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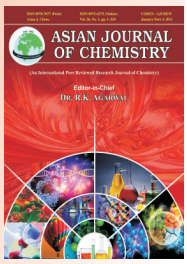

Controlled Grafting of Cellulose by Atom Transfer Radical Polymerization of Butyl Methacrylate†

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Through atom transfer radical polymerization (ATRP) in the solution of 1-allyl-3-methylimidazolium chloride (BMIMCl), which is ionic, cellulose graft poly(butyl methacrylate) copolymers (Cell-PBMA) were prepared. The macroinitiator cellulose chloroacetate (Cell-ClAc) was synthesized through direct acylation of cellulose with chloroacetyl chloride ($ClCH_2COCl$) in 1-allyl-3-methylimidazolium chloride. Afterward, the synthesized Cell-ClAc was used for the ATRP of butyl methacrylate (BMA) mediated by the CuCl and four-dimethyl aminopyridine (DMAP) catalytic system. Employing techniques such as FTIR and NMR, the Cell-ClAc and Cell-PBMA were characterized. Gel permeation chromatography (GPC) was employed for the analysis of the characteristics of the polymerization and the polymer molecular weights distribution. With contact angle measurements, the hydrophobicity of Cell-PBMA was studied. The study demonstrated that the graft copolymerization of Cell-PBMA is a controlled/'living' radical polymerization and the obtained graft polymer has a significant hydrophobic performance, indicating its potential applications as an oil absorption material.

Keywords: Cellulose, Homogeneous, Atom transfer radical polymerization, Graft copolymer, Hydrophobicity.

INTRODUCTION

Cellulose is regarded as the most abundant and renewable biopolymer in nature. It is also one of the promising raw materials for the modern industries and in terms of cost available for the production of various functional materials[1]. However, its supramolecular structure makes it difficult to be processed and also causes its insolubility of cellulose in water and the most common organic solvents. This phenomenon makes physical and/or chemical modification of cellulose necessary before it can be further utilized. To modify celluloses properties and combine the advantages of natural cellulose and synthetic polymers, it is effective to synthesize polymer-grafted cellulose[2-4].

For the synthesis of cellulose based graft copolymers, the most commonly used method has been a radical polymerization with grafting-from approach[5-7]. With this method, the initial radicals are formed on the cellulose chain either with chemical initiators or under irradiation. However, the problems of such method are the poor control of the graft density and length and the formation of unattached homopolymer[8-10]. Recently, considerable attention has been paid to a new field, controlled radical polymerization[11-15]. Several techniques for such polymerizations have been developed. Among those techniques, atom transfer radical polymerization (ATRP) is one of the most widely used[10,16,17]. When applied in graft copolymerization, these techniques show significant advantages such as the ability to polymerize grafts with controlled graft density, length and narrow molecular weight distribution. Another advantage is that there is no homopolymer impurities formed during the polymerization[18-21].

By converting part of the hydroxyl groups of cellulose into halide containing groups, which can initiate the polymerization, cellulose can be converted into an ATRP macroinitiator. Many studies have demonstrated the polymerizations from cellulose-based initiators with ATRP technique[16, 22-29], yet most of those studies on the preparation of cellulose-based graft copolymers by ATRP were carried out in heterogeneous reaction mediums. Relatively few studies on the synthesis of cellulose graft copolymer through a controlled radical polymerization directly from cellulose in its homogeneous solution have been reported.

In this study, homogeneous ATRP was used to produce poly(butyl methacrylate) grafts onto acetylated cellulose in a controlled manner with varying graft densities and lengths. The graft copolymers were dissolved in DMF and Cell-PBMA films were prepared and the hydrophobicity of the films surfaces was studied by contact angle measurements.

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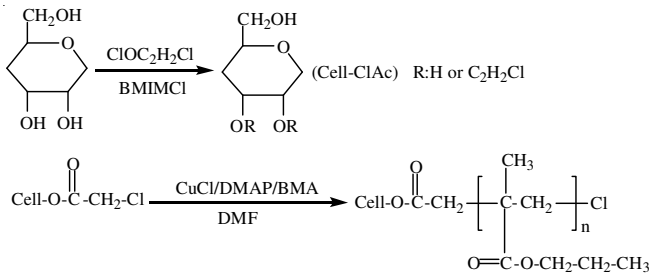
EXPERIMENTAL

Cellulose pulp (DP = 576) was provided by Xinjiang Aoyang Science and Technology Co., Ltd. Ionic liquid (IL) 1-N-butyl-3-methylimidazolium chloride (BMIMCl, m.p. 73 ºC) was purchased from Henan Lihua Pharmaceutical Co., Ltd. Copper(I)chloride was purified by stirring in glacial acetic acid, filtered and washed with ethanol three times and then dried in vacuum at room temperature overnight. Chloroacetyl chloride ($ClCH_2COCl$), 4′-dimethyl aminopyridine (DMAP), butyl methacrylate (BMA) and other reagents were all of analytical grade and were used as received.

Synthesis of macroinitiator for ATRP: Upon drying in vacuum at 50 ºC overnight, cellulose powder (1.0 g, 6.2 mmol) was treated with melted BMIMCl (19.0 g) and stirred at 80 ºC for 12 h and the resulting cellulose/BMIMCl solution was obtained.Then the solution was cooled to room temperature and then 3.5 g (30.99 mmol) of $ClCH_2COCl$ in 10 mL of DMF was added drop wise over a 0.5 h period into the solution at room temperature in a water bath. The reaction mixture was then stirred at room temperature for 8 h in N_2 atmosphere. The mixture was dispersed with deionized water and the resulting precipitate was washed several times with deionized water, dried at 50 ºC in vacuum overnight and 0.87 g of white floccules, as product of macroinitiator (Cell-ClAc), was obtained. The degree of substitution (DS) of Cl was found to be 0.78 (as determined by ^{13}C NMR analysis).

Grafting copolymerization of butyl methacrylate by the Cell-ClAc: The Cell-ClAc was used to initiate the polymerization of BMA *via* ATRP using CuCl/DMAP as a catalyst system, as shown in **Scheme-I**.



Scheme-I: Synthesis procedure of macroiniator Cell-ClAc and cellulose graft copolymers

In a 150 mL round-bottom flask, the Cell-ClAc (0.50 g, 1.76 mmol of Cl) was dissolved in 20 mL of DMF. Then, 4.96 g (0.035 mol) of BMA was added and the solution was evacuated and flushed with nitrogen for 0.5 h. Finally, 0.15 g of DMAP (1.2 mmol) and 0.12 g of CuCl (1.2 mmol) were added and the polymerization was carried out at 60 ºC in nitrogen atmosphere. At different reaction time, a few milliliters of samples were withdrawn from the flask using degassed syringes, in order to determine monomer conversion and molecular weights. The resultant solution was mixed with excessive deionized water and precipitated out as the white floccules. The white floccules, *i.e.*, Cell-PBMA, was washed thoroughly with water and then filtered and dried under vacuum at 50 ºC for 12 h before characterization.

Isolation of the grafted PBMA chains by hydrolysis: The copolymers were hydrolyzed by 70 % H_2SO_4 for 8 h at its boiling point. At the end, the residual polymer was precipitated in excess of hexane, dried by freeze drying and the product was analyzed by GPC.

Characterization: Using a FT-IR (EQUINOX 55 Fourier transform infrared spectrometer, Bruker, Germany), the chemical structure/functional groups of the product were determined. ^1H and ^{13}C NMR spectra were obtained on a NMR spectrometer (JEOL Eclipse 500 MHz and Bruker Avance 300 MHz NMR spectrometer) with DMSO-d_6 as the NMR solvent.

The molecular weights of PBMA were determined through gel permeation chromatography (GPC). For the GPC measurement, a mixture of methanol and water (with a ratio of methanol to water of 7:3) containing 10 mmol/L of lithium bromide was used as an eluent at a flow rate of 0.4 mL/min (Column type: SB-804 HQ, Shodex, Japan). The number-averaged molecular weight (M_n) and weight-averaged molecular weight (M_w) were calculated using poly (ethylene glycol) standards.

Hydrophobic performance testing of Cell–PBMA: A certain amount of Cell-PBMA was dissolved in DMF to form a homogeneous solution and drop casted onto a PVDF surface to prepare a Cell-PBMA film with a film thickness of around 30 μm. The JC 200 ºC contact angle measuring instrument was used for testing the film's contact angle of water to evaluate the hydrophobic properties of Cell-PBMA copolymers.

RESULTS AND DISCUSSION

The Cell-ClAc was prepared by partial esterification of the hydroxyl groups of the glucose units of cellulose with neat $ClOC_2H_2Cl$ in absence of any catalyst. The reaction took place under homogeneous conditions in cellulose/BMIMCl solution at room temperature for 8 h. The ester linkage formed during the reaction resulted in the characteristic peak at 1753 cm^{-1} for the C=O stretching band in the FTIR spectrum, as illustrated in Fig. 1.

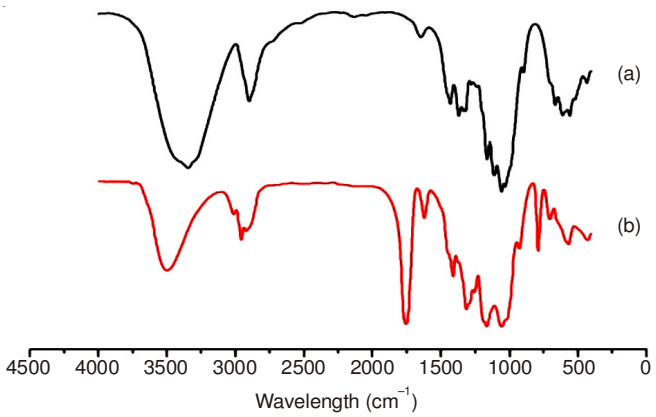


Fig. 1. FT-IR spectra of pure cellulose (a) and Cell-ClAc (b)

The ^{13}C NMR spectroscopy confirmed the substitution of the hydroxyl groups on the cellulose backbone with $ClCH_2COCl$.

Fig. 2 shows that both the methyl carbon from $ClCH_2COCl$ (peak a) and the carbon in glucose (peak b) NMR signals appear and a peak c at 176 ppm attributed to the C=O carbon of $ClCH_2COCl$ is seen in NMR.

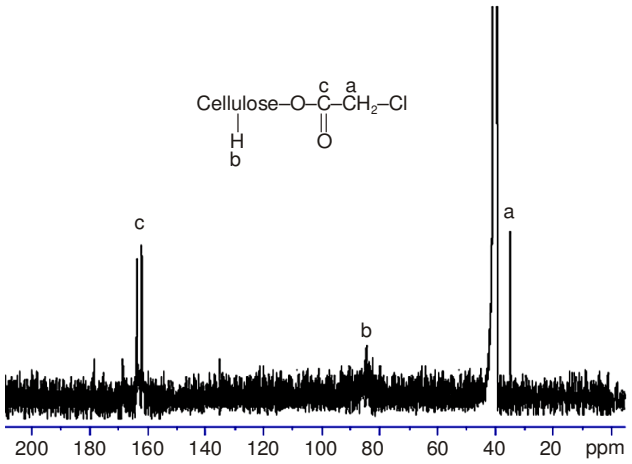


Fig. 2. ^{13}C NMR spectrum of Cell-ClAc

Cellulose is not soluble in organic solvents, but with the acylation of $ClCH_2COCl$, the as-prepared Cell-ClAc can dissolve well in DMF, DMAc, DMSO and THF. The graft copolymerization of BMA to cellulose was carried out in DMF at 60 ºC, [Cell-ClAc]/[BMA]/[DMAP]/[CuCl] = 1:30:0.7:0.70 and the total substitution degree (DS) of Cl is 0.78.

The chemical structure of the Cell-PBMA was determined through FT-IR spectroscopy. As Fig. 3 shows, there is a shift of the peak at 1753 to 1721 cm^{-1}, which is attributable to >C=O functional group in the ester group. The absorptions at 1642 cm^{-1} appeared after grafting, which is due to the free C=O of PBMA. In addition, the absorption peaks of the C-H stretching frequencies of the $-CH_2$ and $-CH_3$ groups and the bending modes of the C-H bonds in $-CH_3$ at 2877, 2960, 1454 and 1376 cm^{-1}, respectively, were distinctly observed, indicating that PBMA has chemically bonded on the cellulose.

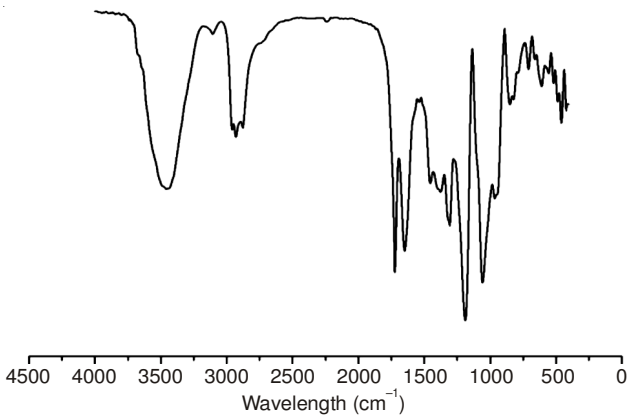


Fig. 3. FT-IR spectra of Cell-PBMA

The structure of the Cell-PBMA was also characterized by ^{1}H NMR spectroscopic analyses. As shown in Fig. 4, the peaks originating from the protons of the cellulose backbone appeared at 3.6-5.5 ppm and the NMR peaks of protons from PBMA appeared at 1.2-2.0 ppm and 0.9 ppm.

The kinetic plot of the reaction is shown in Fig. 5. It can be seen that $\ln([M]_0/[M]_t)$ varies linearly with time. Such variation indicates a constant concentration of propagating radicals, which characterizes the controlled/"living" radical polymerization.

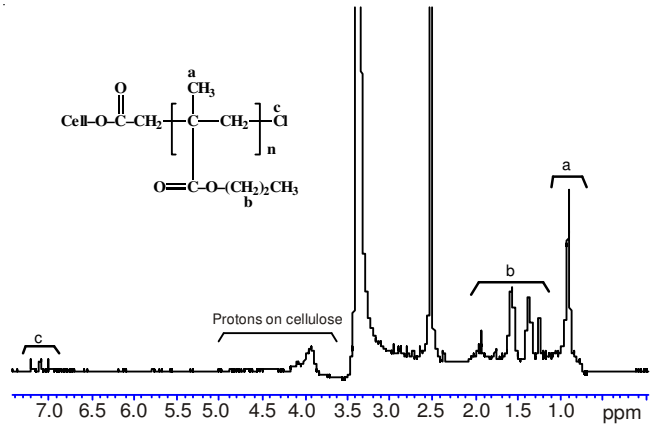


Fig. 4. ^{1}H NMR spectrum of Cell-PBMA

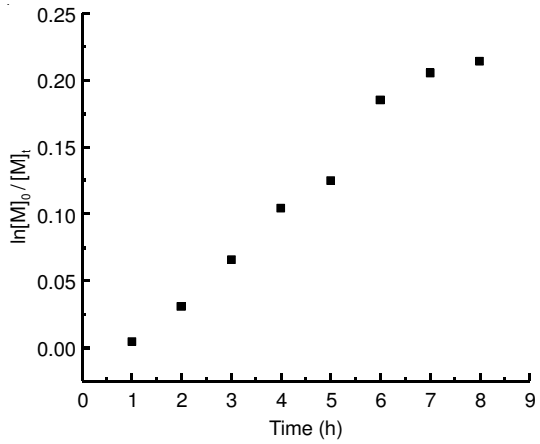


Fig. 5. Semilogarithmic plot of monomer consumption *versus* time for BMA polymerization in DMF initiated by Cell-ClAc. Reaction conditions:[Cell-ClAc]/[BMA]/[DMAP]/[CuCl] = 1:30:0.7:0.7, 60 ºC

Through hydrolysis of the backbone, the grafted PBMA chains were converted into individual molecules so that their molecular weights can be determined. Fig. 6 illustrates the variations of M_n and M_w/M_n with the monomer conversion in the polymerization process. It can be seen that with the monomer conversion, the M_w of the graft copolymer increased in a linear manner, whereas the polydispersity decreased. In addition, it was validated that the graft copolymerization was a controlled/'living radical polymerization.

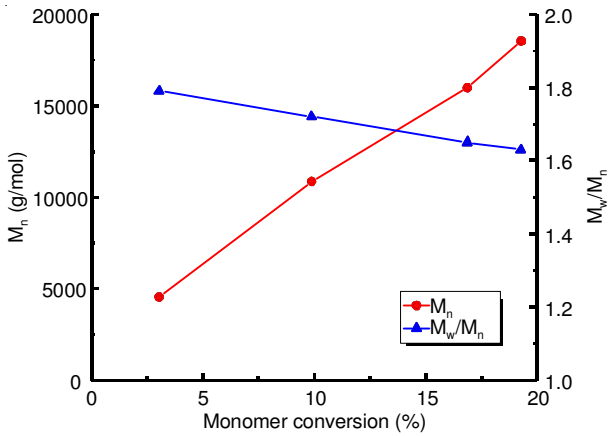


Fig. 6. Variation of the M_n and M_w/M_n of side chain PBMA with the monomer conversion

The hydrophobicity of Cell-PBMA copolymers was studied by testing the contact angles of water on the surfaces of Cell-PBMA films with various monomer conversions.

As shown in Fig. 7, the contact angles on the surfaces of Cell-PBMA films fit between the cellulose film (as measured from surface, prepared using cellulose/BMIMCl solution) and homopolymers film (as measured from surface, prepared using PBMA/DMSO solution). The sample with the highest monomer conversion also of the highest contact angle measured. This can be attributed to the samples higher grafting density, which caused that the hydroxyl groups of cellulose were more hidden and the PBMA grafts more exposed on the surface.

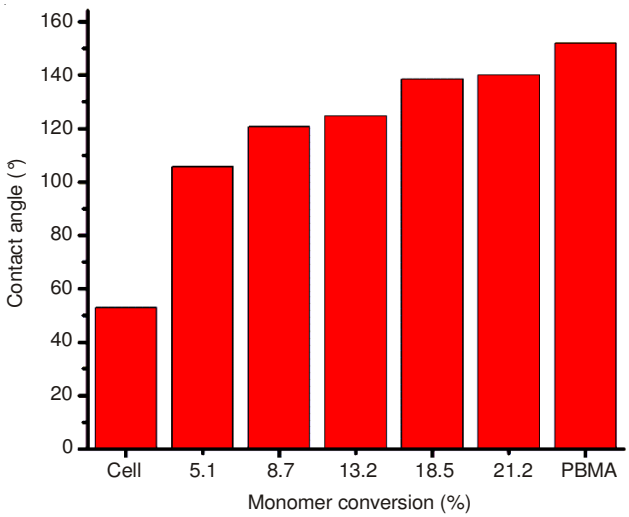


Fig. 7. Water contact angle values of Cell-PBMA films surfaces

Conclusion

In this study, through an ATRP controlled/'living' radical polymerization reaction, the Cell-PBMA was successfully synthesized in homogeneous media. The characterization indicated that the graft copolymerization was efficient and the obtained copolymer was well structured. The synthesized Cell-PBMA was dissolved in DMF to prepare a Cell-PBMA film and the hydrophobicity the films surfaces were studied through contact angle measurements. It was demonstrated that the obtained graft copolymer had significant hydrophobic performance. A new platform is offered for the surface modification of polysaccharide materials to improve their hydrophobic performance. In itself the possibility to prepare a highly efficient oil absorbent from these graft copolymers provides an easy and environmentally friendly method available to various applications.

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