SYNTHESIS AND COMPARISON OF GRAFT COPOLYMERS USING METHACRYLIC MONOMERS AND CELLULOSE VIA ATRP

YUE SHEN,[*] LIN DAI,[*] MING-FEI LI,[*] JING HE,[*] BO WANG[*] and RUN-CANG SUN[*,**]

[*]*Beijing Key Laboratory of Lignocellulosic Chemistry, College of Materials Science and Technology, Beijing Forestry University, Beijing 100083, China*
[**]*State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China*
✉ *Corresponding authors: Jing He, hejing2008@sina.com; Bo Wang, mzlwb@bjfu.edu.cn;*

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Graft copolymers of cellulose and methacrylic monomers were prepared by atom transfer radical polymerization (ATRP) under mild conditions. Cellulose macro-initiator was successfully synthesized by direct acylation of cellulose with 2-bromopropionyl bromide (BIBB) in ionic liquid 1-allyl-3-methyli midazolium chloride, followed by ATRP of 2-hydroxyethyl methacrylate (HEMA) and 2-hydroxypropyl methacrylate (HPMA). Copolymers were obtained via ATRP catalyzed by CuBr/pentamethyl diethylenetriamine (PMDETA). The two grafting copolymers were characterized and compared by GPC, FTIR, ^{1}H NMR, and TGA analyses. The GPC results indicated that the reaction in the CuBr/PMDETA system was a well-controlled and living ATRP process; it exhibited relatively good control over the ATRP. The graft efficiency and graft ratio were higher in DMF. HEMA was more conducive to the ATRP reaction. Compared with cellulose-*g*-PHEMA, cellulose-*g*-PHPMA showed poor thermal stability. The cellulose graft copolymer in solution aggregated and self-assembled into a sphere-like structure.

Keywords: ATRP, cellulose, graft copolymer, ionic liquid

INTRODUCTION

Cellulose has attracted considerable attention as it is abundant, cheap, renewable, and biodegradable.[1,2] With the increasing demand of using cellulose more effectively, modification of cellulose by grafting other molecules of special functional groups on its structure imparts more flexible properties to it.[3,4,5] In recent years, grafting polymers on cellulose using conventional polymerization techniques has been widely studied, such as free radical polymerization, ring-opening polymerization, nitroxide-mediated polymerization, and reversible addition-fragmentation chain transfer polymerization.[6-10] However, the main drawbacks of these reported techniques are the production of an unwanted homopolymer together with the graft copolymer and the undesired chain degradation of the cellulose backbone. In contrast, atom transfer radical polymerization (ATRP) is a robust, versatile, and powerful technique to prevent the formation of homopolymer byproducts in the polymerization.[11,12] As one of the techniques to accurately control the chain length and polydispersity of the polymer, ATRP does not destroy the cellulose backbone due to its mild conditions.

So far, there has been little research on the direct homogeneous graft polymerization on the cellulose backbone through ATRP because of the poor solubility of cellulose in traditional solvents.[13] Recently, ionic liquid (IL) as a solvent in carbohydrate chemistry or a reaction medium of homogeneous cellulose modification, which has good properties including low melting points, wide liquid ranges, and lack of vapor pressure, has been widely reviewed.[14-19] Some ionic liquids, especially those containing the Cl^- anion, are capable of dissolving cellulose.[20-22]

MMA is a commonly used monomer in ATRP reaction.[23] In previous work, cellulose-*g*-MMA was obtained in ionic liquid under mild conditions via ATRP. As one of the multiple stimuli-responsive biodegradable copolymers, it has attracted growing attention due to its behavior

in response to multiple stimuli, such as pH, temperature, and salt.[24] However, there is little research about other hydrophilic methacrylic monomers. 2-hydroxyethyl methacrylate (HEMA) and 2-hydroxypropyl methacrylate (HPMA) were chosen as monomers in this study, due to the excellent biocompatibility, pH-sensitivity, and temperature-sensitivity of their polymers.[25] Macro-initiators could be synthesized by direct homogeneous acylation of cellulose with 2-bromopropionyl bromide (BIBB) in ionic liquid, followed by ATRP procedure in different solvents.

This study aimed at grafting methacrylic monomers (HEMA or HPMA) on non-derivatized cellulose via ATRP under mild conditions. The ATRP was conducted in four different polar aprotic solvents in order to determine the most effective solvent. The objectives of the experiment were: (i) to examine the different monomer grafting efficiency in different solvents; (ii) to compare the synthesis copolymers structure, monomer conversion, and actual polymer molecular weight. The copolymers obtained were characterized by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (^{1}H NMR), thermogravimetric (TGA), and gel permeation chromatography (GPC). Furthermore, the self-assembly or aggregation of the copolymers were also investigated by means of transmission electron (TEM) and atom force microscopy (AFM).

EXPERIMENTAL

Materials

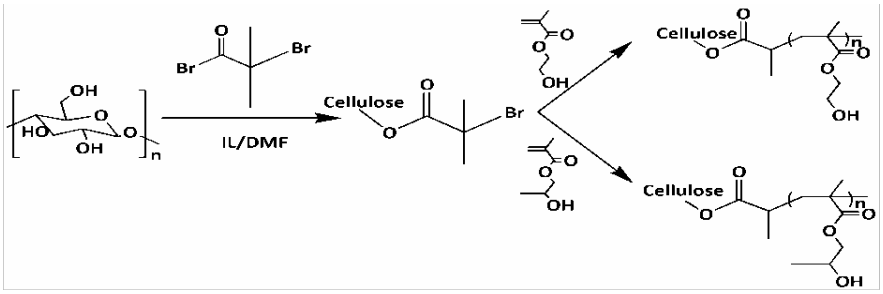
Cellulose with a degree of polymerization (DP) of 130 was supplied by J&K Chemical Reagent, China. Ionic liquid, 1-allyl-3-methylimidazolium chloride ([AMIM]Cl), was prepared according to the literature.[26] HEMA and HPMA were purchased from Beijing Chemical Engineering Plant, China. The monomers were dried over anhydrous $MgSO_4$ and then distilled from CaH_2 under reduced pressure. To remove copper (II), CuBr (Beijing Chemical Reagent Factory) was purified by stirring in glacial acetic acid, filtering, and washing with acetone three times. Then, CuBr was dried in a vacuum at room temperature overnight. *N,N,N′,N′,N′*-pentamethyldiethylene triamine (PMDETA, 98%, Acros Organics) was stirred overnight over CaH_2 and distilled under reduced pressure. 2-Bromopropionyl bromide (98%, Aldrich) was used as received. Other solvents, such as *N,N*-dimethylformamide (DMF), butanone, ethanol, pyridine, and HCl, produced by Beijing Chemical Engineering Plant, were dried and then distilled under reduced pressure.

Synthesis of cellulose-based macro-initiator (Cell-Br)

A total of 1.5 g (5.8 mmol) of cellulose was dispersed in 25.0 g [AMIM]Cl, and the mixture was heated with stirring at 80 °C until the cellulose was completely dissolved, and then cooled to room temperature. 2-Bromopropionyl bromide (10.7 g, 48.3 mmol) in 15.0 mL DMF was added dropwise into the ice-cold cellulose/[AMIM]Cl solution and stirred in a flask under nitrogen. The mixture was left to warm up to room temperature and stirred for 10 h. After the reaction, the resulting solution was poured into an excess of de-ionized water, and the white floccules were precipitated out. The white floccules, Cell-Br, were washed thoroughly with water, and then filtered and dried under vacuum at 50 °C for 12 h before characterization. Scheme 1 illustrates the outline of the synthesis of cellulose-based ATRP macro-initiator.

Synthesis of Cell-*g*-HEMA and Cell-*g*-HPMA

As shown in Scheme 1, Cell-Br was used to initiate the polymerization of HEMA or HPMA via ATRP using CuBr/PMDETA as a catalyst system. Cell-Br (100.0 mg, 0.2 mmol of Br), PMDETA (0.04 g, 0.2 mmol), HEMA (5.2 g, 40 mmol) or HPMA (5.8 g, 40 mmol), and solvents such as DMF (30.0 g) were added into the flask with a stirring bar. After Cell-Br was dissolved completely, CuBr (28.0 mg, 0.2 mmol) was introduced into the flask, which was evacuated and back-filled with N_2 three times and thereafter immersed into an oil bath.



Scheme 1: Synthesis of two monomers from a cellulose substrate via ATRP

The mixture was stirred at 60 °C for a prescribed time. The polymerization was ended by exposing the mixture to air and diluting with distilled water. The polymer was separated from copper by a de-ionized water wash. After filtration and washing, the white solid products were collected and dried at 50 °C under vacuum for 24 h before characterization and comparison.

The grafting efficiency (GE) and grafting ratio (G, wt%) was determined according to the following equations:

$$GE = W_1/W_2 \times 100 \quad (1)$$

$$G = (W_2 - W_3)/W_3 \times 100 \quad (2)$$

where W_1 (g) is the weight of the monomers, W_2 (g) is the dry weight of the graft polymers, and W_3 (g) is the weight of Cell-Br.

Instrumental measurements

The molecular weight and molecular weight distributions of PHEMA and PHPMA on cellulose were determined by GPC equipped with a PL-gel 10 mm Mixed-B 7.5 mm ID column with THF as eluent. The flow rate was 1 mL/min. A series of mono-dispersed polystyrene was used as standard to generate the calibration curve. FTIR spectra (Magna-IR 750, Nicolet, USA) were used to characterize the structure of cellulose and graft copolymers. ^{1}H NMR spectra (Bruker AV300 NMR, Switzerland) of Cell-*g*-PHEMA and Cell-*g*-PHPMA were obtained by using DMSO-d_6 as solvent. Thermal stability determinations of the samples were examined using TGA (DTG-60, Shimadzu, Japan). The samples were heated in an aluminum crucible from 50 to 550 °C at a heating rate of 10 °C/min, while the apparatus was continually flushed with a nitrogen flow of 20 mL/min. All samples were dried under vacuum at 40 °C for 24 h prior to TGA measurements. The aggregate morphology of copolymers was examined with a Hitachi H-9800 TEM (Hitachi, Japan). AFM observation was conducted on an SPM-9600 atomic force microscope (Shimadzu, Japan).

RESULTS AND DISCUSSION

Effect of various solvents and reaction temperatures on ATRP reaction

Table 1 summarizes the experimental results obtained by changing reaction temperatures in different polar aprotic solvents. In an attempt to achieve better control of M_w and polydispersity of the grafted PHEMA and PHPMA on cellulose produced in the CuBr/PMDETA system, several solvents, including DMF, butanone, ethanol, and pyridine, were used in the ATRP at different temperatures. PHEMA and PHPMA were obtained by selective hydrolysis of Cell-*g*-PHEMA and Cell-*g*-HPMA copolymers. Different reaction conditions were attempted to obtain well-defined cellulose graft copolymers. Herein, cellulose-Br is an excellent initiator, and radical–radical coupling of the propagating chains is prone to occur due to the high concentration of chain radicals. Therefore, gels are easily formed and the reaction is quite difficult to control. It can be seen that the macro-initiator cannot be dissolved in ethanol and pyridine and the reaction cannot be performed (Table 1, entry 1 and entry 10). The dilute reaction conditions could maintain a low concentration of radicals, minimize the intermolecular coupling, and render the polymerization controllable. The radical coupling can be reduced by lowering the reaction temperature. However, the viscosity of the reaction mixture was found to increase with a decrease of the temperature. Clearly, the grafting efficiency and graft ratio were the highest at 60 °C (DMF)/70 °C (Butanone).

Therefore, the polymerization temperature was set at 60 °C (DMF)/70 °C (Butanone) in the following experiments. Besides, low molar coupling renders the polymerization controllable. Thus, low molar ratio of monomer to solvent should be used to keep a high dilution of the reaction solution. Figure 1 shows the variation of the GE calculated from different monomers. Both Cell-*g*-PHEMA and Cell-*g*-PHPMA had higher grafting efficiency and graft ratio when DMF was used as solvent. From the above analysis, it was concluded that the polarities of the solvents affected the reaction significantly. Taking into account the effective utilization of the raw materials, DMF was chosen as reaction solvent. Meanwhile, Cell-*g*-PHEMA had higher graft efficiency than Cell-*g*-PHPMA under the same conditions. Thus, it was more conducive to the ATRP reaction. Furthermore, the use of the reaction medium, ionic liquid, allowed a simple process for the separation of the metal complex from the polymer mixture at the end of the polymerization.

The potential of the ionic liquid catalyst mixture recycling and recovering is currently being studied.

Characterization of Cell-*g*-PHEMA and Cell-*g*-PHPMA

Figure 2 shows the FTIR spectra of the non-derivatized cellulose, macro-initiator Cell-Br, Cell-*g*-PHEMA, and Cell-*g*-PHPMA. The stretching vibration of carbonyl in the 2-bromopropionyl group appeared at 1714 cm^{-1} in the FTIR spectrum of Cell-Br, but not in that of

its precursor, which indicates that the 2-bromopropionyl group was introduced onto cellulose chains. In the FTIR spectra of graft copolymers Cell-*g*-PHEMA and Cell-*g*-PHPMA, the bands at 2900 (C-H stretching of methyl and methylene groups), 1710 (the carbonyl group), and 750 cm^{-1} (-OH bending) are the characteristic absorption bands of PHEMA and PHPMA units, which suggests successful grafting reactions. The ^{1}H NMR spectra of the copolymers are given in Figure 3. In Figure 3(a), 1.9, 3.6, and 3.9 ppm are attributed to the hydroxy, methylene, and ester methylene protons. As compared with PHEMA, the characteristic chemical shifts of PHPMA segments are readily identifiable: 1.1, 1.9, and 3.7 ppm are owing to the methyl, hydroxy on the tertiary carbon, and ester methylene protons, respectively. These results confirmed the successful grafting polymerization of HEMA and HPMA on the cellulose backbone.

Table 1
Results of HEMA and HPMA initiated by Cell-Br in different solvents

Entry	Monomer	[M][a]/[I][b]/[Cu(I)]/[PMDETA]	Solvent (wt%)	Temp. (°C)	Time (min)	GE (%)	G (wt%)	M_w [c] (g/mol)
1	HEMA	50:1:1:1	Ethanol	50	10	-	-	-
2	HEMA	50:1:1:1	DMF(44.4)	50	10	gelled	-	-
3	HEMA	200:1:1:1	DMF(68.1)	60	60	19.8	1532	11070
4	HEMA	200:1:1:1	DMF(68.1)	60	120	34.7	2647	16074
5	HEMA	200:1:1:1	DMF(68.1)	60	180	36.5	2809	27306
6	HEMA	200:1:1:1	Butanone(58.5)	70	60	16.6	1266	10300
7	HEMA	200:1:1:1	Butanone(58.5)	70	120	25.3	1930	13079
8	HEMA	200:1:1:1	Butanone(58.5)	70	180	30.8	2350	15403
9	HPMA	50:1:1:1	Pyridine	50	10	-	-	-
10	HPMA	50:1:1:1	DMF(44.4)	50	10	gelled	-	-
11	HPMA	200:1:1:1	DMF(68.1)	60	60	24.6	1962	14737
12	HPMA	200:1:1:1	DMF(68.1)	60	120	35.1	2799	16038
13	HPMA	200:1:1:1	Butanone(58.5)	70	60	14.2	1131	9956
14	HPMA	200:1:1:1	Butanone(58.5)	70	120	23.1	1843	12854
15	HPMA	200:1:1:1	Butanone(58.5)	70	180	27.6	2201	15731

[a] [M] = mole of HEMA (entries 1 to 8), HPMA(entries 9 to 15)
[b] [I] = mole of bromine
[c] M_w obtained from GPC for the grafted chains by hydrolysis of Cell-*g*-PHEMA and Cell-*g*-PHPMA

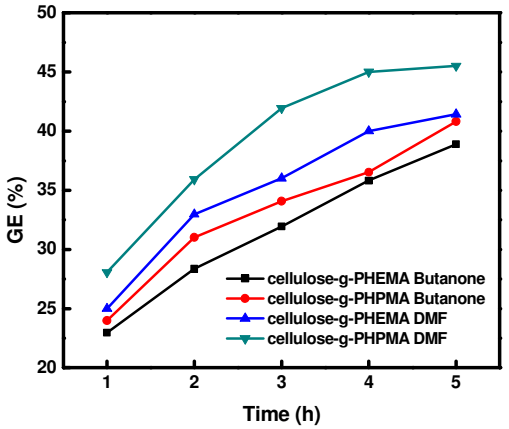


Figure 1: Grafting efficiency of different monomers in DMF and butanone. Conditions: [HEMA] or [HPMA]/[Cell-Br]/[CuBr]/[PMDETA]=200:1:1:1, polymerization temperature was 60 °C (DMF)/70 °C (Butanone)

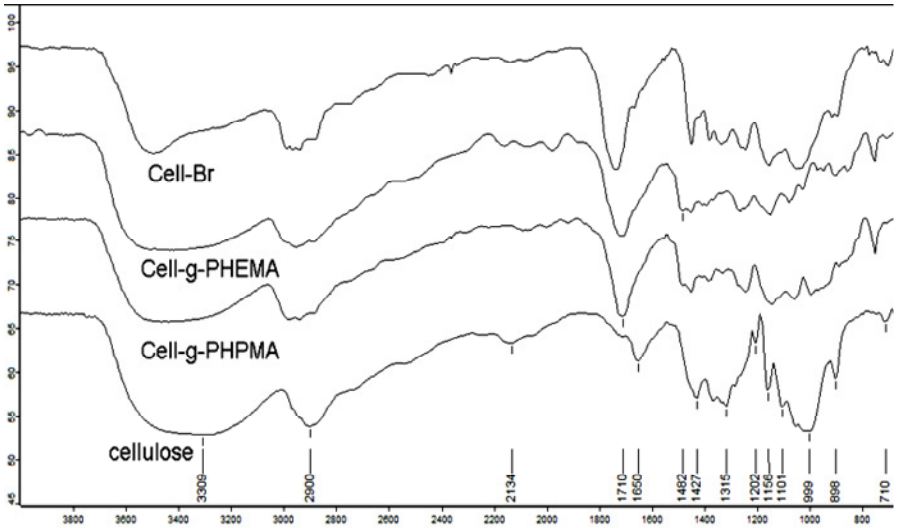


Figure 2: FTIR spectra of cellulose, macro-initiator Cell-Br, Cell-*g*-PHEMA, and Cell-*g*-PHPMA

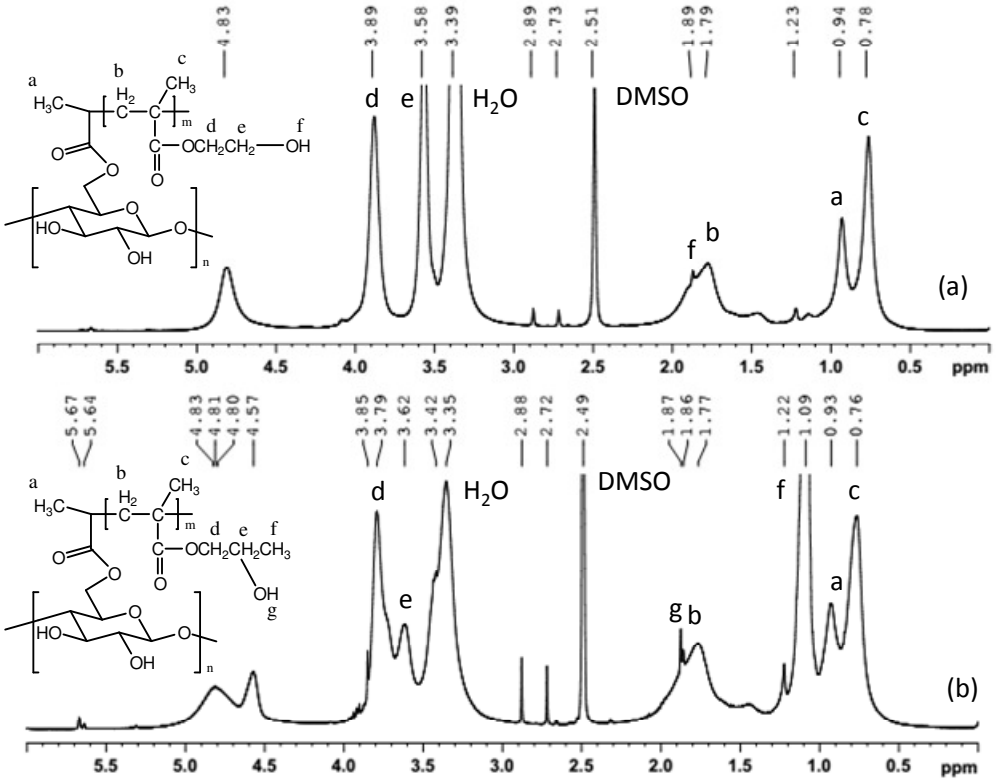


Figure 3: ^{1}H NMR spectra of Cell-*g*-PHEMA (a) and Cell-*g*-PHPMA (b)

Semilogarithmic plots of the monomer conversion of HEMA and HPMA versus the reaction time are shown in Figure 4. A semilogarithmic plot with the linear first-order kinetics can ascertain the "livingness" of atom transfer radical polymerization. It also reflects the constant concentration of propagating radicals. The variation of $\ln(M_o/M_t)$ was linear with time in the period of 60 to 170 min, where M_o was the initial monomer concentration and M_t was the

monomer concentration at time *t*. Therefore, within this period the polymerization was suggested to be first order, and the concentration of the growing radical species in the system was constant with respect to relatively low monomer conversion. After 170 min, a slight curving occurred. A possible reason might be the use of the polar solvent [AMIM]Cl and the decrease of radical concentration, which led to partial termination of the living free radical.

Moreover, the variation of the molecular weight and molecular weight distribution of the side chain PHEMA is shown in Figure 5. Clearly, the number of molecular weights (M_n) of PHEMA increased linearly with the monomer conversion, and the polydispersity decreased during the polymerization process. The M_w/M_n was about 1.62. In previous work, the M_w/M_n of side chain PMMA was about 1.65. The results indicated that the PMDETA system exhibited relatively good control over the ATRP and the reaction in the present system was a well-controlled and living ATRP process. As compared with Cell-*g*-PMMA, Cell-*g*-PHEMA produced the side chain PHEMA with relatively narrow polydispersity.

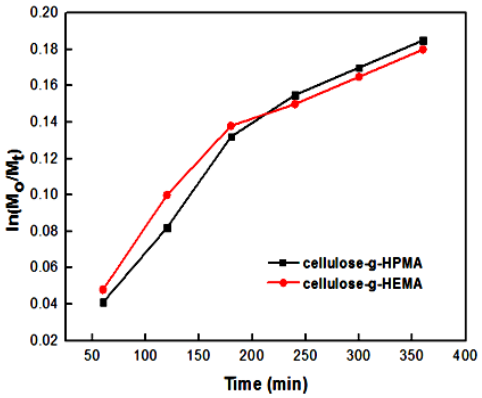


Figure 4: Semilogarithmic plot of monomer consumption versus time for HEMA and HPMA in DMF polymerizing in AmimCl initiated by Cell-Br, [HEMA or HPMA]/Cell-Br/[CuBr]/ [PMDETA]=200:1:1:1, polymerization temperature was 60 °C

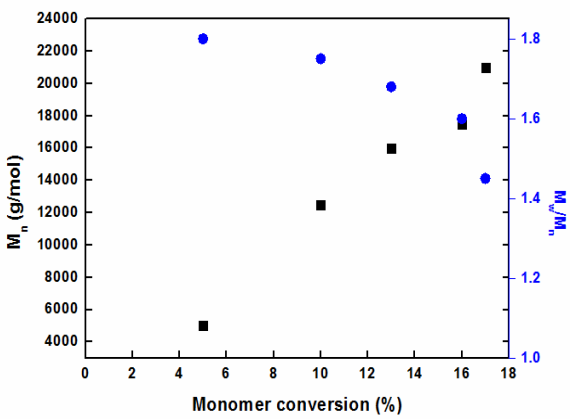


Figure 5: Dependence of the number-average weight (M_n) and polydispersity (M_w/M_n) of side chain PHEMA on monomer conversion

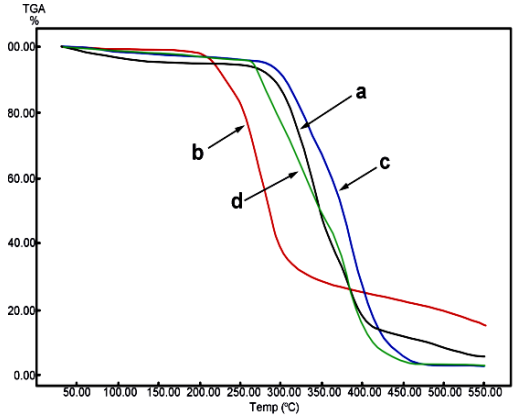


Figure 6: TGA curves of cellulose (a), Cell-Br (b), Cell-*g*-PHEMA (c), and Cell-*g*-PHPMA (d)

Thermal stability of Cell-*g*-PHEMA and Cell-*g*-PHPMA

TGA was used to study the decomposition pattern and the thermal stability of the grafted copolymers. As shown in Figure 6, the thermal decomposition of cellulose (Figure 6(a)) occurred at 270 °C and underwent two stages. After the reaction with 2-bromopropionyl bromide to form the macro-initiator Cell-Br, which underwent its major decomposition step at 300 °C, its thermal

stability decreased significantly (Figure 6(b)). The lowered thermal stability might be the result of introducing the bromoalkyl units, which may eliminate HBr upon heating and the HBr formed catalyzes the further degradation. The TGA of Cell-*g*-PHEMA (Figure 6(c)) displayed higher decomposition temperature than Cell-*g*-PHPMA (Figure 6(d)). This may be on account of a methyl branched-chain in Cell-*g*-PHPMA, which led to poor thermal stability. Cell-*g*-PHPMA underwent its first and major decomposition step at 275 ^{o}C, where 90 wt% of its weight was lost. The second degradation step occurred at 400 ^{o}C, leaving a residue of 5 wt% as the temperature reached 450 ^{o}C. Above 500 ^{o}C, the grafted polymers showed lower stability than cellulose and Cell-Br.

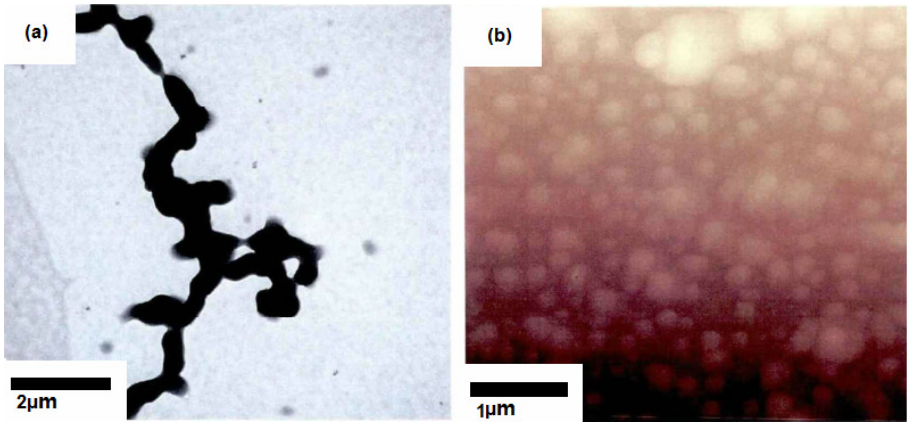


Figure 7: TEM (a) and AFM (b) images for the aggregates formed from Cell-*g*-PHPMA

Morphological characterization of Cell-*g*-PHPMA

The morphology of the aggregates was examined by TEM and AFM (Figure 7). In Figure 7(a), there seems to be a tendency for individual aggregates to stick to each other in the TEM image for the copolymer in DMF. In Figure 7(b), AFM analysis shows that in the selective solvent acetone the average diameter of a single polymer was roughly 200-300 nm, suggesting that the surface morphology of the graft copolymer was approximately spherical, differing from 400 to 600 nm in the TEM image. The main reason was that the polarity of acetone was weaker than DMF, and the forces of the acetone molecule were relatively small.

CONCLUSION

Cellulose was easily converted to an ATRP macro-initiator through direct acylation in ionic liquid [AMIM]Cl. Then, Cell-*g*-PHEMA and Cell-*g*-PHPMA copolymers were synthesized by grafting polymerizations of HEMA and HPMA onto the ATRP macro-initiator, thus leading to hydrophilic-modified cellulose for a variety of potential applications. Both Cell-*g*-PHEMA and Cell-*g*-PHPMA had higher grafting ratio and graft efficiency when DMF was used as solvent. Meanwhile, HEMA was more conducive to the ATRP reaction. The TGA of Cell-*g*-PHEMA showed a higher decomposition temperature than that of Cell-*g*-PHPMA. Moreover, the cellulose graft copolymer in solution could aggregate and self-assemble into a sphere-like structure.

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