The Synthesis of a Macro-initiator from Cellulose in a Zinc-Based Ionic Liquid

Supeno Supeno,[a,b] Rusli Daik,[b,*] and Said M. El-Sheikh [c]

The synthesis of a macro-initiator from cellulose in mixtures of zinc-based ionic liquid and polar solvents including deep eutectic solvent, dimethylformamide, acetone, and tetrahydrofuran (THF) was studied. The results of FTIR and NMR spectroscopies indicated that the cellulose-based macro-initiator can only be obtained in an inert ether solvent, THF. When the amounts of cellulose and zinc-based ionic liquid were fixed at 0.5 g and 18 mL, respectively, the degree of substitution of the cellulose-based macro-initiator obtained was increased from 11.0% to 17.4% as the reaction temperature was increased from room temperature to 40 °C, as calculated from TGA thermograms. When the amount of cellulose was cut in half, a degree of substitution of 27.5% was achieved due to lower viscosity and better homogeneity of the reaction medium. A green, new, and relatively cheap approach has been shown to be suitable for synthesizing a cellulose-based macro-initiator.

Keywords: Cellulose macro-initiator; Zinc-based ionic liquid; Polar solvent; Green chemistry

Contact information: a: Cenderawasih University, Jayapura, Papua, Indonesia; b: School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia; c: Nano-Structured Materials Division, Advanced Materials Department, Central Metallurgical Research and Development Institute, Cairo, Egypt;
** Corresponding author: rusli@ukm.my*

INTRODUCTION

Cellulose, which is the most abundant biomaterial, has attracted more attention due to its biodegradable, biocompatible, and renewable character (Chang *et al*. 2010). These advantages have led to modification of cellulose and its derivatives to give new materials for such applications as sorption, coating, membrane, and drug delivery agents (Nishio 2006). Of these modifications, atom transfer radical polymerization (ATRP) has been extensively studied for graft copolymerization of vinyl monomers onto cellulose and cellulose derivatives, in which the formation of macro-initiators is a prerequisite (Meng *et al*. 2009). This method can yield copolymer with controlled graft density and length as well as narrow molecular weight distribution (Nurmi *et al*. 2007). In addition, the formation of homopolymer is insignificant in the polymerization process (Pyun *et al*. 2003).

Macro-initiator formation is important in the synthesis of cellulose graft copolymers via the ATRP method. One of the common reactions used in the synthesis of a cellulose-based macro-initiator is acylation, in which an acyl halide, such as 2-bromo-isobutyrylbromide, reacts with the hydroxyl group of cellulose to form an ester functional group, either with or without a catalyst (Meng *et al*. 2009; Lin *et al*. 2009; Xiao *et al*. 2011; Wang *et al*. 2011; Hiltunen *et al*. 2012; Zhong *et al*. 2012).

There have been many reports describing the synthesis of cellulose-based macro-initiators under green conditions either heterogeneously or homogeneously. Recently, an ionic liquid medium has been shown to provide the homogeneously green condition in synthesizing cellulose-based macro-initiator. For instance, the macro-initiator of cellulose bromopropionyl ester was synthesized in an ionic liquid 1-allyl-3-methylimidazolium chloride (AMIMCl) medium at room temperature without using a catalyst. It was found that the degree of substitution (DS) was 0.74. In addition, the macro-initiator was easily separated from the ionic liquid just by washing it with plenty of water (Xin *et al*. 2011). However this was costly due to the price of the ionic liquid.

There are other types of the ionic liquids called deep eutectic solvents (DES). This kind of solvent is relatively cheap and has been used in the modification of cellulose. Abbott *et al*. (2005) reported the acetylation of cellulose and monosaccharides using a Lewis acidic ionic liquid. They synthesized cellulose acetate by mixing cellulose and acetic anhydride in a zinc-based ionic liquid at 90 ^oC. The range of the degree of substitution was 0.14 to 0.31. Moreover, Duan *et al*. (2006) reported the use of zinc-based ionic liquid, a green and moisture-stable catalyst for carbonyl group protection, by converting it into acetyls at room temperature. Acetylization of various aldehydes with neopentyl glycol in Lewis acidic ionic liquids (choline chloride. x $ZnCl_2$) can achieve up to a 97% conversion. This reaction was easily conducted at room temperature due to the low boiling points of the alcohol and aldehyde involved.

To date, the synthesis of macro-initiator from cellulose in a zinc-based ionic liquid for ATRP grafting purposes has not yet been reported. In addition to contributing to a green approach, zinc-based ionic liquid is cheap, easy to prepare, and possible to recover. Furthermore, it is capable of dissolving cellulose. Thus, it can provide homogeneous conditions for synthesizing a cellulose-based macro-initiator. This paper reports the synthesis of a macro-initiator from dissolved cellulose in a zinc-based ionic liquid, which was then diluted in either dimethylformide (DMF), acetone, or tetrahydrofuran (THF). These solvents were required to maintain the liquid state when introducing 2-bromoisobutyryl bromide at a low temperature into ionic liquid.

EXPERIMENTAL

Materials

Microcrystalline cellulose (Across) (MCC) was dried at 40 ^oC in vacuum for approximately two days. N,N dimethylformamide (99.5%, Systerm) (DMF), tetrahydrofuran (100%, J.T. Baker) (THF), and acetone (99.5%, Systerm) were dried over alumina prior to use. Zinc chloride (ACS reagent, Merck), choline chloride (> 99%, Aldrich) (ChCl), urea (99%, Systerm), and 2-bromoisobutyryl bromide (98%, Aldrich) (BiBBr) were used as received.

Preparation of Choline Chloride/Urea Eutectic-based Ionic Liquid

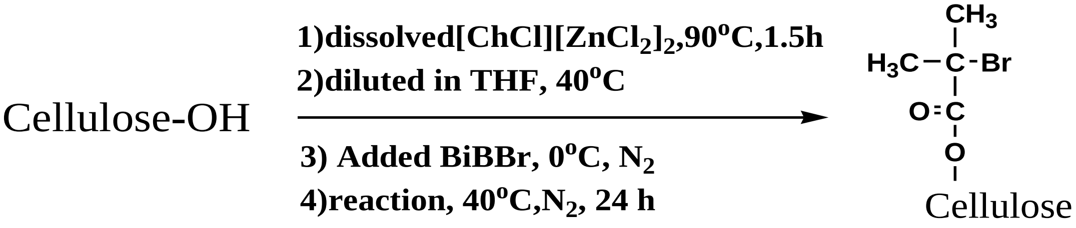
This ionic liquid preparation was carried out according to Abbot *et al.* (2003). Choline chloride was mixed with urea in a molar ratio of 1:2. This mixture was heated to about 100 ^oC with stirring until a clear, colorless liquid was obtained.

Preparation of Zinc-based Ionic Liquid ($[ChCl][ZnCl_2]_2$)

The zinc-based ionic liquid was prepared according to the procedure reported by Duan *et al*. (2006) and is briefly described as follows: choline chloride was mixed with zinc chloride in a molar ratio of 1:2. This mixture was heated to about 100 °C with stirring until a clear colorless liquid was obtained.

Synthesis of Microcrystalline Cellulose 2-Bromoisobutyryl (MCC-BiB) Macro-initiator

The preparation of the macro-initiator was carried out as follows: MCC (0.5 g) was dissolved in a zinc-based ionic liquid (18 mL) under stirring at 90 °C for 1.5 h in a 100-mL three-necked round-bottom flask. This solution was then diluted with 30 mL of a polar solvent (*e.g.*, THF). Diluted BiBBr (2.4 mL in 10 mL of THF) was added to the solution drop-wise with stirring at 0 °C in an ice/water bath under sparging of N_2 gas. The solution was then moved to a silicon oil bath at 40 °C for 24 h under stirring and sparging of N_2 gas. Deionized water was later added to the final solution to precipitate the macro-initiator. The product was then filtered and washed with deionized water until a neutral pH was achieved. Finally, the products were dried at 40 °C in a vacuum oven.



Scheme 1. Synthesis procedure of MCC-BiB macro-initiator

Characterization

The MCC-BiB macro-initiator was characterized by FTIR (Perkin Elmer 2000 FTIR) and ^{1}H and ^{13}C NMR (JEOL 400 NMR spectrometer). The degradation of the macro-initiator was studied by the TGA of SDTA 851 Mettler Toledo at a temperature range of 30 to 600 °C, a heating rate of 10 °C/min and nitrogen gas.

RESULTS AND DISCUSSION

Synthesis of MCC-BiB Macroinitiator

The results of the MCC-BiB macro-initiator synthesis in various polar solvents are presented in Table 1.

Table 1. Results and Reaction Conditions of the Homogeneous Acylation of Cellulose by BiBBr in Diluted [ChCl][ZnCl$_2$]$_2$

No	Solvent added	Melting Point (^{o}C)	Reaction Temp.(^{o}C)	Formation of macro-initiator
1	DES*	12.0	60	No
2	DMF	-61.0	40	No
3	Acetone	-95.0	40	No
4	THF	-108.4	40	Yes

* a mixture of choline chloride and urea with 1:2 mole ratio \

Table 1 shows that only THF was able to provide suitable conditions for the formation of the cellulose-based macro-initiator catalyzed by [ChCl][ZnCl$_2$]$_2$ near ambient temperatures. These results were clarified by FTIR, TGA, and NMR analysis. A possible explanation is related to the presence of carbonyl groups in the structure of DMF and acetone. The [ChCl][ZnCl$_2$]$_2$ catalyst can activate the carbonyl group to undergo reactions such as acetalization. Duan *et al*. (2006) reported that the acetalization reaction of aldehydes or acetones in Lewis acidic ionic liquids (choline chloride. x ZnCl$_2$) can achieve up to a 97% conversion. DES is a good solvent for cellulose (Miller 2008). Thus, DES can provide homogeneous reaction conditions. However, DES contains urea, which has carbonyl and amine groups. Therefore, in addition to the acetalization reaction, DES will also undergo the Schotten-Baumann reaction, the reaction between amine or alcohol and acyl halide (Lindstrom 2007). THF is a cyclic ether with a five-membered ring structure. It is inert (Chang *et al*. 1987) and thus only supports the acylation reaction between cellulose and BiBBr catalyzed by [ChCl][ZnCl$_2$]$_2$.

Characterization of MCC-BiB Macroinitiator

Figure 1 presents the FTIR spectra of the MCC and MCC-BiB. The summary of bands of FTIR spectra are given in Table 2.

Table 2. FTIR bands of MCC and MCC-BiB

Material	Wave number (cm^{-1})						
	O-H stretching	C-H stretching	C=O Stretching	Absorbed water	CH$_3$ bending	C-O-C stretching	C-O stretching
MCC	3351	2901	-	1641	-	1164	1060
MCC-BiB	3349	2902	1735	1640	1372	1163	1060

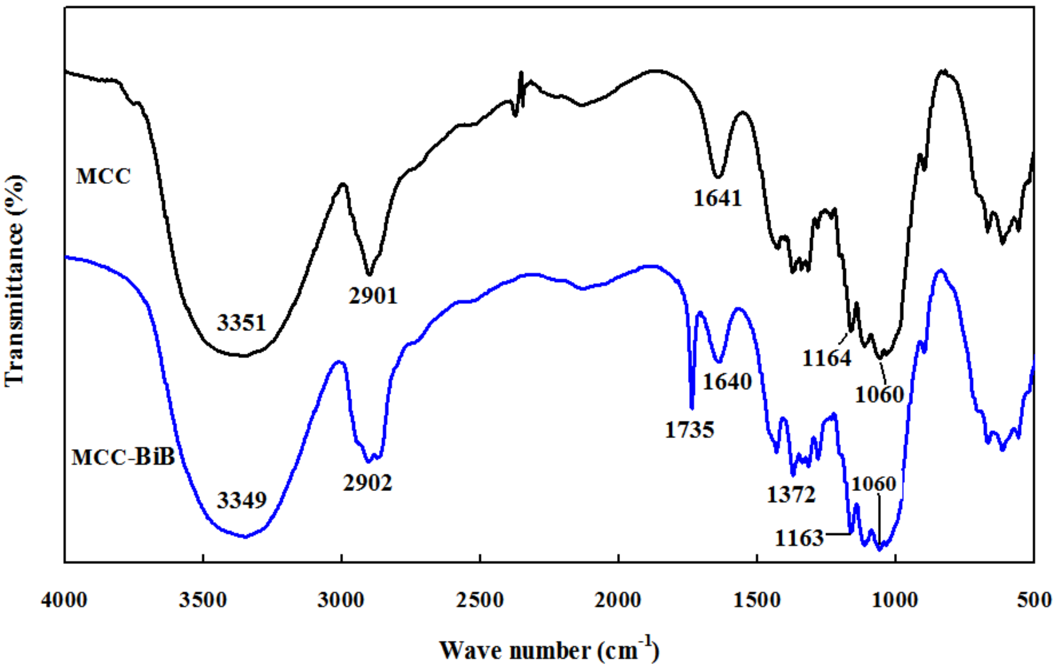


Fig. 1. FTIR spectra of MCC and the MCC-BiB macro-initiator

The broad bands with strong intensity in the region of 3351 to 3349 m^{-1} are assigned to the O-H bond stretching vibration of the alcohol groups. The medium peaks around 2901 cm^{-1} corresponded to the C-H bond stretching of alkane group. The sharp peak at 1735 cm^{-1} and the small peak at 1372 cm^{-1} in the FTIR spectrum of MCC-BiB are attributed to the stretching vibration of C=O and to the bending vibration of CH_3, respectively. These peaks indicate that 2-bromoiso-butyryloxyl was bonded to MCC. The bands with medium intensity around 1641 cm^{-1} were believed to be due to tightly absorbed water by MCC (Shamsuri and Daik 2012). The C-O-C bond stretching of ether group and the C-O bond stretching of alcohol group are found around 1164 and at 1060 cm^{-1}, respectively.

The presence of the BiB groups on the MCC chains was further clarified by NMR spectroscopy. Figure 2 shows the ^{1}H NMR and ^{13}C NMR spectra of MCC-BiB.

The proton chemical shift in the range of 1.4 to 2.0 ppm can be attributed to the methyl protons of the bromoisobutyryl group. The peaks in the range of 3.6 to 3.7 ppm can be attributed to the methylene protons of MCC. In the ^{13}C NMR spectrum of MCC-BiB, peaks for the methyl carbon (1), the quaternary carbon (2) and carbonyl group (9) of the BiB groups, and the methylene carbon (3) of MCC were observed at 30.8, 58.2, 171.7, and 66.1 ppm, respectively. These NMR spectra are in agreement with the data reported by Meng *et al*. (2009), in which the cellulose micro-initiator was synthesized by using the ionic liquid of 1-allyl-3-methylimidazolium chloride.

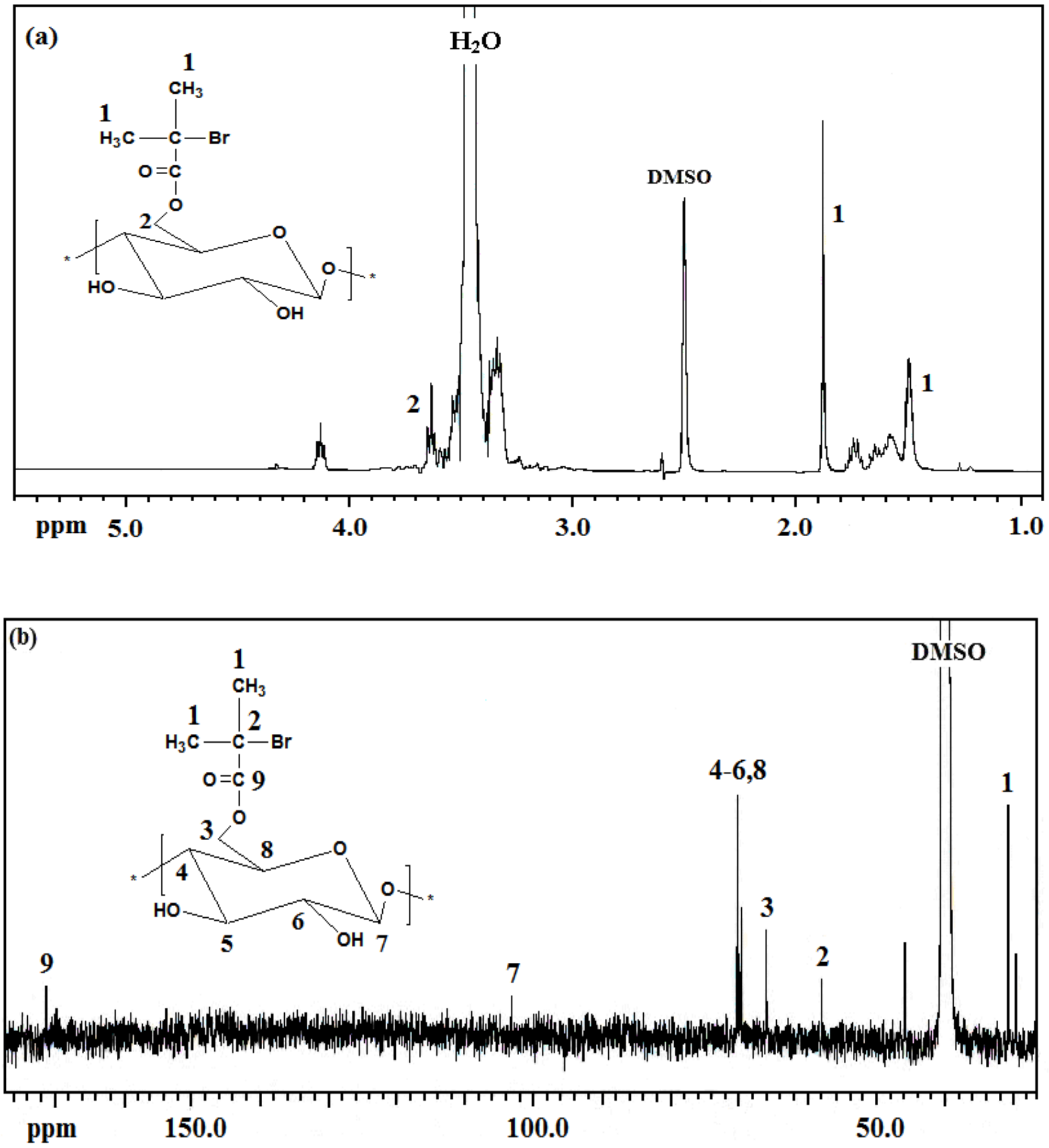


Fig. 2. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of MCC-BiB in DMSO-d_6

Figure 3 shows the TGA thermograms of the MCC-BiB macro-initiator (1, 2, 3, 4) and MCC. Both of the thermograms exhibited a small weight loss at a low temperature range (up 110 ^{o}C) due to the evaporation of absorbed water. At higher temperatures, the MCC underwent only one sharp weight loss, at around 342 ^{o}C, which can be attributed to the degradation of MCC (T_d).

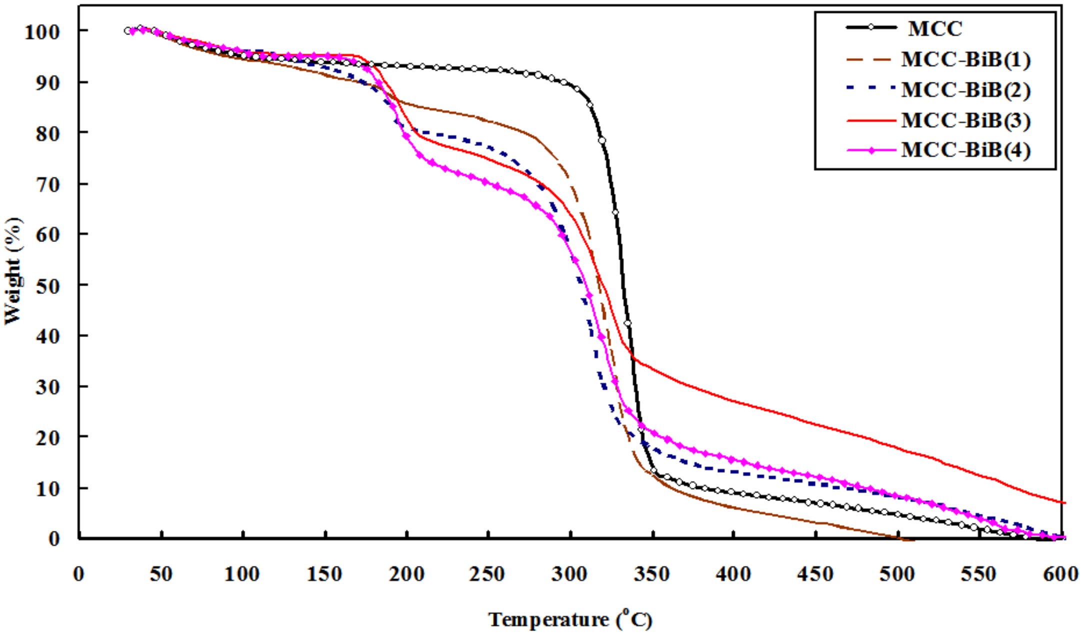


Fig. 3. TGA thermograms of MCC-BiB macroinitiator (1, 2, 3, 4) and MCC. The number (1, 2, 3, and 4) refer to the synthesis conditions as given in Table 3.

The MCC-BiB, however, underwent two steps of degradation**.** For example the MCC-BiB (2), the first step was in the range of 150 to 245 °C and corresponded to 15.1% of the weight loss. This weight loss resulted from the degradation of the BiB groups. Xiao *et al*. (2010) reported that the BiB degraded within a temperature range of 150 to 275 °C with an 11.7% weight loss. The second weight loss was found at around 313 °C, which was lower than that of the degradation temperature of MCC (342 °C). This was believed to be the partial degradation of the MCC when it was dissolved in the zinc-based ionic liquid at a high temperature. The dissolved MCC underwent partially thermal depolymerization catalyzed by the Lewis acid catalyst of zinc chloride (Domvoglou *et al.* 2010). According to the TGA data of MCC-BiB (2), the amount of BiB in MCC-BiB was 15.1% (wt) and 77.8% (wt) for amount of MCC. By converting these percentages to moles and then calculating the mole ratio of BiB in MCC-BiB executively, this would give a 17.4% degree of substitution of BiB on MCC.

The effect of the reaction parameters, such as temperature, and the molar ratio of BiBBr to the MCC, on the formation of the macro-initiator was investigated, and the results are presented in Table 3.

Table 3. Results and Reaction Conditions of the Homogeneous Acylation of Cellulose by BiBBr in Mixtures of [ChCl][$ZnCl_2$]$_2$ and THF for 24 Hours

No	Weight of cellulose (g)	[ChCl][$ZnCl_2$]$_2$ added (mL)	BiBBr added (mL)	Reaction temp.(°C)	BiB* (wt%)	MCC* (wt%)	DS** (%)
1	0.50	18	2.4	Room temp.	9.4	82.8	11.0
2	0.50	18	2.4	40	15.1	77.8	17.4
3	0.50	18	4.8	40	16.9	77.0	19.2
4	0.25	18	2.4	40	24.6	71.0	27.5

* as calculated from the TGA thermograms; ** DS - degree of substitution

Table 3 shows that the amount of MCC-BiB increased as the reaction temperature increased. This was caused by thermodynamic and kinetic factors. In terms of thermodynamics, the fact that more MCC-BiB was produced at a higher temperature could be explained based on the value of the standard enthalpy change of the reaction ($\Delta_r H^o$), as follows:

$$\text{Cel-OH} + \text{Br-COC(CH}_3)_2\text{Br} \xrightarrow{[\text{ChCl}][\text{ZnCl}_2]_2} \text{Cel-O-COC(CH}_3)_2\text{Br} + \text{H-Br}, \quad \Delta_r H^o(\text{kJ/mol})$$

The $\Delta_r H^o$ value as calculated from the bond energy data (Lide *et al*. 2009) was 24 kJ/mol, which means that the reaction was an endothermic process. Generally, the higher the temperature, the faster the reaction occurs. Thus, both the thermodynamic and kinetic factors require higher temperatures to promote a faster reaction. However, this work was carried out only at 40 ^{o}C due to the low boiling point of THF. The different amounts of BiBBr did not significantly affect the amount of MCC-BiB produced. The results presented in Table 2 also indicate that more of the macro-initiator was produced when there was less cellulose in the reaction medium. This was due to the better homogeneity and lower viscosity of the reaction medium when less cellulose was used.

CONCLUSIONS

1. A new and relatively cheap approach to the formation of an MCC-BiB macro-initiator was successfully carried out in mixtures of zinc-based ionic liquid and THF.
2. The FTIR and ^{1}H and ^{13}C NMR spectra confirmed the presence of bromoisobutyryl on the cellulose chains.
3. The amount of the MCC-BiB micro-initiator was quantified using TGA. It was found that more macro-initiator was formed at a higher temperature.

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