SYNTHESIS OF CELLULOSE-GRAFT-POLY(METHYL METHACRYLATE) VIA HOMOGENEOUS ATRP

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Cellulose-graft-poly(methylmethacrylate) (cellulose-g-PMMA) copolymers were prepared by homogeneous atom transfer radical polymerization (ATRP) under mild conditions, in an attempt to develop an efficient way to modify the surface of cellulose. A cellulose macro-initiator was successfully synthesized by direct homogeneous acylation of cellulose with 2-bromopropionyl bromide in a room temperature ionic liquid (RTIL), 1-allyl-3-methylimidazolium chloride ([AMIM]Cl). Copolymers were obtained via ATRP of methyl methacrylate (MMA) with CuBr/penta-methyldiethylenetriamine (PMDETA) as catalyst and N,N-dimethyl-formamide (DMF) as solvent without homopolymer byproduct. The grafting copolymers were characterized by ^{1}H-NMR, ^{13}C-NMR, and FTIR. The grafted PMMA chain was obtained by the hydrolysis of the cellulose backbone and analyzed by GPC and TGA measurements. In addition, the assemblies or aggregates formed by cellulose-g-PMMA copolymers were studied by means of TEM and AFM. The results indicated that the graft polymerization occurred from the cellulose backbone and the obtained copolymers had grafted polymer chains with well-controlled molecular weight and polydispersity; the cellulose graft copolymer in solution could aggregate and self-assemble into sphere-like structures.

Keywords: Cellulose; ATRP; Graft polymerization; Ionic liquid

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INTRODUCTION

Cellulose is one of the most abundant, inexpensive, nontoxic, and renewable biomacromolecules in nature and is widely applied in areas as diverse as composite materials, textiles, drug delivery systems, and personal care products (Roy et al. 2009). However, cellulose lacks some properties that synthetic polymers have in some applications and has some inherent drawbacks, such as poor solubility in common solvents, poor crease resistance, poor dimensional stability, etc. (Nishio et al. 2006). Modification by graft polymerization provides a means of altering the physical and chemical properties of cellulose and increasing its functionality. Many techniques for graft copolymerization of various monomers on the cellulose backbone have been developed, such as free radical polymerization (Khan 2004; Khan 2005; Srivastava 2006), ring-opening polymerization (Hafren et al. 2005), nitroxide-mediated polymerization (NMP) (Daly et al. 2001), reversible addition–fragmentation chain transfer (RAFT) polymerization (Roy et al. 2005), and atom transfer radical polymerization (ATRP) (Carlmark and Malmstrom 2002). ATRP was independently discovered by Matyjaszewski and Sawamoto in 1995

(Wang and Matyjaszewski 1995), and it has been shown to be a robust and versatile technique to accurately control the chain length and polydispersity of the polymer, and could be used to synthesize well-defined copolymers (Braunecker and Matyjaszewski 2007). It is generally believed that the living/controlled nature of ATRP is due to the relatively low radical concentration in the reaction system, which suppresses the termination relative to propagation. Among all of the above mentioned techniques, ATRP is widely used with respect to the modification of the surface properties of cellulose and cellulose derivatives (Shen and Yong 2004; Vlcek et al. 2006; Ostmark et al. 2007; Tang et al. 2007).

However, it is extremely difficult to dissolve cellulose in water and most common organic solvents because of its stiff molecules and close chain packing via numerous intermolecular and intramolecular hydrogen bonds (Zhang et al. 2005), which makes the graft polymerization of cellulose difficult to process. Although ATRP grafting from cellulose in the solid state (Carlmark and Malmstrom 2002) or suspensions of micro-crystalline cellulose (Harrisson et al. 2011) have been reported, the processes were relatively complicated and the reaction times were much longer. Recently, room temperature ionic liquids (RTILs) have been found to be environmentally friendly and powerful solvents for cellulose and considered as desirable homogeneous media for the acylation of cellulose (Schlufter et al. 2006; El Seoud et al. 2007). The direct homo-geneous graft polymerization of cellulose backbone through ATRP using ionic liquids as cellulose solvents has been reported (Sui et al. 2008; Lin et al. 2009; Meng et al. 2009). Nevertheless, it could be found that the monomer conversions were relatively low.

In this paper, cellulose macroinitiator was synthesized through homogeneous acylation of underivatized cellulose with 2-bromopropiomyl bromide in ionic liquid [AMIM]Cl (1-allyl-3-methyl imidazolium chloride). Then, the graft copolymerization of methyl methacrylate (MMA) by ATRP in the medium of DMF (N,N'-dimethyl formamide) was carried out. The outlines of the synthesis of cellulose-based ATRP macroinitiator and cellulose-g-PMMA copolymer are illustrated in Schemes 1 and 2, respectively. The preliminary studies on the thermal stability and the morphology of the graft copolymer in different solutions were also studied.

EXPERIMENTAL

Materials

Cellulose with a degree of polymerization (DP) of 130 was used. Ionic liquid [AMIM]Cl was synthesized according to the literature procedures (Wu et al. 2004). Both cellulose and [AMIM]Cl were dried before use. Methyl methacrylate (MMA) was purchased from Beijing Chemical Engineering Plant (Beijing, China) and was dried over anhydrous $MgSO_4$ and then distilled from CaH_2 under reduced pressure. To remove copper(II), CuBr (Beijing Chemical Regent Factory) was stirred in glacial acetic acid, filtered, and washed with acetone for three times and then dried under vacuum at room temperature for 12 h. N,N,N′,N′,N′-pentamethyldiethylenetriamine (PMDETA, 98%, Acros Organics) was stirred overnight over CaH_2 and distilled under reduced pressure. N,N'-dimethyl formamide (DMF, Beijing Chemical Engineering Plant) was dried and

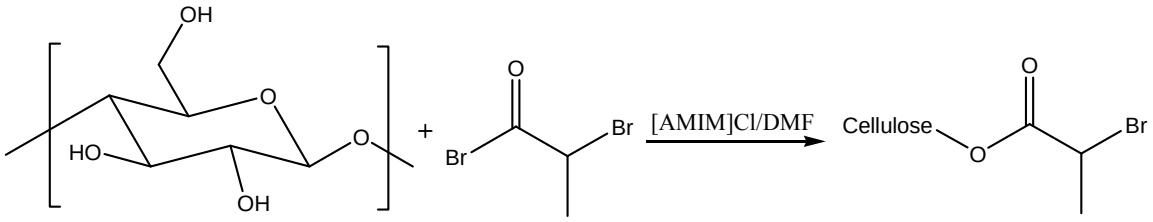
distilled under reduced pressure. 2-bromopropionyl bromide (98%, Aldrich), HCl (38%, analytically pure), allyl chloride (98%, Acros), N- methylimidazole (99%, J&K Chemical Reagent Co., Ltd), and ethyl ether (Beijing Chemical Reagent Factory) were all used as received.

Synthesis of Macro-Initiator Cellulose 2-Bromopropionyl (Cell-Br)

The preparation of the cellulose-based macro-initiator Cell-Br was carried out according to the procedure shown in Scheme 1. A total of 1.0 g (5.8 mmol) of cellulose was dispersed in 20.0 g of [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 (7.1 g, 32.2 mmol) in 10.0 mL of DMF was added dropwise into the ice-cold cellulose/[AMIM]Cl solution and stirred in a flask under nitrogen. After that the mixture was left to warm up to room temperature and stirred for 10 h. The resulting solution was poured into an excess of deionized water, and the white floccules were precipitated. 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. The degree of substitution of the Cell-Br was calculated according to Eq. 1,

$$DS = (I_1/3) / (I_2/7) \quad (1)$$

where I_1 is the integration value of CH_3 and I_2 is the integration value of cellulose backbone from the ^1H NMR spectrum of Cell-Br.



Scheme 1. Synthesis of the macroinitiator Cell-Br

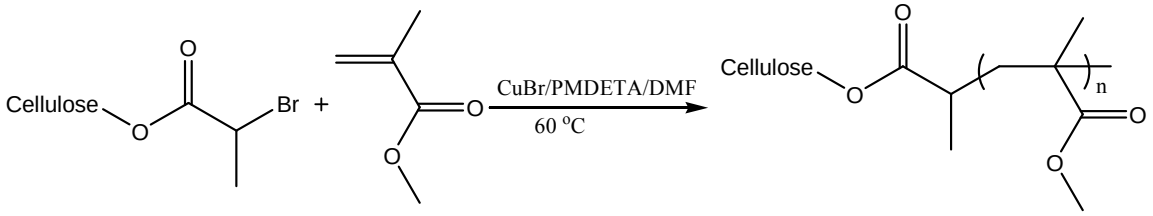
Synthesis of Cellulose-g-PMMA Copolymer

The macroinitiator Cell-Br was used to initiate the polymerization of MMA via ATRP using CuBr/PMDETA as a catalyst system. As shown in Scheme 2, Cell-Br (50.0 mg, 0.1 mmol of Br), MMA (2.43 g, 24.0 mmol), PMDETA (0.02 g, 0.1 mmol), and DMF (15.0 g) were added into a dried flask with a magnetic stirring bar. After the macroinitiator was dissolved completely, Cu(I)Br (14.0 mg, 0.10 mmol) was introduced into the flask, and then the reaction system was evacuated and back-filled with nitrogen 3 times. Thereafter, the flask was immersed into an oil bath at 60 °C for a prescribed time period. The polymerization was stopped by exposing the mixture to air and diluted with distilled water. After filtering and washing, the white solid products were collected and dried at 50 °C under vacuum for 12 h before characterization.

To estimate the graft ratio, the cellulose-g-PMMA samples were weighed before and after the graft polymerization with PMMA. The graft ratio (G, wt %) was calculated according to Eq. 2,

$$G = (W_2\text{-}W_1) / W_1 * 100 \quad (2)$$

where W_1 (g) is the dry weight of the Cell-Br sample and W_2 (g) is the dry weight of the cellulose -g-PMMA sample.



Scheme 2. Synthesis of cellulose graft copolymer

Analytical Methods

The chemical structure of the macro-initiator Cell-Br was characterized with a Tensor 27 FTIR spectrophotometer in the range of 4000 to 400 cm^{-1}. The NMR spectra were recorded at 25 °C on a Bruker AVIII 400 MHz spectrometer.

The molecular weight distributions of PMMA obtained by hydrolysis of Cell–PMMA were measured on a gel permeation chromatography (GPC) (equipped with a PL-gel 10 mm Mixed-B 7.5 mm ID column) with THF as the eluent. The flow rate was 1 mL/min. A series of monodispersed polystyrene were used as the standard to generate the calibration curve.

Thermal stability determinations of the samples were performed using thermo-gravimetric analysis (TGA) (DTG-60, Shimadzu, Japan). Samples were heated in an aluminum crucible 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 aggregated and self-assembled morphology of Cell–PMMA was examined by transmission electron microscopy (TEM) (Hitachi H-9800) and Atom Force Microscopy (AFM) (SHIMADZU SPM-9600). In order to observe the aggregated morphology of Cell–PMMA in a good solvent, samples were prepared as follows: one drop of Cell–PMMA solution in DMF (W/V = 1/100) was placed onto a copper TEM grid coated with carbon film, and the assembly was self-dried at room temperature. In order to observe the aggregated morphology of Cell–PMMA in selected solvent, 5mL of Cell–PMMA solution in DMF (W/V = 1/100) was slowly dropped into 95 mL acetone under stirring to obtain the solution of Cell–PMMA in acetone. Then one drop of this solution was placed onto a newly cleaved fresh mica surface for AFM analysis.

RESULTS AND DISCUSSION

Synthesis of Macro-Initiator Cell-Br

The homogeneous acylation of cellulose with 2-bromopropionyl bromide was readily carried out in the ionic liquid [AMIM[Cl at about 0 °C. An excess of 2-bromo-

propionyl bromide was required under such relatively mild reaction conditions in order to achieve a high grafting degree. The formation of Cell-Br was confirmed by FT-IR, NMR, and thermogravimetric analysis. Comparing with the virgin cellulose, the incorporation of bromo-ester groups would lead to suppression of the hydrogen-bonding interactions between cellulose chains; therefore, its solubility in solvents was increased significantly.

Figure 1 displays the FT-IR spectra for the virgin cellulose (a) and Cell-Br (b). The stretching vibration of carbonyl in 2-bromopropionyl group appeared at 1730 cm^{-1} in the FT-IR spectrum of cell-Br, which indicated that the 2-bromopropionyl group was introduced into cellulose chains. Moreover, the broad stretching band of hydroxyl groups at 3500 cm^{-1} for Cell-Br (b) was significantly reduced compared with that of cellulose (a), which also indicated the partial substitution of hydroxyl groups by acylation.

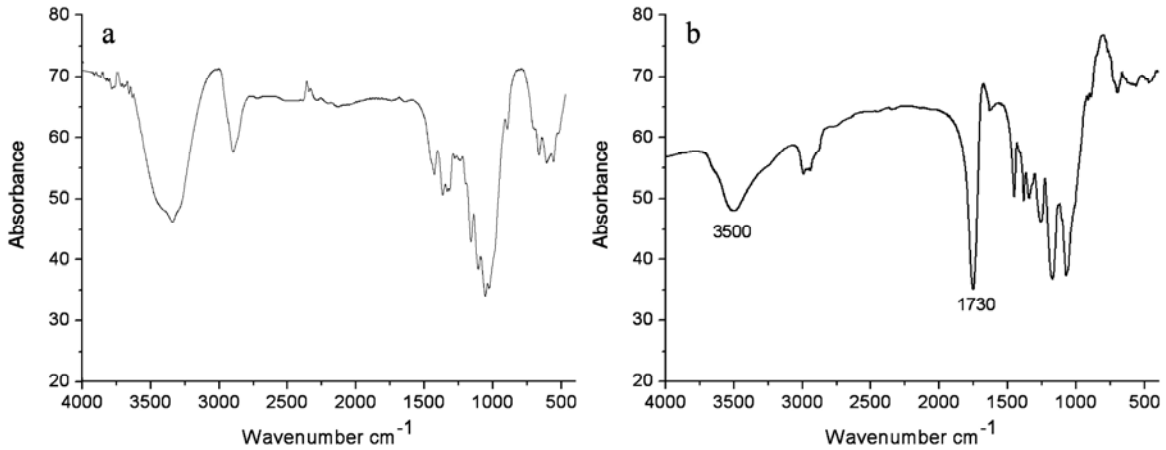


Fig. 1. FTIR spectra of virgin cellulose (a) and macroinitiator Cell-Br (b)

The acylation was further confirmed by ^{1}H NMR (Fig. 2). The chemical shift in the range of 1.40 to 1.70 ppm could be attributed to the methyl protons of the bromopropionyl group. The signals at 3.6 to 5.8 ppm are due to the cellulose backbone. The DS of cell-Br was calculated to be 0.74 (Eq. 1). In the ^{13}C NMR spectrum (Fig. 3), the chemical shift of carbonyl carbon appeared in the range 160.0 to 171.0 ppm. Those at the range of 62 to 102 ppm are due to the cellulose backbone, and the signal at 21.6 ppm is attributed to the acetate methyl carbons. However, the signals at 120 to 140 ppm also showed the presence of minor traces of aromatic residues, most likely due to lignin. The signals for carbon atoms in the cellulose backbone, for example, C-1 (d4), presented multiple peaks instead of singlet, indicating the substitution on different hydroxyl groups of cellulose.

Synthesis of Cellulose-g-PMMA Copolymers

The bromoester groups formed from the reaction of the hydroxyl groups on the cellulose backbone with 2-bromopropionyl bromide are known to be efficient initiators of ATRP. A series of polymerizations was conducted using CuBr/PMDETA as the catalyst system and Cell-Br as the macroinitiator. DMF was used as the solvent because the macroinitiator Cell-Br dissolved well in DMF. Therefore, a homogeneous reaction solution was obtained, which is important for ensuring the uniform distribution of grafting polymer chains in the cellulose macromolecules.

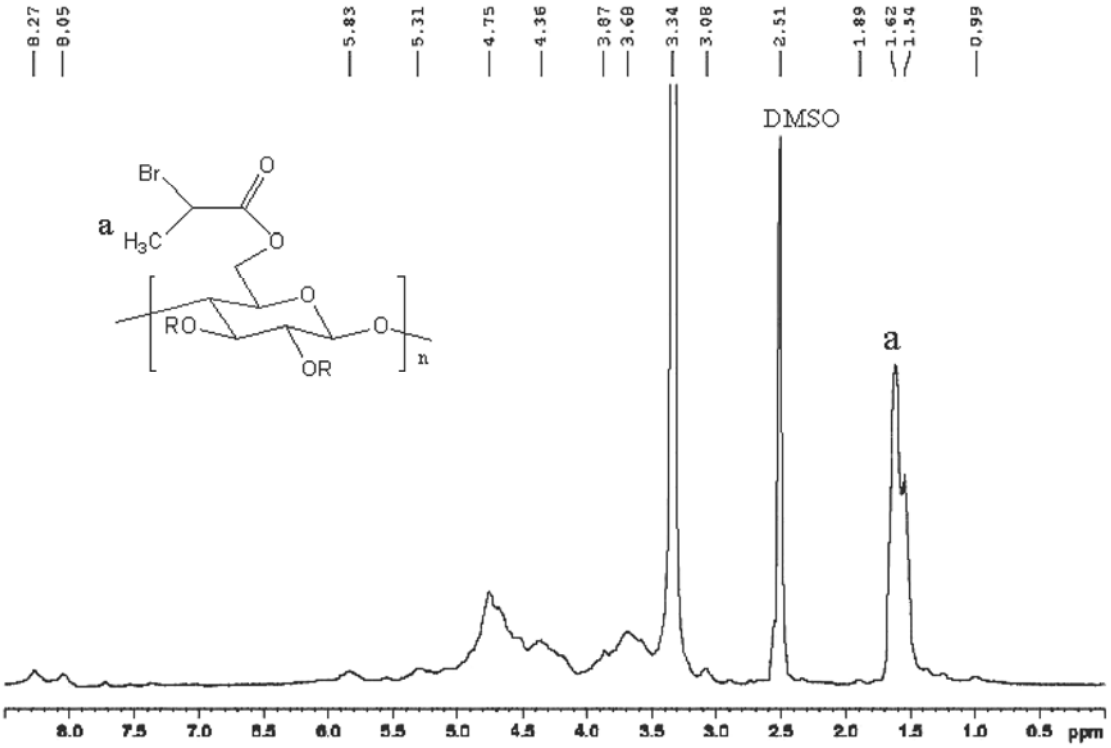


Fig. 2. [1]H NMR spectrum of macroinitiator Cell-Br in DMSO-d_6

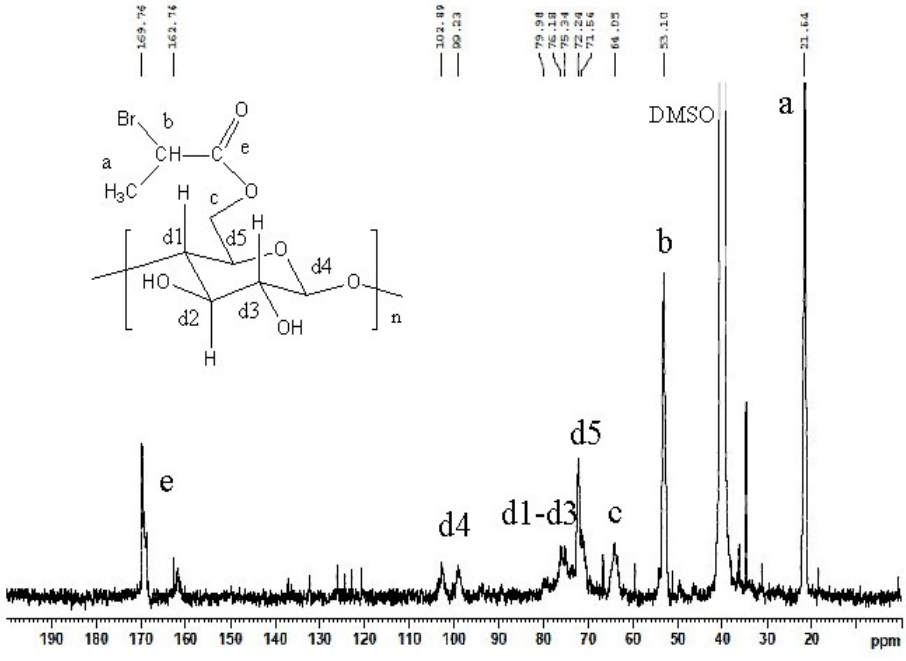


Fig. 3. [13]C NMR spectrum of macroinitiator Cell-Br in DMSO-d_6

Table 1 summarizes the experimental results obtained by changing the reaction conditions. As Cell-Br is a multifunctional initiator, radical-radical coupling of the propagating chains may occur to form crosslinks readily due to a high concentration of chain radicals in the local area. Hence, gels are easily formed and the reaction is quite difficult to control. Therefore, a low molar ratio of monomer to solvent should be used to keep a high dilution of the reaction solution. The dilute reaction conditions could maintain a low concentration of radicals, minimize the intermolecular coupling, and render the polymerization controllable. The radical coupling can also be reduced by lowering the reaction temperature. However, at too low temperature, such as 50 ^{o}C, the product cellulose-g-PMMA copolymer had a low graft ratio. Therefore, the polymerization temperature was set at 60 ^{o}C. The viscosity of the polymerization mixture was found to increase progressively with an increase of the conversion. The graft ratio was quite high, and the monomer conversion increased with the reacting time. The fast polymerization could be attributed to the homogeneous solution that was used, which would allow easy diffusion of the monomer molecules to the cellulose macroinitiation sites. In the present work, the highest monomer conversion was 37.8%, which was higher than the values reported in previous articles (Sui et al. 2008; Lin et al. 2009; Meng et al. 2009).

Table 1. Results and Reaction Conditions of ATRP of MMA Initiated by Cell-Br

No.	[M]/[I][a]/[Cu(Ⅰ)]/[PMDETA]	Solvent (wt %)	Temp (^{o}C)	Time (min)	Conversion (%)	Graft Ratio (wt %)
1	50:1:1:1	44.4	50	30	gelled	
2	100:1:1:1	68.1	50	60	16.3	1254
3	100:1:1:1	68.1	60	120	33.5	2578
4	200:1:1:1	68.1	60	60	23.4	1800
5	200:1:1:1	68.1	60	180	37.8	2909
6	200:1:1:1	68.1	70	60	34.1	2624
7	300:1:1:1	68.1	80	10	gelled	

[a] [I] = mole of bromine, calculated from ^{1}H-NMR of Cell-Br

The FTIR spectrum of cellulose-g-PMMA copolymer is shown in Fig. 4. The wide absorption at 3447 cm^{-1} was attributable to the hydroxyl stretching vibrations of cellulose and the absorption bands at 2961 and 2953 cm^{-1} originated from C-H stretching of methyl and methylene groups, respectively. The absorption band at 1730 cm^{-1} corresponded to the carbonyl group of PMMA. The signals at 1450, 1385, 1243, and 1149 cm^{-1} represented the C-H and C-O bending or stretching frequencies. The absorbance at 750 cm^{-1} was attributed to O-H bending vibration of hydroxyl. These results confirmed that the PMMA chain had been grafted onto the surface of cellulose successfully.

The ^{1}H NMR spectrum of the copolymer is given in Fig. 5. The characteristic chemical shifts of PMMA segments were readily identifiable: the signals at 0.75, 0.95, and 3.57 ppm were attributed to the methyl, methylene, and tertiary carbon protons in PMMA, respectively. These results confirmed the successful grafting polymerization of MMA on the cellulose backbone.

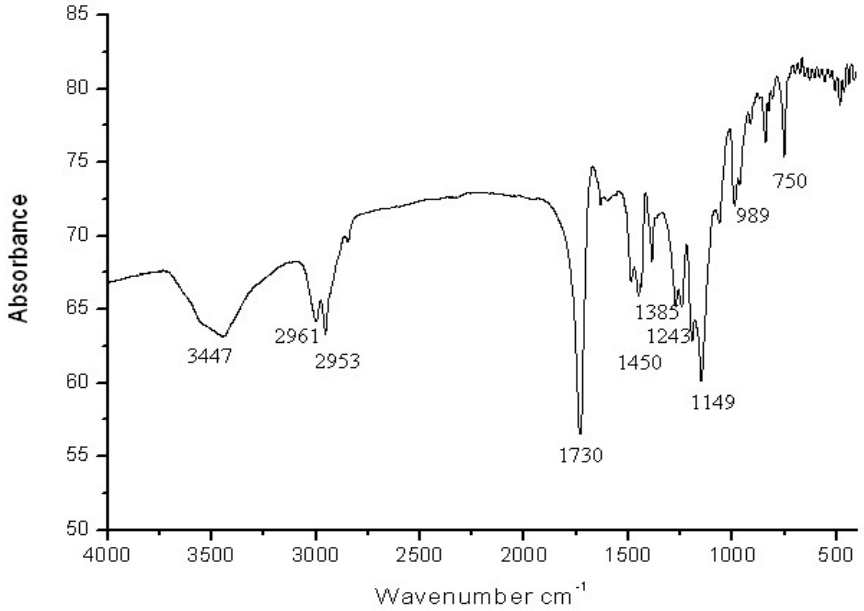


Fig. 4. FTIR spectrum of cellulose-g-PMMA (conversation 37.8%)

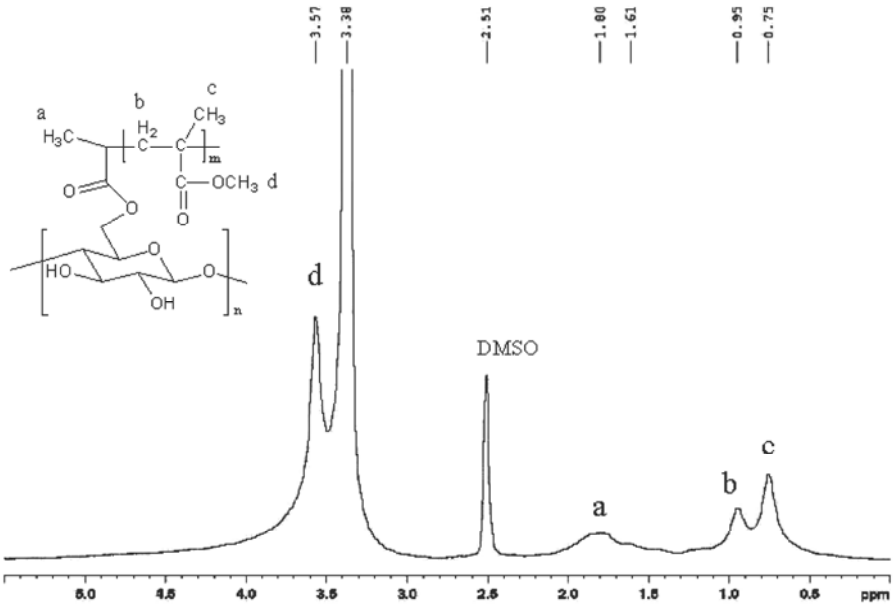


Fig. 5. ^{1}H NMR spectrum of cellulose-g-PMMA (conversation 37.8%) in DMSO-d_6

The signals of the cellulose backbones hydrogen were very weak, even under high temperature and higher concentration. As a result, the integration of the hydrogen was inaccurate. Therefore, the molecular weight of the grafting copolymer was carried out by the GPC method. The polymerization kinetics of MMA grafted on cellulose was studied. The monomer conversion was determined by weighing the samples. A semilogarithmic plot of the monomer conversion of MMA versus the reaction time is shown in Fig. 6 (a).

At the initiating stage, a curvature was observed, which provided evidence of termination due to the impact of the close proximity of the initiators. The variation of $\ln([M]_o/[M]_t)$ of MMA was linear with time in the period of 25 to 200 min, where $[M]_o$ was the initial monomer concentration and $[M]_t$ was the monomer concentration at time *t*. This indicated that the radical concentration is stable in the system during the polymerization when the monomer conversion is low, and within this period the polymerization was thought to be first order. After 200 min, the variation of $\ln([M]_0/[M]_t)$ of MMA was no-linear with time, and a slight curving occurred. This might be caused by the decrease of the radical concentration, resulting in partial termination of living free radicals, or the polar solvent (DMF) used. The variation of the molecular weight and molecular weight distribution of the side chain PMMA is shown in Fig. 6(b), which confirmed the polymerization kinetics again. PMMA was obtained by selectively hydrolysis of Cell–g-PMMA copolymers. The number average molecular weight of PMMA increased with monomer conversion, whereas the polydispersity decreased during the polymerization process, and the M_w/M_n was about 1.65. The preceding results suggested that the polymerization was a well-controlled and living process. This was in line with the results of Lin et al. (2009) and Meng et al. (2009).

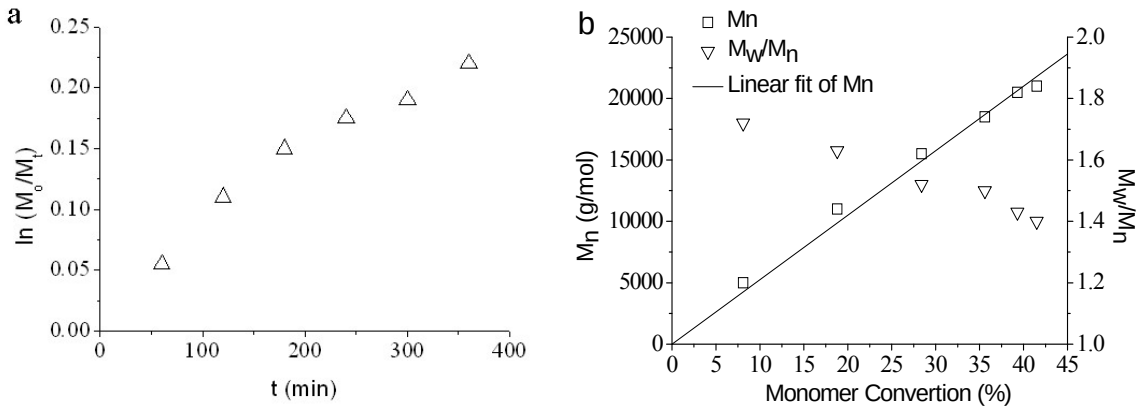


Fig. 6. Semilogarithmic plot of monomer consumption versus time for MMA polymerizing in DMF initiated by Cell-Br (a). Dependence of the number-average molecular weight and polydispersities (M_w/M_n) of side chain PMMA (b) on monomer conversion. [MMA]/[Cell-Br (DS=0.74)]/[CuCl]/[PMDETA] = 200:1:1:1, polymerization temperature was 60 °C (conversation 37.8%)

Thermogravimetric analysis (TGA) was used to study the decomposition pattern and the thermal stability of the grafted copolymers (Fig. 7). As shown in Fig. 7 a, the thermal decomposition of cellulose occurred by a one-step mechanism, displaying maximum degradation at 370 °C. After reaction with 2-bromopropionyl bromide to form the macroinitiator Cell-Br, its thermal stability decreased significantly (Fig. 7 b). Cell-Br underwent its major decomposition step at 290 °C.

The lowered thermal stability might be a result of the introduction of the bromoalkyl units, which may eliminate HBr upon heating and the HBr formed catalyzes the further degradation. TGA of cellulose-g-PMMA (Fig. 7 c) displayed higher decomposition temperature than homo PMMA (Fig.7 d).

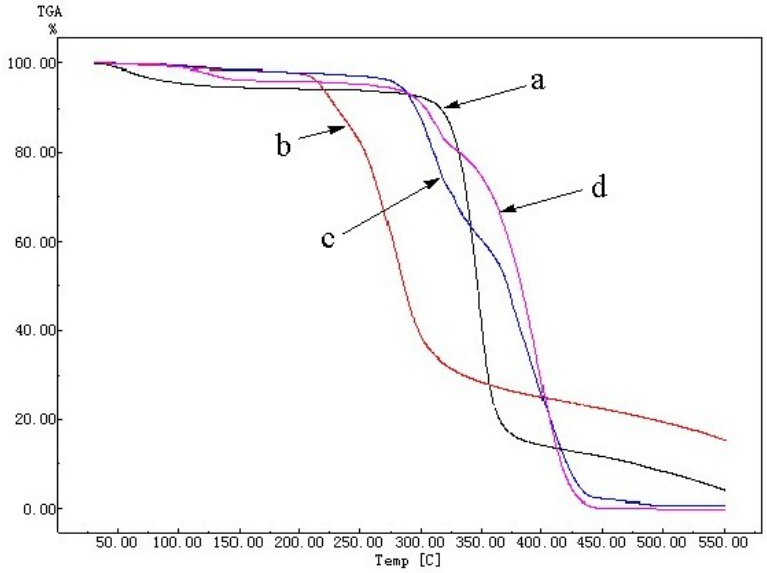


Fig. 7. TGA curves of virgin cellulose (a), Cell-Br (b), cellulose-*g*-PMMA (conversation 37.8%) (c), and PMMA (d)

The Morphology of Lignocellulose Grafted Copolymer Cell–PMMA

The morphology of the aggregates was examined by TEM and AFM. As shown in Fig. 8, solid spherical aggregates with diameters about 500 nm were observed by TEM in DMF. Particles gathered into a linear form. As shown in Fig. 9, in the selective solvent acetone, the average diameter of sphere-like particulates was roughly 100 nm. It was clear that the small particles gathered into huge independently sphere-like particles. A possible reason might be that the polarity of acetone was weaker than DMF, which means the forces acting upon a molecule of acetone were relatively small. To some extent, this indicated the tendency of aggregation of Cell-g-PMMA copolymers in solution.

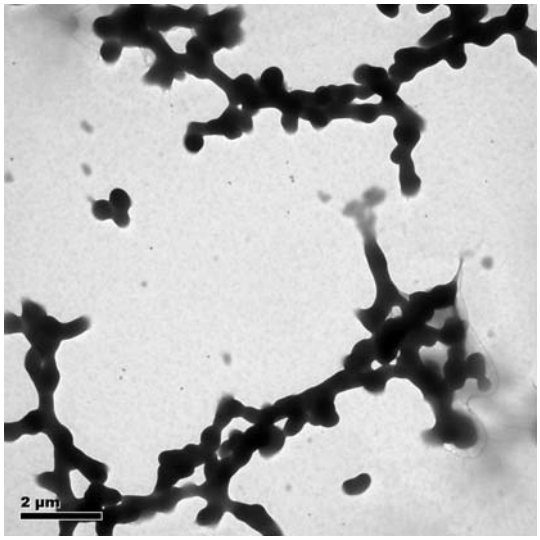


Fig. 8. TEM image for the aggregates formed from cellulose-g-PMMA (conversation 37.8%) in DMF

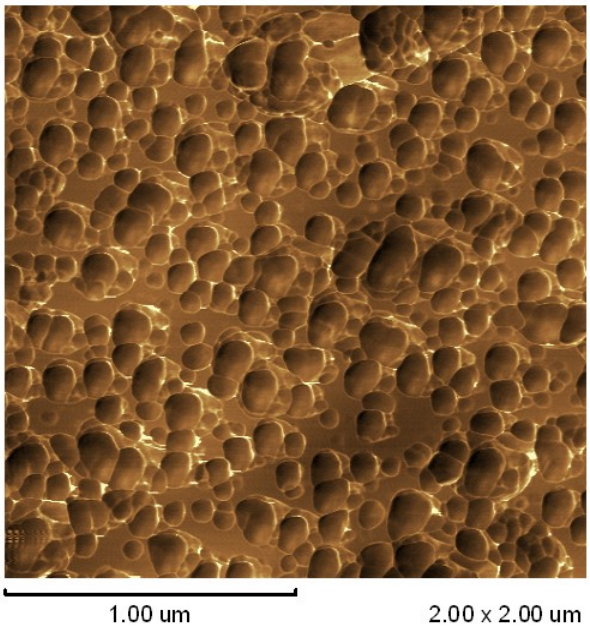


Fig. 9. AFM image for the aggregates formed from cellulose-g-PMMA (conversation 37.8%) in acetone

CONCLUSIONS

A new and convenient method for graft modification of cellulose directly onto its backbone under a homogeneous condition has been successfully carried out. The macroinitiator for ATRP was synthesized by direct homogenous acylation of cellulose in the ionic liquid [AMIM]Cl. The hydroxyl groups on the cellulose were partially converted into tertiary bromoester groups by reaction with 2-bromopropionyl bromide in the absence of any catalysts and protecting group chemistry. Graft copolymers of cellulose were obtained by ATRP of MMA under mild controllable conditions in DMF with a relatively low polydispersity, around 1.65, and the highest monomer conversion was 37.8%. The obtained graft copolymer Cellulose-g-PMMA showed good thermal stability, and the copolymer could aggregate and self-assemble into spherical particles with 500 nm diameter in DMF and 100 nm diameter in the selective solvent acetone. The same synthetic methodology could be employed for a wide range of underivatized polysaccharides to afford new biomaterials with desired properties, which could be applied in a wide range of areas, such as packaging, coatings, adhesives, biomedical polymers, tissue engineering, active surfaces, and engineering applications, etc.

ACKNOWLEDGEMENTS

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