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Preparation of cellulose graft poly(methyl methacrylate) copolymers by atom transfer radical polymerization in an ionic liquid

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ABSTRACT

Cellulose graft poly(methyl methacrylate) copolymers were prepared by atom transfer radical polymerization (ATRP) in an ionic liquid. Cellulose chloroacetate, as a macroinitiator, was first synthesized by direct acylation of cellulose with chloroacetyl chloride without any catalysts under mild conditions in an ionic liquid, 1-allyl-3-methylimidazolium chloride (BMIMCl). Then, the macroinitiator was used for the ATRP of MMA mediated by the CuBr and 2,2′-bipyridine (bpy) catalysis system. The copolymerization was carried out in BMIMCl without homopolymer byproduct. The polymers were easily separated from the catalyst when the ionic liquid was used as reaction medium. The grafting copolymers were characterized by means of ^{1}H NMR, AFM and GPC. The results showed that the obtained copolymers had grafted polymer chains with well-controlled molecular weight and polydispersity, and the polymerization was a "living/controlled" system. Further, through AFM observation, it was found that the cellulose graft copolymer in solution could aggregate and self-assembly into sphere-like polymeric structure.

1. Introduction

Cellulose has been widely studied during the past decades due to its abundance, inexpensive, and attractive properties such as nontoxic, biodegradable, renewable and thus acceptable from the environmental point of view. However, cellulose lacks some properties that synthetic polymers have in some applications although it has many useful properties. Modification of cellulose by graft polymerization provides a significant route to combine the advantages of natural and synthetic macromolecules for a wide range of potential applications (Nishio, 2006).

Graft copolymerization of cellulose using various conventional techniques has been studied quite extensively (Barsbay et al., 2007; Gupta & Khandekar, 2003; Gupta & Sahoo, 2001; Gurdag, Guclu, & Ozgumus, 2001; Lu, Yi, Li, & Ha, 2001; Mais, Binder, Knaus, & Gruber, 2000; Okieimen, 2003). Most of the techniques used are based on free radical polymerization methods, where free radical sites are produced along the cellulose backbone either by chemical means or by irradiation (Campbell, Williams, & Stannett, 1969; Misra, Mehta, & Khetarpal, 1984). In the presence of vinyl monomers, the polymeric chain grows from these radical sites through a "grafting-from" approach. The main drawbacks of these methods include the production of unwanted homopolymer together with the graft copolymer and the undesired chain degradation of the cellulose backbone.

With the advent of controlled free radical polymerization techniques, it is now possible to synthesize polymers with predetermined molecular weight and low polydispersity for a great variety of vinyl monomers. Atom transfer radical polymerization (ATRP) (Wang & Matyjaszewski, 1995) is one of the techniques to accurately control the chain length and polydispersity of the polymer, and could be used to synthesize well-defined copolymers. The living/controlled nature of ATRP is due to the relatively low radical concentration in the reaction system, which suppress the termination relative to propagation (Matyjaszewski, 1998; Patten & Matyjaszewski, 1999; Xia & Matyjaszewski, 1999).

Ionic liquids (IL), a series of organic salts that are liquid at or near room temperature, are considered to be environmentally friendly alternatives to volatile organic compounds (VOC) due to their nonvolatile, nonflammable, thermally stable, chemically inert and recyclable properties. It was first used as reaction medium of ATRP by Haddleton and his coworkers (Carmichael et al., 2005), in which, 1-butyl-3-methylimidazolium hexafluorophosphate was reported as solvent for copper-mediated ATRP of methyl methacrylate (MMA) in the presence of *N*-propyl-2-pyridylmethanimine as ligand. The reaction was relatively fast, but the molecular weights were higher than the theoretical values, and the polydispersity index was $M_w/M_n > 1.35$ in all five reported experiments.

In this study, ATRP was used to synthesize the graft copolymer of cellulose with PMMA using an ionic liquid BMIMCl as a reaction medium. In the synthesis process, the cellulose has been modified to serve as a macroinitiator that initiates the ATRP of MMA. The copolymers were characterized by ^{1}H NMR and AFM. The living

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nature of the polymerization was discussed. The preliminary study on the morphology of the graft copolymer in solution was also presented.

2. Experimental

2.1. Materials

Cotton linter (Cell-OH) was used as the cellulose material; Ionic liquid (IL) 1-*N*-butyl-3-methylimidazolium chloride (BMIMCl, mp. 73 °C), was purchased from Henan Lihua Pharmaceutical Co., Ltd.; CuBr was purified by stirring in glacial acetic acid, filtering, and washing with ethanol three times, followed by drying in vacuum at room temperature overnight; chloroacetyl chloride, 2,2′-bipyridine (bpy), methyl methacrylate (MMA) and other reagents were all analytical grade and used as received.

2.2. Synthesis of cellulose-based macroinitiator

In a typical reaction procedure, 5 folds amount of chloroacetyl chloride was added with a pipet into about 15 g cellulose/BMIMCl solutions (containing 3% of cellulose by weight) in flask. The mixture was heated in oil bath for a certain time under N_2 atmosphere with stirring. Under the conditions for the acetylation, the system remained completely homogeneous as the reaction proceeded. To obtain a reasonable reaction speed, a relatively high temperature (50 °C) was adopted. As the reaction was complete, the products were isolated by precipitation into excess de-ionized water and precipitated out the white floccules. The white floccules, that are Cell-ClAc, was washed thoroughly with water, then filtered and freeze-dried. The DS (degree of substitution) of the product was analyzed by 1H NMR method in DMSO-d6. The result is confirmed by the mass increase due to acylation. The structure of products was characterized by FT-IR and NMR.

2.3. ATRP grafting onto cellulose in BMIMCl

The macroinitiator Cell-ClAc was used to initiate the polymerization of MMA via ATRP using CuBr/bpy as a catalyst system. Cellulose-AcCl was added to molten BMIMCl in a three-neck flask. The mixture was stirred with a stirring bar at 90 °C for 5 h. When the macroinitiator was dissolved completely, bpy and MMA was introduced into the flask, and then Cu(I)Br was added. The flask was evacuated and back-filled with nitrogen for three times and thereafter immersed into an oil bath. The polymerization was allowed to react at 60 °C for a prescribed time period. Cell-ClAc, CuBr, bpy and the monomer were used at a molar ratio of 1:1:1:100. The monomer conversion was determined by ^{1}H NMR. At a certain interval time, an amount of reaction mixture was withdrawn from the flask with degassed syringes and poured into excessive de-ionized water to precipitate out the solid products. After filtering and washing, the white solid products were collected and freeze-dried before characterization. The polymerization was stopped by exposing the mixture to air and the copolymer was precipitated into de-ionized water, washed and freeze-dried. The polymer was separated from copper by a simple de-ionized water wash.

2.4. Characterization

2.4.1. Fourier transform infrared spectra (FT-IR)

IR spectra were recorded on a Spectrum GX Infrared spectrophotometer (USA PE Company) using KBr pellets.

2.4.2. Nuclear magnetic resonance spectroscopy (NMR)

^{1}H NMR and ^{13}C NMR spectra of samples were obtained on a Bruck-DRX 400 NMR spectrometer with DMSO-d_6 as solvent.

2.4.3. Gel permeation chromatography (GPC)

The molecular weight and molecular weight distributions of PMMA obtained by hydrolysis of Cell-PMMA were measured on a gel permeation chromatography (GPC) (equipped with a Waters 515 pump, three columns Styragel HT3, StyragelHT4, and Styragel HT5, and a 2414 differential refractometer detector) with THF as the eluent, the flow rate was 1 mL/min. the hydrolysis procedure was as follows: 0.04 g cellulose-*g*-PMMA sample was immersed into a round-bottomed flask containing 15 mL of 1.5 M HCl aqueous solution. The flask was stirred at 90 °C for 72 h. The reaction mixture was filtered to separate the solid cellulose particles, and the HCl aqueous solution was removed by evaporation.

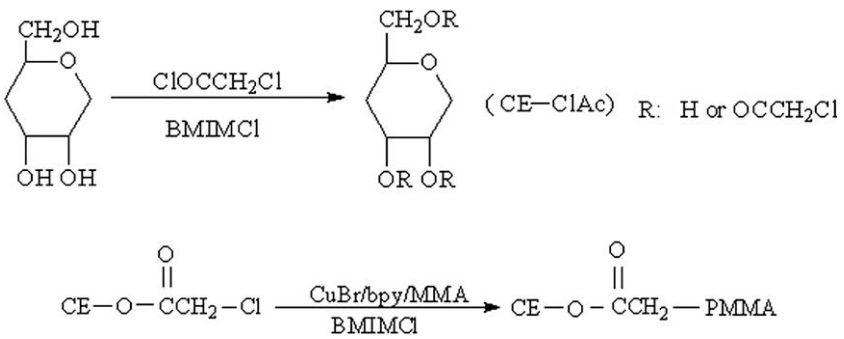
2.4.4. Atom force microscopy (AFM)

The aggregated and self-assembly morphology of Cell-PMMA was examined by atomic force microscope (AFM). In order to observe the aggregated morphology of Cell-PMMA in good solvent, samples were prepared according to reference (Meng, Gao, & Zhang, 2009): 2009): 5 mL Cell-PMMA solution in DMSO (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 and was self-dried at room temperature.

3. Results and discussion

3.1. Synthesis of cellulose chloroacetate (Cell-ClAc) macroinitiator

The macroinitiator Cell-ClAc was synthesized by homogeneous acylation of cellulose with chloroacetyl chloride in BMIMCl as shown in Scheme 1. The homogeneous chloroacylation of cellulose with chloroacetyl chloride can be readily carried out in ionic liquid BMIMCl even at room temperature. To obtain a reasonable reaction speed, a relatively high temperature was adopted.



Scheme 1. Synthesis procedure of macroinitiator Cell-ClAc and cellulose graft copolymers.

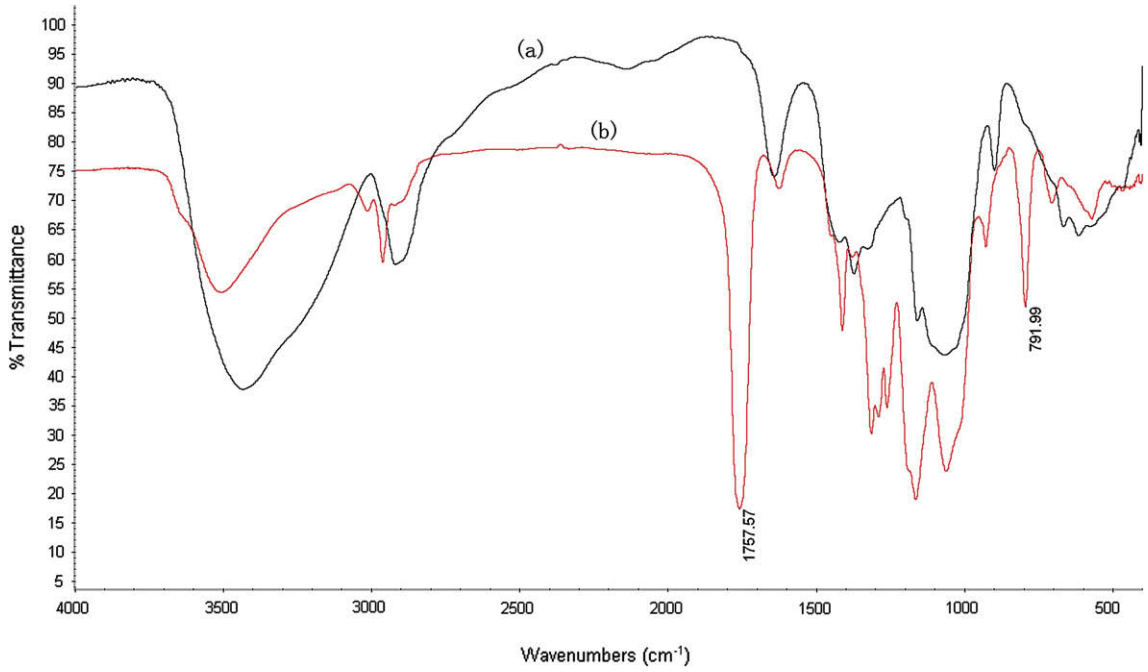


Fig. 1. FT-IR spectra of underivatized cellulose and macroinitiator Cell-AcCl (DS = 1.11).

Fig. 1 displays the FT-IR spectra for the native cellulose (a) and Cell-ClAc (b). In can be seen that the stretching vibration of carbonyl (—C=O) appeared at 1750 cm^{-1} and C—Cl stretching appeared at 790 cm^{-1} in the FT-IR spectrum of Cell-ClAc (b), but not in that of native cellulose (a), which indicates that the chloroacetyl group has been attached to cellulose.

The introduction of the chloroacetyl groups on cellulose chains was further confirmed by NMR measurement (Fig. 2). The chemical shift at δ = 4.237 ppm in ^{1}H NMR (Fig. 2(a)) could be attributed to the ethyl protons of chloroacetyl group. In the ^{13}C NMR spectrum (Fig. 2(b)), the chemical shift of carbonyl carbon appeared in the range of 165–171 ppm.

The effect of reaction parameters, such as reaction time, reaction temperature and the molar ratio of chloroacetyl chloride/AGU, on the DS of chloroacetyl group was investigated and shown in Table 1. It can be seen that increasing the ratio of chloroacetyl chloride to cellulose and extending the reaction time may raise the degree of substitution of chloroacetyl group. The highest DS value achieved was 1.87. The reaction could be also accelerated through raising the temperature, but the temperature might not exceed 50 °C, because the reaction product HCl may cause the acid hydrolysis of cellulose at higher temperature. It should be noticed that, in previous studies using cellulose derivatives as the starting materials, the higher DS of chloroacetyl group was very difficult to obtain, the reaction time was longer than 12 h, and its values were still less than 0.5 (Mehmet Coskun & Mehmet Mürsit Temüz, 2005), which is mainly due to the occupation on hydroxyl groups of cellulose by ester or ether groups. Obviously, homogeneous acylation of underivatized cellulose with chloroacetyl chloride may give a relatively higher DS of chloroacetyl group.

3.2. Preparation of cellulose-g-PMMA copolymers

The chloroacetate groups formed from the reaction of the hydroxyl groups on the cellulose backbone with chloroacetyl chloride were known to be an efficient initiator of ATRP (Kamigaito, Ando, & Sawamoto, 2001). A series of polymerizations were conducted using CuBr/bpy as the catalyst system and Cell-ClAc as the macroinitiator, ionic liquid BMIMCl as reaction medium. The reaction of grafting on cellulose is indicated in Scheme 1. Chloroacetate groups here act as initiator sites.

The graft copolymers Cell-PMMA was characterized by ^{1}H NMR analysis (Fig. 3). The chemical shift of proton at 3.677 ppm can be observed, which is attributed to protons of —OCH_3 in PMMA.

Because cellulose-ClAc is an excellent initiator (Kamigaito et al., 2001; Mehmet Coskun et al., 2005), radical–radical coupling of the propagating chains is prone to occur due to high concentration of chain radicals (Qin, Matyjaszewski, Xu, & Sheiko, 2003). Therefore, gels are easily formed and the reaction is quite difficult to control. The dilute reaction conditions could maintain a low concentration of radicals, minimize the intermolecular coupling and render the polymerization controllable. Thus, low molar ratio of monomer to solvent should be used to keep high dilution of the reaction solution. The radical coupling can also be reduced by lowering the reaction temperature. But the viscosity of the reaction mixture was found to increase with a decrease of the temperature, so the polymerization temperature was set at 60 °C. Different reaction conditions were attempted to obtain well-defined cellulose graft copolymers. Table 2 shows the experimental results obtained by changing the reaction conditions.

The "livingness" of atom transfer radical polymerization process can be ascertained from a semilogarithmic plot with the linear first-order kinetics, which reflects the constant concentration of propagating radicals. Semilogarithmic plots of the monomer conversion versus the reaction time for MMA copolymerization with Cell-ClAc macroinitiator is shown in Fig. 4. The variation of $\ln([M]_0/[M]_t)$ is linear with time in the period of 25–180 min, where $[M]_0$ is the initial monomer concentration and $[M]_t$ is the monomer concentration at time t, which indicates that within this period the polymerization is of first-order with respect to the monomer. That is, the concentration of the growing radical species in the system is constant during the polymerization. After 180 min, a slight curving occurred. The possible reason might be the polar solvent BMIMCl used and the decrease of radical concentration, which is due to partial termination of living free radicals.

Fig. 5 shows the variation of the molecular weight and its distribution of the side chain PMMA obtained by selectively hydrolysis of cellulose in Cell-PMMA copolymers. The molecular weight of

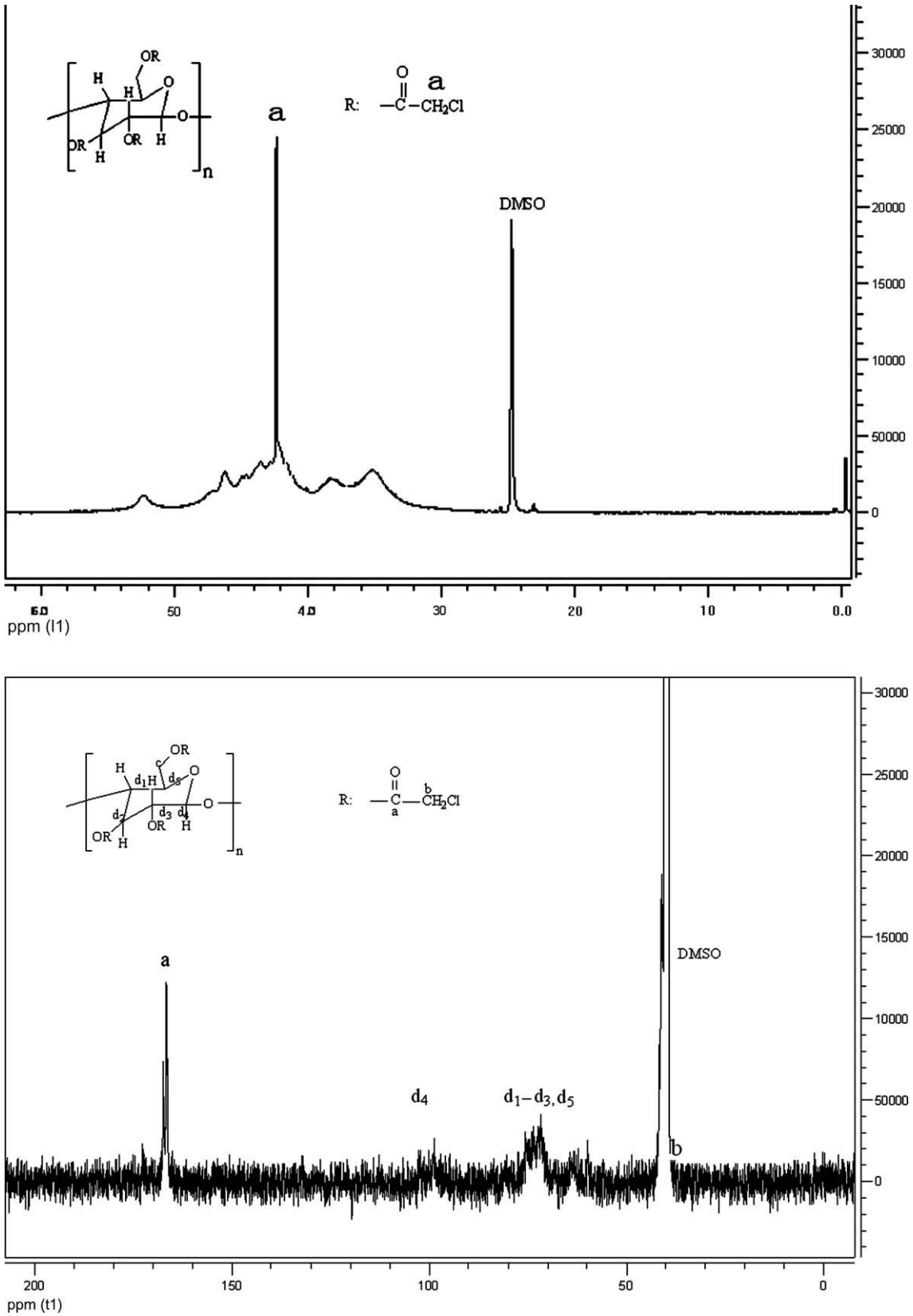


Fig. 2. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of Cell-AcCl (DS = 1.11) in DMSO-d_6.

the graft copolymer is increased with the monomer conversion, and the M_w/M_n is about 1.6, which is decreased after the grafting polymerization. These results confirm again that the graft copolymerization is living and controlled.

Above discussion indicates that the graft copolymerization of MMA onto the cellulose backbone by ATRP was accomplished successfully in the ionic liquid BMIMCl. At the end of graft copolymerization in this way, homopolymer was not observed in the

Table 1
Conditions and results of the homogeneous chloroacylation of cellulose in BMIMCl.

No.	Molar ratio[a]	Temp. (°C)	Time (h)	DS[b]
1	3:1	30	1	0.33
2	3:1	50	2	0.59
3	5:1	30	2	0.65
4	5:1	40	1	0.74
5	5:1	50	2	1.11
6	5:1	50	5	1.87

[a] Molar ratio: chloroacetyl chloride/anhydroglucose unit (AGU).
[b] Calculated from ^{1}H NMR of Cell-ClAc.

medium. Consequently, there was no problem over separating the graft copolymer from the homopolymer. This is an important advantage over conventional radical polymerization where homopolymerization and graft copolymerization occur simultaneously. Further, ionic liquids allow a simple process for separation of the metal complex from the polymer mixture at the end of the polymerization, and the ability to recover and reuse the catalyst dissolved in the ionic liquids for subsequent polymerizations was also reported by Sarbu and Matyjaszewski (2001).

3.3. The morphology of cellulose grafted copolymer Cell-PMMA in solution

The morphology of Cell-PMMA graft copolymer was studied by tapping mode AFM. AFM image in Fig. 6 shows the spherical morphology of the aggregates of cellulose-*g*-PMMA copolymers after the solvent is evaporated at the room temperature. The copolymer in acetone formed discrete, spherical particles and the average diameters of sphere-like particulates derived from the selective solvent acetone is roughly 50–100 nm. It indicates the tendency of aggregation of Cell-PMMA copolymers in solution.

4. Conclusions

The ATRP of MMA from cellulose-based macroinitiator was successfully carried out in an ionic liquid, BMIMCl. The macroinitiator for ATRP was synthesized by direct homogenous acylation of cellulose in an ionic liquid BMIMCl. The hydroxyl groups on the cellulose were partially converted into chloroacetyl groups by reaction with chloroacetyl chloride in the absence of any catalysts and protecting group chemistry. The DS of chloroacetyl group could be controlled by

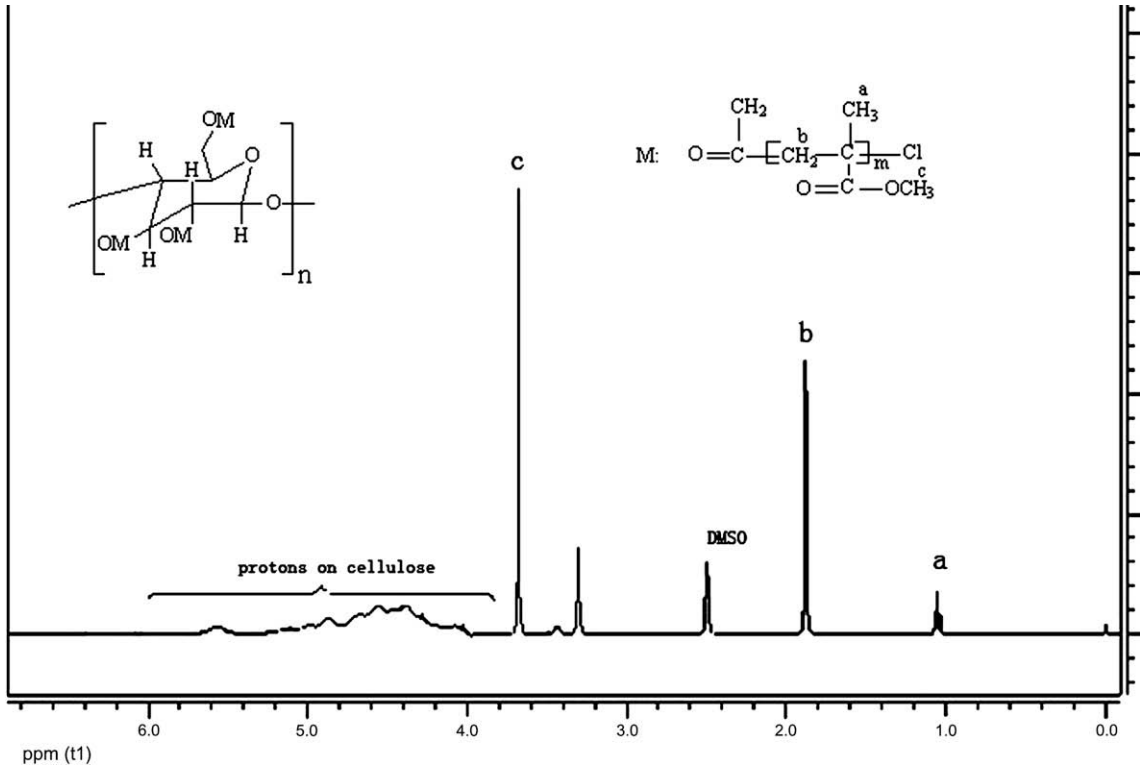


Fig. 3. ^{1}H NMR of Cell-PMMA in DMSO-d_6.

Table 2
Results and experiment conditions of ATRP of MMA onto Cell-ClAc in BMIMCl.

No.	[*M*]/[*I*][a]/[Cu(I)]/[Pby]	Solvent (wt%)	Temp. (°C)	Time (min)	Conversion (%)	M_n[b] (g/mol)	M_w/M_n
1	50:1:1:1	44.4	50	30	Gelled		
2	100:1:1:1	68.1	60	120	10.6	11000	1.74
3	100:1:1:1	68.1	60	180	14.2	15500	1.66
4	200:1:1:1	68.1	60	240	15.3	31000	1.61
5	200:1:1:1	68.1	80	30	Gelled		
6	300:1:1:1	68.1	70	300	15.5	47000	1.52

[a] [*I*] = mole of chloroacetate group, calculated from ^{1}H NMR of Cell-ClAc.
[b] Obtained from GPC for the grafted chains by hydrolysis of Cell-PMMA.

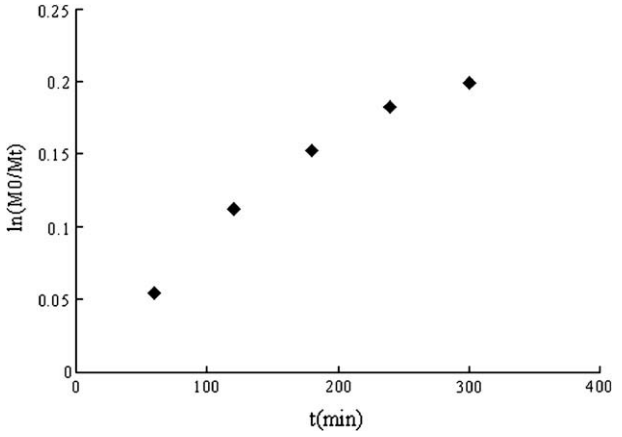


Fig. 4. Semilogarithmic plot of monomer consumption versus time for MMA polymerizing in BMIMCl initiated by Cell-ClAc. Cell-ClAc (DS = 1.11)/[CuBr]/[Bpy]/[MMA] = 1:1:1:100, polymerization temperature is 60 °C.

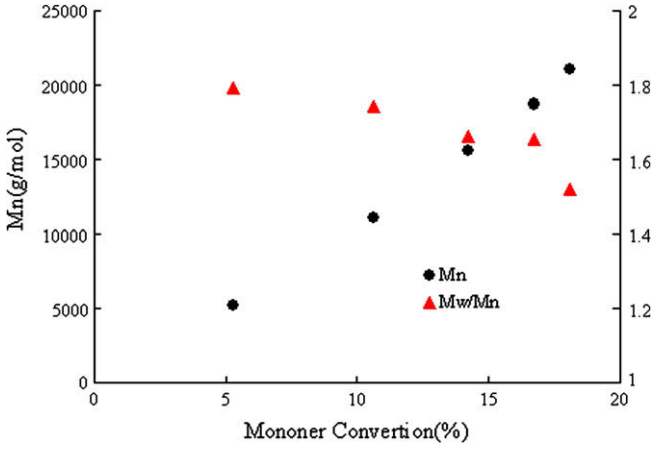


Fig. 5. The variation of the M_n and M_w/M_n of side chain PMMA with the monomer conversion.

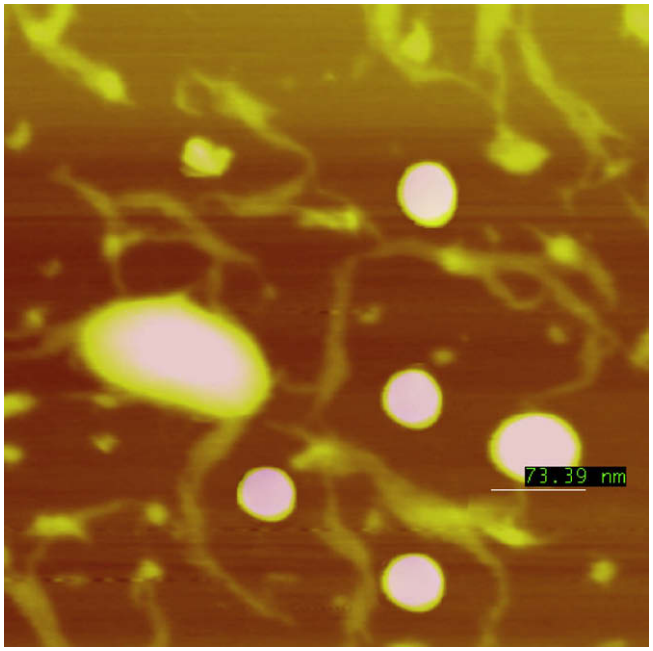


Fig. 6. AFM image for Cell-PMMA in solvent acetone, after solvent evaporation.

varying the reacting time, molar ratio of acylation reagent to cellulose and reaction temperature. The chloroacetyl groups on the cellulose are efficient for "graft from" copolymerization. Graft copolymers of cellulose have been obtained by ATRP of MMA under mild controllable conditions. The resulting polymers had relatively low polydispersity, from 1.5 to 1.8, and the Cell-PMMA could aggregate and self-assemble in selective solution, forming discrete, spherical particles with 50–100 nm diameters. Further, the use of the reaction medium, ionic liquid BMIMCl, allows a simple process for separation of the metal complex from the polymer mixture at the end of the polymerization. The polymer is recovered essentially copper free by a simple solvent wash. Optimization of this process and the potential to recycle the recovered ionic liquid–catalyst mixture are currently in progress.

Acknowledgements

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References

Barsbay, Murat, Gueven, Olgun, Stenzel, Martina H., Davis, Thomas P., Barner-Kowollik, Christopher, & Barner, Leonie (2007). Verification of controlled grafting of styrene from cellulose via radiation-induced raft polymerization. *Macromolecules, 40*(20), 7140–7147.

Campbell, D., Williams, J. L., & Stannett, V. (1969). The preparation and characterization of some cellulose graft copolymers. V. ESR study of preirradiation grafting of styrene to cellulose acetate. *Journal of Polymer Science Part A-1: Polymer Chemistry, 7*(12), 429–437.

Carmichael, A. J., Haddleton, D. M., Bon, S. A. F., et al. (2005). Copper(I) mediated living radical polymerisation in an ionic liquid. *Chemical Communication*, 1237–1238.

Gupta, K. C., & Khandekar, Keerti (2003). Temperature-responsive cellulose by ceric(iv) ion-initiated graft copolymerization of *n*-isopropylacrylamide. *Biomacromolecules, 4*(3), 758–765.

Gupta, K. C., & Sahoo, Sujata (2001). Graft copolymerization of acrylonitrile and ethyl methacrylate comonomers on cellulose using ceric ions. *Biomacromolecules, 2*(1), 239–247.

Gurdag, G., Guclu, G., & Ozgumus, S. (2001). Graft copolymerization of acrylic acid onto cellulose: Effects of pretreatments and crosslinking agent. *Journal of Applied Polymer Science, 80*(12), 2267–2272.

Kamigaito, M., Ando, T., & Sawamoto, M. (2001). Metal-catalyzed living radical polymerization. *Chemical Reviews, 101*, 3689.

Lu, J., Yi, M., Li, J. Q., & Ha, H. F. (2001). Preirradiation grafting polymerization of DMAEMA onto cotton cellulose fabrics. *Journal of Applied Polymer Science, 81*(14), 3578–3581.

Mais, Ursula, Binder, Wolfgang H., Knaus, Simone, & Gruber, Heinrich (2000). Synthesis and ^{13}C CP MAS NMR spectroscopy of cellulose-graft-poly(*N*-acetylethylenimine). *Macromolecular Chemistry and Physics, 201*(16), 2115–2122.

Matyjaszewski, K. (1998). Radical nature of cu-catalyzed controlled radical polymerizations (atom transfer radical polymerization). *Macromolecules, 31*(15), 4710–4717.

Mehmet Coskun & Mehmet Mürsit Temüz, (2005). Grafting studies onto cellulose by atom-transfer radical polymerization. *Polymer International,* 54, 342–347.

Meng, T., Gao, X., & Zhang, J. (2009). Graft copolymers prepared by atom transfer radical polymerization (ATRP) from cellulose. *Polymer, 50*(2), 447–454.

Misra, B. N., Mehta, I. K., & Khetarpal, R. C. (1984). Grafting onto cellulose. VIII. Graft copolymerization of poly(ethylacrylate) onto cellulose by use of redox initiators. Comparison of initiator reactivities. *Journal of Polymer Science: Polymer Chemistry Edition, 22*(11), 2767–2775.

Nishio, Yoshiyuki (2006). Material functionalization of cellulose and related polysaccharides via diverse microcompositions. *Advances in Polymer Science, 205*, 97–151.

Okieimen, F. E. (2003). Preparation, characterization, and properties of cellulose–polyacrylamide graft copolymers. *Journal of Applied Polymer Science, 89*(4), 913–923.

Patten, T. E., & Matyjaszewski, K. (1999). Copper(I)-catalyzed atom transfer radical polymerization. *Accounts of Chemical Research, 32*(10), 895–903.

Qin, S. H., Matyjaszewski, K., Xu, H., & Sheiko, S. S. (2003). Synthesis and visualization of densely grafted molecular brushes with crystallizable poly(octadecyl methacrylate) block segments. *Macromolecules, 36*, 605–612.

Sarbu, T., & Matyjaszewski, K. (2001). ATRP of methyl methacrylate in the presence of ionic liquids with ferrous and cuprous anions. *Macromolecular Chemistry and Physics, 202*, 3379–3391.

Wang, J. S., & Matyjaszewski, K. (1995). Controlled/"living" radical polymerization–halogen atom transfer radical polymerization promoted by a Cu(I)/Cu(II) redox process. *Macromolecules, 28*(23), 7901–7910.

Xia, J. H., & Matyjaszewski, K. (1999). Controlled/"living" radical polymerization. Atom transfer radical polymerization catalyzed by copper(I) and picolylamine complexes. *Macromolecules, 32*(8), 2434–2437.