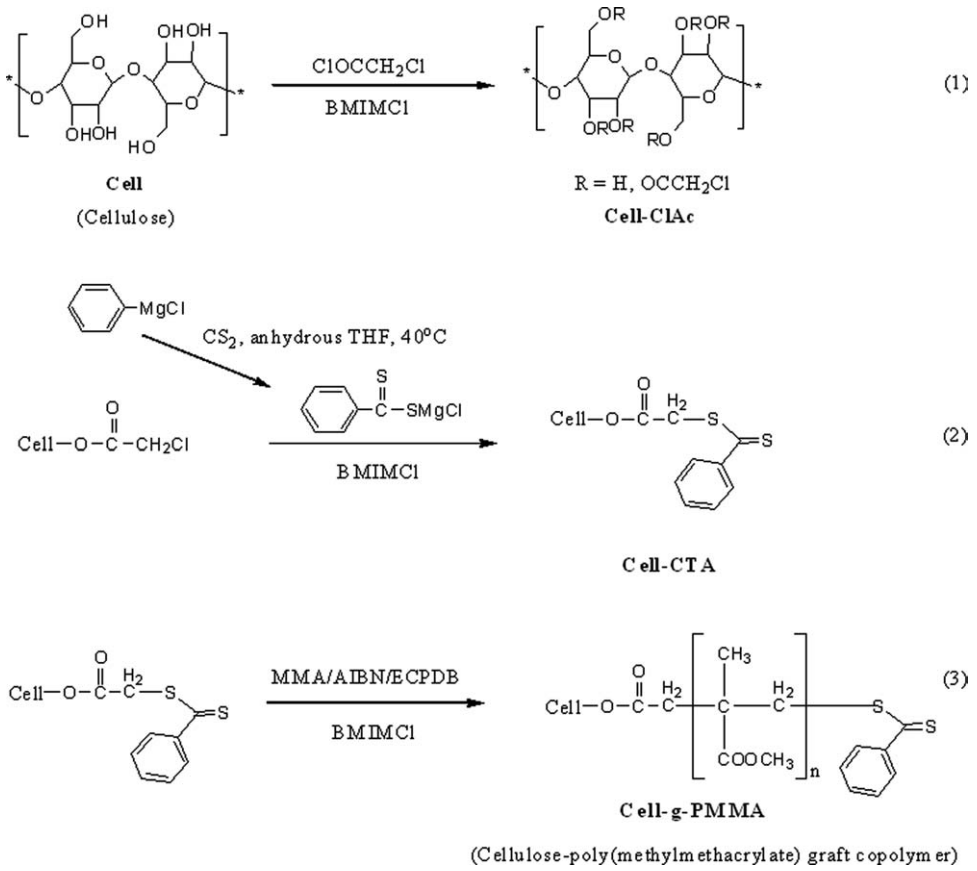
INTRODUCTION

Cellulose is the most abundant renewable polymer resource available today that has been used as a raw material to access a wide spectrum of products.[1] Among these cellulose-based materials, cellulose graft copolymers have gained a substantial interest in the last few decades due to the unique properties they endow which make possible their use in a wide range of applications such as medical, pharmaceutical, textiles, filtration, composites, among others.[2] Polymer grafting on cellulose can be accomplished by two main strategies, namely, the "grafting-onto" and "grafting-from." The grafting-onto method requires attachment of presynthesized and well-characterized polymer chains onto cellulose hydroxyl groups. However, steric hindrance can prevent optimal attachment because the polymer chains must diffuse through grafted "brushes" to reactive sites. Therefore, the grafting-onto method produces grafts with low surface grafting densities. To increase the grafting density on cellulose, the "grafting from" approach is employed. Polymer chains are formed by in situ initiated polymerization from substrate-immobilized initiators. Such polymerization methods have included conventional radical polymerizations, ionic polymerizations, and ring opening polymerizations.

Recent advances in controlled/living free radical polymerizations such as nitroxide-mediated polymerization, atom transfer radical polymerization (ATRP), and reversible addition fragmentation chain transfer (RAFT) polymerization allow also synthesis of graft copolymers from cellulose.[2] Recently, RAFT polymerization has merged as a powerful and useful living polymerization method for synthesizing well-defined, sophisticated graft polymer features (e.g., block, graft, comb, and star) and controlling the polymerization of numerous vinyl monomers [e.g., molecular weight and polydispersity indices (PDIs)] over mild reaction conditions. RAFT has been applied to graft various monomers onto solid supports such as silica particles,[3] silicon wafers,[4] carbon nanotubes,[5] rigid poly(propylene),[6] gold nanoparticles,[7,8] and core-shell microspheres.[9] Additionally, RAFT has been reported to graft different vinyl monomers on different cellulosic fibers.[10–15]

However, typical organic chemistry reactions for cellulose, including polymer grafting, are challenging because of its insolubility in water and in most organic solvents due to the highly dense hydrogen bonded network. Thus, most syntheses, including those cited above, are heterogeneous reactions carried out at the solid or swollen state. "Activation" (swelling cellulose) allows



Scheme 1. The preparation of Cell-AcCl, Cell-CTA, and cellulose graft copolymer.

synthesis of cellulose derivatives with surface substitution patterns and tuned reactivity. For more complete reactions, specific solvents have been developed to dissolve cellulosic fibers. These solvents mainly act by breaking down hydrogen bonds to dislocate cellulose fibers to "individual" cellulose chains.[16] For example, LiCl in DMA is one of the most important cellulose reaction solvents.

Recently, ionic liquids (ILs) have emerged as promising solvents due to strong solvation properties and wide liquid ranges and are thus considered to be viable for cellulose modifications.[17,18] Polymerizations of vinyl monomers via conventional or controlled/living radical polymerizations, including RAFT, have already been conducted in ILs.[19–24] Well-defined polymers with narrow polydispersities have been obtained and the rate of polymerization was enhanced compared to typical solvents. However, no example has been reported for simultaneous grafting and RAFT polymerization of polymer chains from cellulose in ILs. We herein provide the first report of grafting methylmethacrylate (MMA) from cellulose by RAFT using an ionic liquid (BMIMCl) as the reaction medium. The introduction of PMMA chains on cellulose fiber can improve the hydrophilic property of cellulose fiber and thus widen its application area.

EXPERIMENTAL

Materials

Cotton linter fibers (cellulose) were used. The IL 1-*N*-butyl-3-methylimidazolium chloride (BMIMCl, mp. 73°C) was purchased from Henan Lihua Pharmaceutical Co. Phenylmagnesium chloride (25 wt % solution in tetrahydrofuran) and carbon disulfide (99.9+%) were used as received. 2,2′-Azobis(isobutyronitrile) (AIBN, 97%) was purified by ethanol recrystallization, dried in a vacuum oven, and stored in a freezer. 2-(Ethoxycarbonyl) prop-2-yl dithiobenzoate (ECPDB) was synthesized according to the procedure available in the literature.[25] MMA was dried over anhydrous magnesium sulfate and vacuum distilled before use. All other reagents used were ACS analytical grade and used as received.

Preparation of Cellulose-Supported Chain-Transfer Agent (Cell-CTA)

The Cell-CTA was obtained by converting a cellulose-based ATRP initiator (Cell-ClAc) to Cell-CTA (see Scheme 1): (i) preparation of cellulose-based ATRP initiator (Cell-AcCl): 15 g (92.6 mmol of anhydroglucose unit) of cellulose were dissolved in BMMCl at 3% weight concentration and fivefold of chloroacetyl chloride was added. The mixture was heated and stirred for 2 h at 50°C under N_2. After the reaction was completed, the products were precipitated with excess water and washed thoroughly with water, filtered, and freeze-dried; (ii) the conversion of Cell-ClAc to Cell-CTA: A sample of Cell-ClAc previously prepared was reacted with bis(thiobenzoyl) disulphide prepared as reported by Roy et al. [9b] Briefly, 20 mL (0.15 mol) of phenylmagnesium chloride were added to a three-neck round-bottom flask containing anhydrous THF (100 mL) under nitrogen. An

Table I. Results of the Element Analyses and the DS

	C (%)	H (%)	Cl (%)	S (%)	DS_1[a]	DS_2[b]
Cell-AcCl	38.32	3.89	21.76	0	1.87	2.01
Cell-CTA	54.02	4.63	10.54	15.49	0.84	0.96

[a]DS obtained from EA, [b]DS calculated from ^{1}H-NMR.

excess of carbon disulfide (45 mL, 0.75 mol) was then added dropwise into the flask creating a dark brown solution that was heated at 40°C for 3 h. The resultant dark brown solution was transferred to another flask containing Cell-ClAc (4.0 g). The reaction was conducted at 80°C over 24 h. The product was thoroughly washed with THF and extracted by using a mixture of THF and methanol in a Soxhlet apparatus to remove unreacted RAFT agent. The resulting orange solid residue was labeled Cell-CTA.

Synthesis of Cellulose-*g*-Poly(MMA) Copolymer by RAFT

A typical graft polymerization reaction involved dissolving the Cell-CTA in BMIMCl in a septum-sealed flask. A prescribed concentration of MMA monomers, initiator (AIBN) previously dissolved in 6 mL of DMSO and free CTA (ECDPB, dissolved in 6 mL of DMSO) were then added to the flask. The molar ratio of monomer, Cell-CTA, free CTA, and initiator was 300 : 1 : 1 : 0.1. The reaction mixture was degassed with nitrogen for 15 min and heated to 60°C. The reaction was ceased after 5 h by cooling the mixture in an ice-water bath. The mixture was poured into de-ionized water to precipitate the solid. After filtering and washing, the solid was washed with THF (5 × 150 mL) to remove surface contaminants such as unreacted monomer, ungrafted (free) homopolymer, and initiator. The product was the subjected to Soxhlet extraction with THF for 36 h to remove free homopolymer. Finally, the cellulose-*g*-poly(MMA) sample was freeze dried. To calculate graft ratio, the Cell-CTA samples were weighed before and after polymerization with poly(MMA). The graft ratio (*G*, wt %) was calculated:

$$\text{Grafting ratio}(\%) = \frac{\text{Weight}_{\text{graft}} - \text{Weight}_{\text{cell-CTA}}}{\text{Weight}_{\text{cell-CTA}}} \times 100 \qquad (1)$$

where "$\text{weight}_{\text{graft}}$" is the dry weight of each Cell-CTA sample after grafting with MMA and "$\text{weight}_{\text{Cell-CTA}}$" is the initial weight of each Cell-CTA sample.

Characterization

Fourier Transform Infrared Spectroscopy. Fourier transform infrared spectra of the unmodified cellulose and modified cellulose were obtained by a Spectrum GX Infrared spectrophotometer (USA, Perkin-Elmer Co.) using KBr pellets. About 2 mg of samples were mixed with 200 mg of spectroscopic grade KBr, and the FTIR spectra were recorded with a detector at 4 cm^{-1} resolution and 32 scans per sample in a range of 4,000–400 cm^{-1}.

Elemental Analyses. The modified cellulose samples were analyzed by elemental analyses (EAs) for C, H, N, Cl, and S. C, H, and N contents were determined by combustion followed by chromatographic separation and thermal conductivity detection using a Carlo Erba EA 1108 Elemental Analyzer. The degree of substitution (DS_1) of Cell-ClAc and Cell-CTA were calculated from Cl and S, respectively (Table I).

Chlorine Analysis. The completely dried test samples (5–10 mg) were combusted by the Schoniger oxygen flask combustion method.[26] The combusted products were washed into a flask with 5–10 mL of water. One drop of bromophenol blue (0.1% in ethanol) was added. Nitric acid solution was added dropwise until yellow, and 0.5 mL excess nitric acid was added. Then 50 mL of ethanol and diphenyl carbazone indicator (0.1% in ethanol) was added. Finally, chlorine was determined as chloride anion by titration using 0.05*M* mercuric nitrate (in water) to a purple end point. A blank determination was also carried out and subtracted from the sample titration.

Sulfur Analysis. The completely dried test sample (5–10 mg) was combusted by the Schoniger oxygen flask combustion method.[26] The combusted products were washed into a flask with 5–10 mL of propan-2-ol, and 30 mL of propan-2-ol was added to the flask. Then 0.2 mL of thorin solution (0.2% in water) and 0.25 mL of methylene blue solution (0.02% in water) were added. Finally, sulfur was analyzed as sulfate anion by titration using 0.05*M* barium perchlorate solution (in 95% propan-2-ol) until a definite end point (from green to pink). A blank determination was also carried out and subtracted from the sample titration.

^{1}H-Nuclear Magnetic Resonance Spectroscopy. ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a NMR spectrometer (Bruker, DRX 400 MHz). DMSO-d_6 was used as a solvent and tetramethylsilane (TMS) as reference.

Gel Permeation Chromatography. The molecular weight and molecular weight distributions of PMMA obtained by hydrolysis of Cell-PMMA were measured on a gel permeation

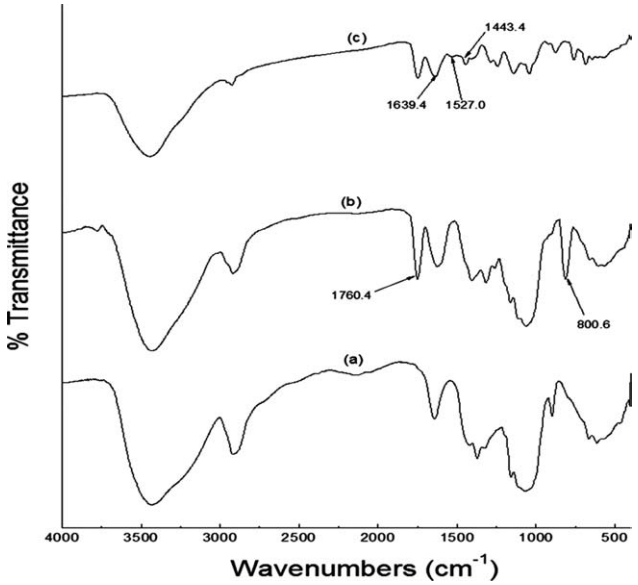


Figure 1. FTIR spectra of (a) unmodified cellulose, (b) cellulose chloracetate (Cell-AcCl), and (c) cellulose-based RAFT chain transfer agent (Cell-CTA).

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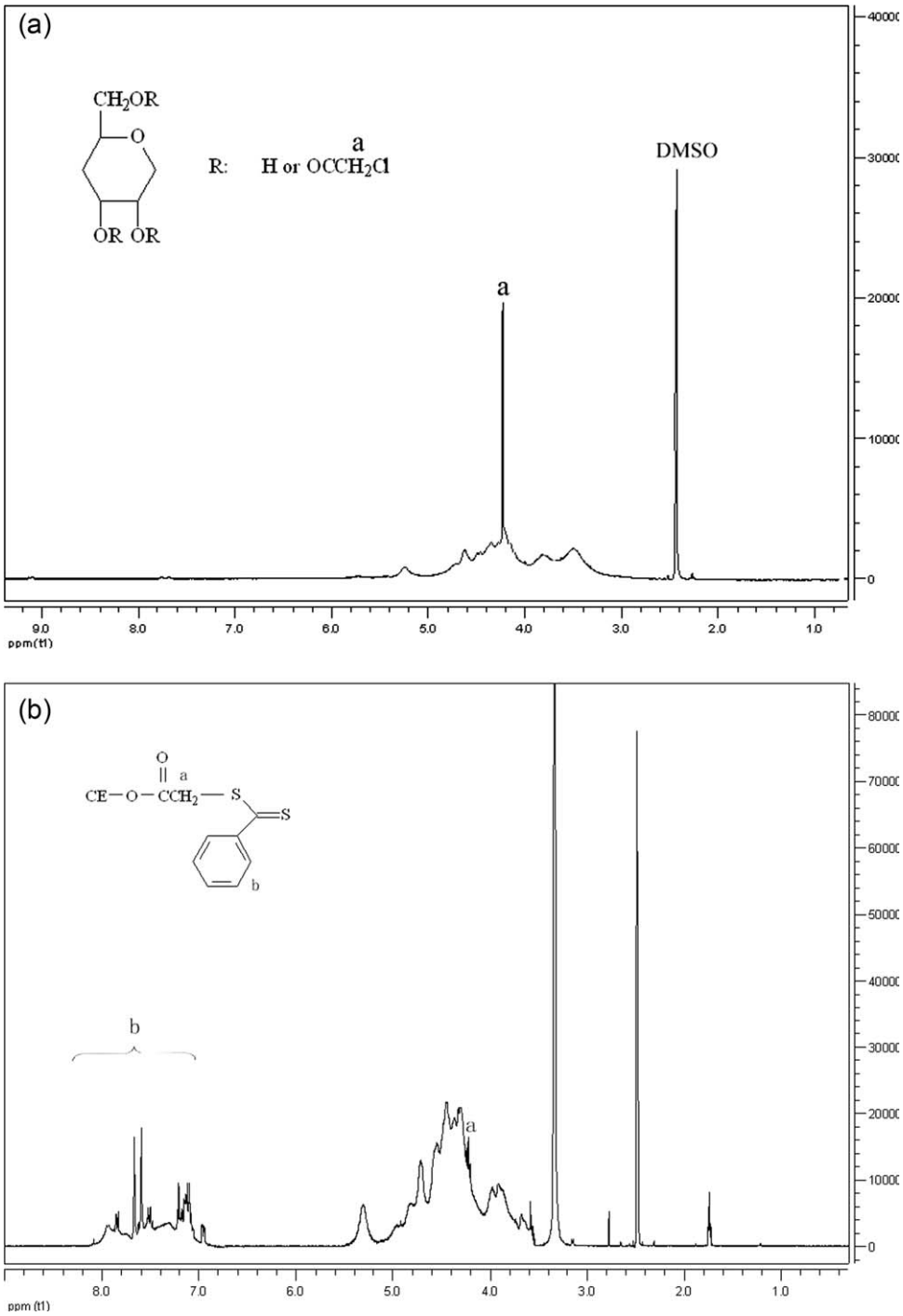

Figure 2. ^{1}H-NMR spectra of Cell-ClAc (a) and Cell-CAT agents (b) in DMSO-d_6.

chromatography (GPC) (equipped with a Waters 515 pump, three columns Styragel HT3, Styragel HT4, and Styragel HT5, and a 2414 differential refractometer detector) with THF as the eluent, the flow rate was 1 mL/min. The hydrolysis involved immersing 0.04 g cellulose-*g*-PMMA sample into a flask containing 15 mL of 1.5*M* HCl. The flask was stirred at 90°C for 72 h and filtered to separate solid cellulose particles. The HCl solution was removed by evaporation.

Contact Angle Measurements. The degree of hydrophobicity of cellulose-*g*-poly(MMA) copolymers was appraised using a contact angle meter (Dataphysics OCA40 Micro). A drop of water was placed on the copolymer surface, and the contact angle was determined at room temperature.

Scanning Electron Microscopy. Scanning electron microscopy (SEM) photomicrographs of the cellulose before and after modification were observed by a Quanta 200 environmental

scanning electron microscope (Philips-FEI Co., Holland) operated at an accelerating voltage of 5 kV, and the dried samples were coated with a gold layer using a diode sputter coating unit. Electron micrographs of each sample were recorded at a magnification of 500×.

RESULTS AND DISCUSSION

Preparation of the RAFT Macromolecular Initiator

The RAFT-mediated grafting and polymerization required immobilization of a RAFT initiator on cellulose chains. The hydroxyl groups of the cellulose were treated with chloroacetyl chloride and converted to the corresponding thio-carbonyl-thio groups and the resultant compound was used as the RAFT agent for graft polymerization. The synthetic routes are in Scheme 1. A cellulose ester, cellulose chloroacetate (Cell-AcCl), was synthesized by homogeneous acylation of cellulose with chloroacetyl chloride in BMIMCl (Step 1). This reaction was conducted in BMIMCl without catalyst, unlike what has been previously reported.[27] The success of this reaction was confirmed by EAs, FTIR, and ^{1}H-NMR. spectrum of Cell-CTA [Figure 1(c)] indicated the presence of C=S stretching bands at 1267 and 1526 cm^{-1}, and C=C stretching bands for the aromatic ring at 1640 and 1443 cm^{-1} which together confirm the grafting of thio-carbonyl-thio groups on cellulose. The chloroacetate groups formed by reaction of the hydroxyl groups on the cellulose backbone and chloroacetyl chloride are efficient initiators for ATRP.[28] Similar conversion into RAFT agents has already been reported.[29]

$$\mathrm{Cl\%} = M_{\mathrm{Cl}} \times \mathrm{DS}_1 / [M_{\mathrm{CE}} + (M_1 - M_{\mathrm{Cl}} - 1) \times \mathrm{DS}_1] \quad (2)$$

$$\mathrm{S\%} = 2 \times M_{\mathrm{s}} / [M_{\mathrm{Cell\text{-}ClAc}} + (M_2 - M_{\mathrm{MgCl}} - M_{\mathrm{Cl}}) \times \mathrm{DS}_2] \quad (3)$$

where M_{Cl}, M_{CE}, M_1, M_{S}, $M_{\mathrm{Cell\text{-}ClAc}}$, M_2, and $M_{\mathrm{MgCl_2}}$, are the molecular weight of Cl, cellulose, chloroacetyl chloride, S, Cell-ClAc, bis(thiobenzoyl) disulphide and $MgCl_2$, respectively; DS_1 and DS_2 are the DS of Cell-ClAc and Cell-CTA, respectively.

The introduction of the chloroacetyl groups onto cellulose and the conversion into thio-carbonyl-thio compound were also confirmed by ^{1}H-NMR (Figure 2). The chemical shift at δ = 4.237 ppm in ^{1}H-NMR [Figure 2(a)] belongs to the ethyl protons of the chloroacetyl group and the aromatic protons are at δ = 7.2–8.0 ppm [Figure 2(b)].

The DS of the Cell-ClAc and Cell-CTA could also be calculated from ^{1}H-NMR by the following equations:

$$\mathrm{DS\ Cell\text{-}ClAc} = \left(\int \mathrm{chloroacetyl}/2\right) \Big/ \left(\int \mathrm{cell}/7\right) \quad (4)$$

$$\mathrm{DS\ Cell\text{-}CTA} = \left(\int \mathrm{aromatic}/5\right) \Big/ \left(\int \mathrm{cell}/7\right) \quad (5)$$

where $\int$ chloroacetyl represents the integrals of peaks assigned to hydrogen atoms which are bonded to the chloroacetyl group of Cell-ClAc [assigned a in Figure 2(a)], $\int$ aromatic represents the integrals of peaks assigned to hydrogen atoms which are bonded to the aromatic protons of Cell-CTA [assigned b in Figure 2(b)] and $\int$ Cell represents the integrals of peaks assigned to hydrogen atoms which are bonded to the carbon atom of cellulose backbone (approximately at δ = 3.5–5.2). However, the hydrogen atoms peaks bonded to the chloroacetyl and cellulose backbone were poorly separated and this calculation should only be considered to rough estimation. And the obtained DS_2 (DSCell-ClAc = 2.01; DSCell-CTA = 0.96) might not agree completely with the data obtained by EA analysis, higher than the DPs calculated from EA analysis.

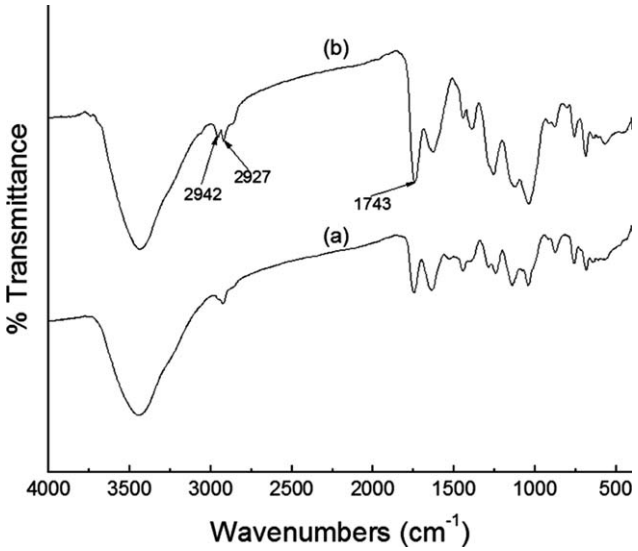

Figure 3. FTIR spectra of cellulose-based RAFT chain transfer agent (Cell-CTA) (a) and cellulose-based grafting copolymer (Cell-*g*-PMMA) (b).

Graft Polymerization

A series of cellulose-*g*-poly(MMA) copolymers were prepared by RAFT in BMIMCl (Scheme 1) which were studied by FTIR and ^{1}H-NMR. Although the characteristic absorbance bands of poly(MMA) appear in the same regions as the bands of the Cell-CTA samples [Figure 3(a)], the FTIR spectra of the grafted samples [Figure 3(b)] show intense characteristic peaks at 2927 and 2942 cm^{-1} due to C—H symmetric and asymmetric stretching of —CH_3 and —CH_2—. Moreover, the intense absorbance band at 1743 cm^{-1} associated with Cell-CTA is characteristic for the C=O stretch and supports the grafting.

The grafting of poly(MMA) was confirmed by ^{1}H-NMR (Figure 4). The chemical shift at 3.68 ppm is due to the protons of —OCH_3 in PMMA. The grafting ratio of poly(MMA) onto cellulose was calculated by gravimetry. Table II shows the results for different reaction conditions studied. By increasing the ratio of monomer to Cell-CTA or extending polymerization time, the ratio of the grafting increased as well as the molecular weight of the grafted chains. However, it seems that the increase in the concentration of the monomer for similar polymerization times do not enhance grafting. This is because the efficiency of the grafting is controlled by saturation kinetics, similar to what has been reported by Roy[11] who found at the same polymerization time, the increase in the monomer concentration (from 1/3 to 1/1, monomer/solvent (v/v)) decreased the grafting ratio from 23% to 21%. The theoretical number average molecular weight, $M_{n,\ \mathrm{theo}}$, was calculated using following the equation:

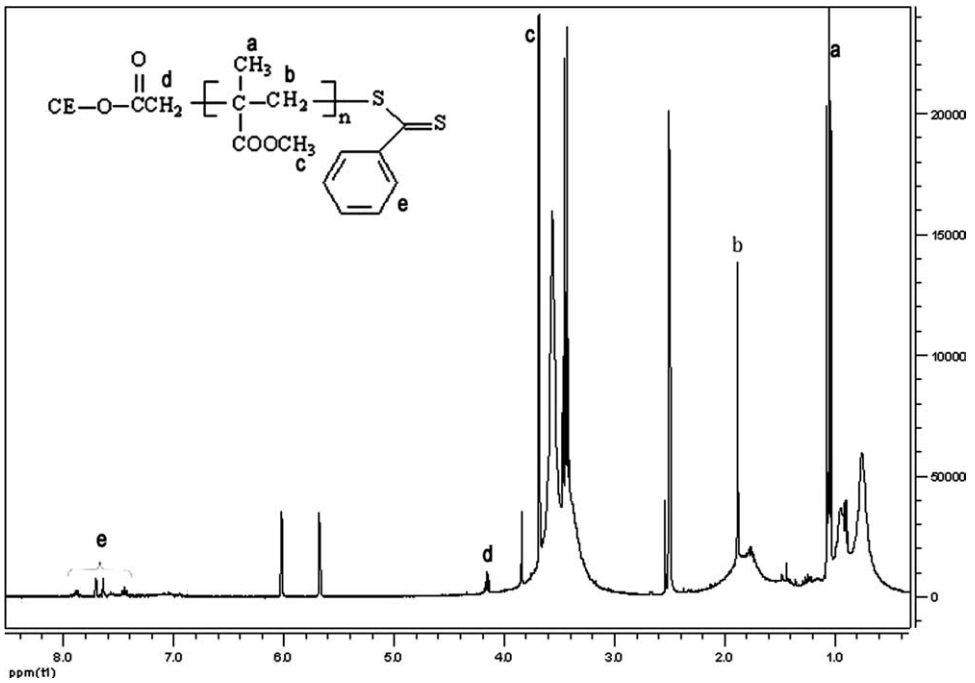

Figure 4. ^{1}H-NMR of cellulose-*g*-PMMA in DMSO-d_6.

$$M_{n,\text{theo}} = M_{CTA} + (n^0_m / n^0_{CTA}) \times M_M \times \text{conversion} \quad (6)$$

where $M_{n,\text{theo}}$ is the theoretical number-average molecular weight of the polymer, n^0_m, number of moles of the monomer initially present in the system, $M_{M,}$ molecular weight of the monomer, n^0_{CTA}, number of moles of CTA initially present in the system and $M_{CTA,}$ molecular weight of the CTA. It should be mentioned here that the experimental molecular weights are generally higher than the corresponding theoretical values, especially at the beginning of polymerizations (Table II). The reason for this may be that the establishment of the RAFT equilibrium is slow, while the calculation of theoretical molecular weight is based on a fast establishment of the main RAFT mechanism.

Compared to the RAFT reaction of MMA in anhydrous THF,[14] the same graft polymerization in IL showed an increase in polymerization rate. Similar observation was also reported by Thurecht et al.[30] by comparing the free radical polymerization of MMA in [BMIM]PF_6 and in toluene. Their results showed that the reaction in IL was faster than in toluene which is may be due to higher polarity of the IL. Similarly, Harrisson[31,32] has also demonstrated the same behavior by investigating the magnitude and effect of solvent on the propagation rate. The rate constants of the propagation of MMA were measured by using a pulsed laser polymerization technique and found to be approximately twice that of bulk MMA in 50 vol % [BMIM]PF_6. Other polar aprotic solvents such as DMF led to a 40% increase in propagation rate relative to bulk MMA[33] while an 80% increase was observed in DMSO.[34] The increase in propagation rate was likely due to increasing medium polarity.

The good solubility of the graft copolymer as well as the starting cellulosic material in the IL seems also to enhance the polymerization efficiency. Ma et al.[35] have demonstrated that a well-controlled RAFT polymerization of MMA worked much better in [(DD)MIM]BF_4, but not in [BMIM]BF_4 and they attributed

Table II. Experimental Conditions and Results of RAFT in BMIMCl[a]

Exp. No.	[M] : [Cell-CTA] : [AIBN] (mole ratio)	Time (h)	Graft ratio (%)[b]	Monomer conversion (%)[c]	M_n (g mol^{-1})[d]	$M_{n,\text{theo}}$ (g mol^{-1})[e]
1	50:1 : 0.1	5	0.72	3.6	3000	684
2	100 : 1 : 0.1	8	4.27	11.8	10,000	2684
3	300 : 1 : 0.1	4	11.80	11.4	9000	7164
4	300 : 1 : 0.1	8	12.93	12.8	10,000	8004
5	300 : 1 : 0.1	12	17.12	16.4	12,000	10,164
6	300 : 1 : 0.1	24	25.11	24.3	15,000	14,904
7	300 : 1 : 0.1	36	28.96	28.8	18,000	17,604

[a]The amount of BMIMCl used in the system was about 30/1 (BMIMCl/Cell-CTA, g/g), [b]Graft ratio was calculated according to eq. (1), [c]Monomer conversion was determined by ^{1}H-NMR analysis, [d]Obtained from GPC of the grafted chains by hydrolysis of copolymer, [e]Calculated from the monomer conversion using eq. (6).

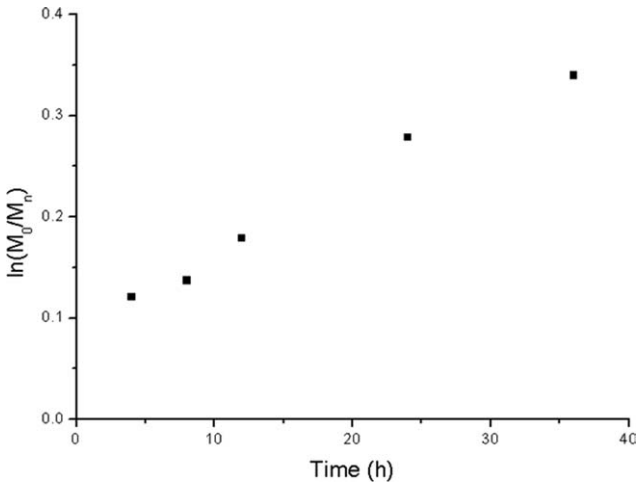

Figure 5. Semilogarithmic plot of monomer consumption versus time for MMA polymerization in BMIMCl initiated by AIBN and Cell-CTA at 60°C.

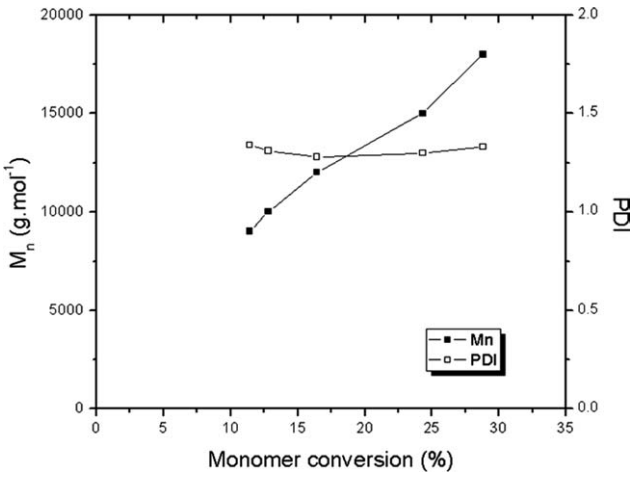

Figure 6. The variation of the molecular weight (M_n) and corresponding PDIs of grafted PMMA chains with respect to monomer conversion for MMA polymerization in BMIMCl initiated by AIBN and Cell-CTA at 60°C.

this difference to the poor solubility of poly(MMA) in [BMIM]BF_4. Other studies particularly of free-radical polymerizations[36] established the role that ILs play in affecting molecular weights and polymerization rates. Such studies demonstrated that the rate constants for the polymerization of MMA in [BMIM]PF_6 increased with polarity and decreased with viscosity as the IL concentration increased. A recent study of BMA polymerization in twenty nine ILs correlated higher degrees of polymerization with solvent viscosity and demonstrated that higher degrees of polymerization were obtained in imidazolium- rather than pyridinium- or ammonium-based ILs.[37]

Figure 5 shows semilogarithmic plots of monomer conversion versus time. The variation of $\ln([M]_0/[M]_t)$ is linear with time which indicate that the polymerization reaction is first-ordered reaction with respect to the monomer. This result confirms that the PMMA-cellulose graft copolymerization in BMIMCl is a living and controlled polymerization. Similar results were obtained by Perrier et al. on the RAFT grafting of poly(styrene), poly(methylmethacrylate), and poly(methylacrylate) from cellulosic fibers in heterogeneous conditions using self-prepared chain transfer agents (CTAs).[10]

The variation of molecular weight and PMMA chains distribution obtained by selective hydrolysis of the copolymer is shown in Figure 6. A linear increase in molecular weight (M_n) with conversion of the monomer is ascribed to the living nature of RAFT.[37] The PDIs, as low as 1.3, were similar to results by Chen et al.,[14] in which the RAFT copolymers showed narrow PDIs less than <1.32, further supporting ideal "living" radical behavior.

Assessment of the Hydrophobicity of Cellulose-*g*-PMMA Copolymers

The degree of surface hydrophobicity of cell-*g*-PMMA was investigated by static contact angle measurements. The raw cellulose,

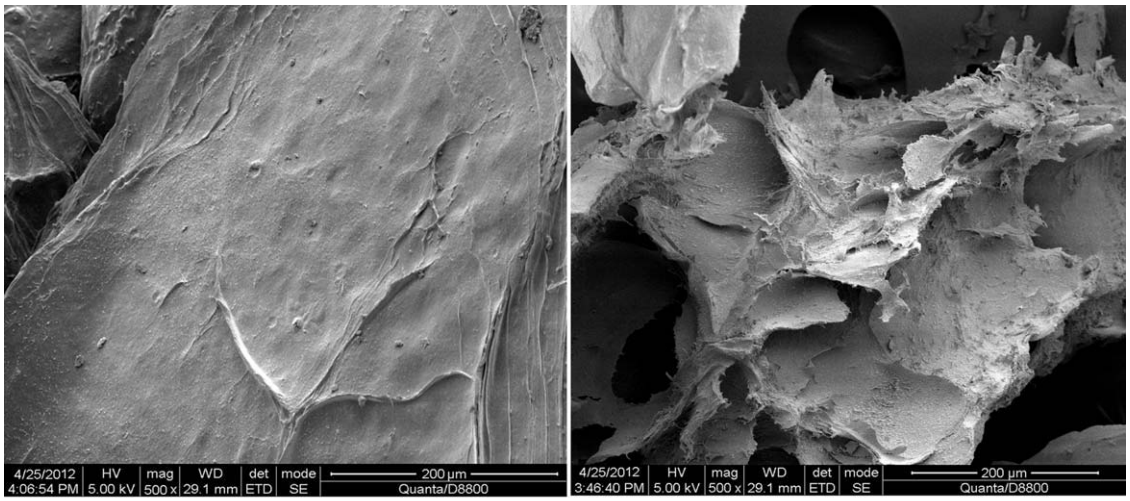

Figure 7. SEM photomicrographs of (a) unmodified cellulose fiber and (b) cellulose-*g*-PMMA, 25% graft ratio.

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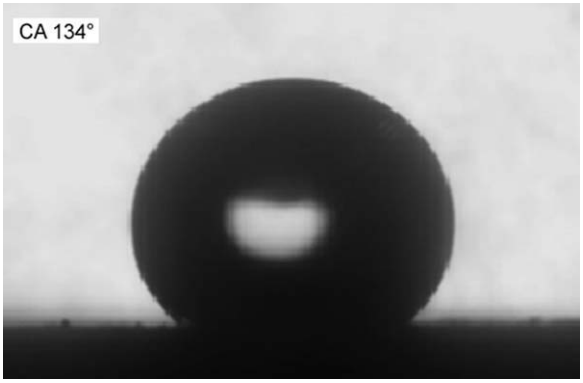

Figure 8. Water droplet on cellulose-*g*-PMMA copolymer (25% graft ratio) surface.

however, adsorbed water very quickly, rendering measurement of the static contact angle impossible. However, the cellulose-*g*-PMMA samples did not adsorb water at all. Static contact angle values for all the graft copolymers were found to be around 130°, thus demonstrating the increase in hydrophobicity of the modified cellulose surface. Figure 7 illustrates the hydrophobic nature of the cellulose-*g*-PMMA copolymer with a graft ratio of 25%.

Scanning Electron Microscopy

SEM micrographs of unmodified cellulose and cellulose-*g*-PMMA copolymers are shown in Figure 8, from which it is evident that the grafted cellulose has different structural features compared with the unmodified cellulose.

Comparison Between ATRP and RAFT Synthesis of Cellulose-*g*-PMMA Copolymers Conducted in BMIMCl

The synthesis of cellulose-*g*-PMMA via ATRP method initiated by Cell-Cl, which were conducted in BMIMCl, was investigated by our previous work.[38] The detailed synthetic procedure and the polymerization data can be found in Ref. 38. The differences between ATRP and RAFT methods were quantitatively compared, and the results are presented in Table III and Figure 9.

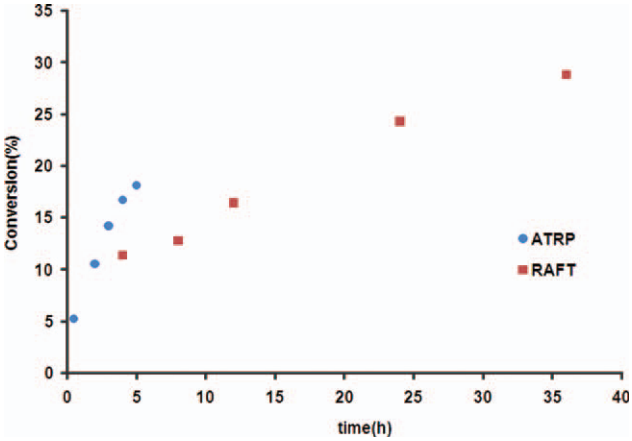

Figure 9. Plots of monomer conversion versus time for MMA polymerization under ATRP and RAFT methods. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The polymerization of MMA was very fast under ATRP conditions, under which the monomer undergoes 10.6% conversion in 120 min in the presence of CuBr/bpy catalytic system producing a polymer with a PDI value of 1.74. Even by varying the ratio of monomer to initiator and the reaction temperature, the polymer produced always had a broader PDI value of >1.5. And the polymerization via RAFT method produced a polymer with a PDI value of 1.28 in 12 h. From the results obtained, it was evident that the copolymer prepared by ATRP produces broader polydispersity values (1.52–1.79) compared with the copolymer prepared through RAFT (1.28–1.46). Thus, it could be concluded that the polymerization was rapid and also less controlled under ATRP conditions.

Table III. Controlled Radical Polymerization of MMA via ATRP and RAFT Methods[a]

Polymerization	Entry	[M] : [Cell-Cl] or [Cell-CTA]	Time (h)	Monomer conversion (%)[b]	M_n (g mol^{-1})[c]	PDI
ATRP	1	100 : 1	0.5	5.3	5200	1.79
	2	100 : 1	2	10.6	11,000	1.74
	3	100 : 1	3	14.2	15,500	1.66
	4	100 : 1	4	16.7	18,700	1.65
	5	100 : 1	5	18.1	21,000	1.52
	6	200 : 1	4	15.3	31,000	1.61
RAFT	1	50 : 1 : 0.1	5	3.6	3000	1.46
	2	100 : 1 : 0.1	8	11.8	10,000	1.38
	3	300 : 1 : 0.1	4	11.4	9000	1.34
	4	300 : 1 : 0.1	8	12.8	10,000	1.31
	5	300 : 1 : 0.1	12	16.4	12,000	1.28
	6	300 : 1 : 0.1	24	24.3	15,000	1.30
	7	300 : 1 : 0.1	36	28.8	18,000	1.33

[a]The polymerization temperature was 60°C both for ATRP and RAFT, [b]Monomer conversion was determined by ^{1}H-NMR analysis, [c]Obtained from GPC of the grafted chains by hydrolysis of copolymer.

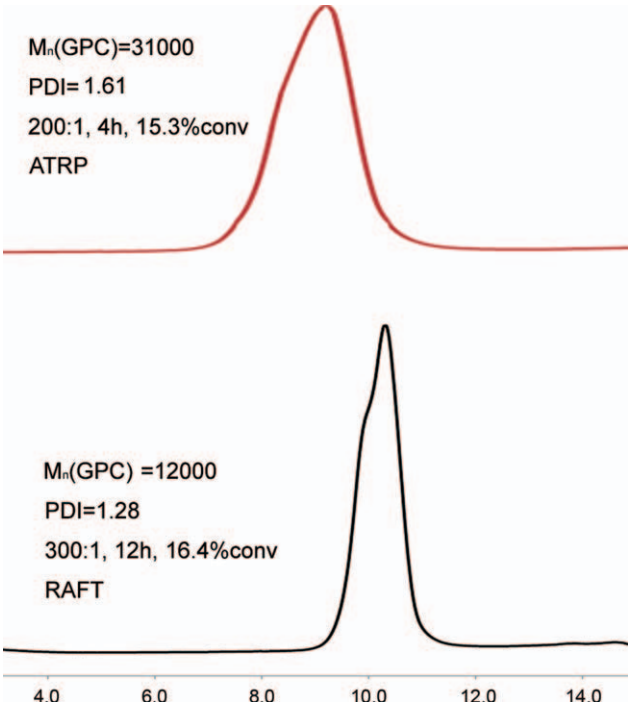

Figure 10. GPC traces of PMMA cleaved from copolymers synthesized under ATRP and RAFT methods. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The GPC traces of the PMMA cleaved from copolymers synthesized using both methods are shown in Figure 10. In principle, the polymerization through RAFT offers some unique advantages including the possibilities of minimum number of dead chains along with thio-carbonyl-thio end groups,[39] control in the rate of polymerization and also less competitive termination.

Recycling of IL Solvent

In general, the most pernicious drawback associated with the intelligent use of ILs is their reuse. The successful development of any industrially relevant process based on ILs hinges on approximately 99+% recovery of the ILs because of the high costs of production. Fortunately, a number of successful industrial efforts have already proven to meet this stringent requirement and at the lab scale it therefore ceases to be the odious barrier it was several years ago. The recycling of IL was possible by simply reducing the pressure and subsequently distilling to remove water, the residual monomer and initiator. The recycling method has not been optimized and a number of other possibilities such as using aqueous biphasic systems (ABS) to recycle or concentrate IL from aqueous solution have to be explored. Systematic studies are currently in progress. We were able to successfully demonstrate that our ILs could be used as a reaction medium over a number of cycles without suffering any adverse effects to their solvation power and reactivity enhancement of the RAFT polymerization. This latter finding is consistent not only with the industrial efforts currently in operation, but with the great number of research efforts underway around the global green research community.

CONCLUSIONS

This study reports the first illustration for the graft copolymerization of MMA onto cellulose by RAFT in a typical IL (BMIMCl). It showed high polymerization rate when BMIMCl was used as the reaction medium, while a controlled/living polymerization character was proven for cellulose-CTA-mediated RAFT polymerization in the IL by first-order kinetics of the copolymerization, linear increase in M_n with conversion, and PDIs that were approximately 1.3. Compared to the polymerization of MMA initiated by Cell-Cl in BMIMCl, it suggested that the polymerization of MMA via ATRP was less controlled. The immobilization of CTAs onto cellulose in a green, recoverable solvent represents a distinct advantage in the ability to prepare well-defined graft cellulose copolymers.

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