REGIOSELECTIVITY IN THE ACYLATION OF CELLULOSE WITH 2-BROMOISOBUTYRYL BROMIDE UNDER HOMOGENEOUS CONDITIONS

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A cellulose-based macroinitiator, cellulose-BiB, was prepared homogeneously by acylation of the hydroxyl groups of cotton cellulose with 2-bromoisobutyryl bromide (BrBiB) in N,N-dimethyl acetamide/lithium chloride (DMAc/LiCl) system. The effects of the molar ratio of BrBiB/anhydroglucose unit (AGU), reaction temperature, and reaction time on the degree of substitution (DS) were investigated in detail. The investigation was focused on the reactivity of the three hydroxyl groups at different position during the partial homogeneous acylation process. The results revealed that the DS of the cellulose-BiB increased with the increase of the molar ratio of BrBiB/AGU and the reaction time. At equivalent accessibility, the homogeneous acylation favored substitution at the C6 position, showing a regioselectivity of C6-OH>>C3-OH>C2-OH for the cotton dissolving pulp. Moreover, the 2-bromoisobutyryl bromide groups could be regioselectively introduced into the AGU of cellulose by controlling the reaction time.

Keywords: cellulose-based macroinitiator, DMAc/LiCl, homogeneous acylation, 2-bromoisobutyryl bromide, regioselectivity

INTRODUCTION

Cellulose is the most abundant natural resource in the world and possesses biocompatibility, biodegradability, renewability, and the ability to be modified easily.[1] It has been considered an ideal material that can replace traditional non-renewable resources, such as coal, fossil oil, and natural gas. However, cellulose also has certain drawbacks,[2] which prevent its wider scale application in various fields. Chemical modification of cellulose by etherification, esterification, or graft polymerization allows avoiding its intrinsic shortcomings and endows it with more flexible properties, opening the way to many advanced applications.[3] Nowadays, cellulose-based materials have been widely used in food, bioengineering, coating, papermaking, and other industry areas.[4-6] Modifications by graft polymerization provide a means of altering the physical and chemical properties of cellulose and increasing its functionality.[7] Specific molecules are usually grafted onto the cellulose backbone to impart specific properties onto the cellulose substrate, without destroying its intrinsic properties.[8] The free radical graft copolymerization consisting of initiation, propagation and termination is the main method to prepare cellulose graft copolymers. However, the traditional free radical graft copolymerization has a defect of poor control on the synthetic products, such as molecular weight and the polydispersity of the grafted chain.[1] With the development of polymer synthesis chemistry, controlled/"living" radical polymerization

methods have been put forward, which are able to minimize chain transfer and to control the molecular weight and polydispersity.[9] Atom transfer radical polymerization (ATRP) is one of the most convenient controlled/"living" radical polymerization methods to prepare well-defined polymers.[10] A lot of investigations have been carried out on using ATRP polymerization methods to prepare cellulose graft copolymers with chemically different grafts, as well as tunable lengths and densities of grafts.[4,5,10,11] However, in order to prepare cellulose graft copolymers by ATRP, the cellulose or cellulose derivatives must be modified into macroinitiators through attachment of alkyl bromide (or chloride) groups along the cellulose chains.[5,11]

The physicochemical properties of cellulose-based graft copolymers, such as viscosity, solubility, flocculation behavior, thermal property and so on, strongly depend on the grafting density of the copolymers, the molecular parameters of grafts,[12] and also the distribution of the grafts along the cellulose chain.[13] Therefore, the synthesis of cellulose-based macroinitiators with a predetermined number of initiation sites and different regioselectivity is very important for preparing cellulose graft copolymers with well-defined structure by ATRP. Theoretically, comb-shaped graft copolymers can be achieved by using the cellulose-based macroinitiator regioselectively substituted at C6-OH as the ATRP initiator sites. If the cellulose-based macroinitiator is regioselectively substituted at both C6-OH and C3-OH or at both C6-OH and C2-OH, asymmetric centipede-like copolymers can be obtained. Ifuku and Kadla[10] prepared a highly regioselective cellulose macroinitiator (6-*O*-bromoisobutyryl-2,3-di-*O*-methyl cellulose) for the first time, and then the regioselective copolymerization of *N*-isopropylacrylamide (NIPAM) onto cellulose was successfully achieved by ATRP using the regioselective C6 cellulosic macroinitiator. Moreover, the synthesis of particular regioselectively substituted cellulose-based macroinitiator is of critical importance for the synthesis of cellulose-based graft copolymers with superior properties for various applications.

Initiation groups in the cellulose-based macroinitiators are typically attached through acylation of cellulose hydroxyl groups by suitable organic acid derivatives.[12] Due to the lower steric hindrance of the primary OH at C6 and the greater acidity of the OH group at C2,[14] the hydroxyl groups of anhydroglucose unit (AGU) at C2, C3, and C6 position exhibit different reaction activities. The reaction medium also has an important effect on the distribution of the substituent. In solid-phase acetylation, no regio-selective reactivity was observed by Yamamoto *et al*.[15] among the three kinds of OH groups. The heterogeneous synthesis of cellulose acetate in methanol had a partial DS order of C3>C2>C6.[16] Under homogeneous conditions, the modification of cellulose is much more uniform and the degree of substitution and the substitution pattern can be better controlled. A kind of well-soluble bacterial cellulose derivatives prepared under homogeneous and mild reaction conditions showed a distribution of the acetyl moieties in the order O-6 > O-3 > O-2.[17] Homogeneous acetylation of cellulose with acetic anhydride at relatively high concentration in ionic liquid showed a reactivity order of C6-OH>C3-OH>C2-OH.[18] However, a different partial substitution of C6-OH>C2-OH>C3-OH occurred in the homogeneous acylation of cellulose with benzoyl chloride in ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl).[19] Xu *et al*. investigated the homogeneous acylations of cellulose with bulky acid chlorides, such as pivaloyl chloride and adamantoyl chloride in DMAc/LiCl and demonstrated a reactivity order of C6-OH>C2-OH>C3-OH.[14] Therefore, it is vital to choose appropriate reaction conditions to synthetize cellulose-based macroinitiators of certain distribution of substituent. The 2-bromoisobutyryl bromide (BrBiB) is the most important acylation reagent applied to prepare cellulose-based macroinitiators for ATRP.[1,4,5,20,21] However, although much research has been devoted to the acylation of cellulose with BrBiB,[5,6,11] little efforts have been made towards the regioselectivity of the acylation reaction. In the present paper, the hydroxyl groups of the cellulose were treated with BrBiB in DMAc/LiCl to synthesize the cellulose-based macroinitiators, cellulose-BiB. Also, an attempt was made to clarify the reactivity difference of the three hydroxyl groups, C2-OH, C3-OH, and C6-OH during homogeneous acylation of cellulose.

EXPERIMENTAL

Materials

The cellulose material used for the synthesis of the cellulose-based macroinitiator was cotton dissolving pulp with a degree of polymerization (DP) of 500. It was obtained from Shandong Silver Hawk Chemical Fibre Co., Ltd. and was dried in a vacuum drying oven for 24 h before use. Lithium chloride (LiCl) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. 2-bromoisobutyloyl bromide (BrBiB) acquired from Shanghai Bangcheng Chemical Co., Ltd. was used without further purification. *N,N*-dimethyl acetamide (DMAc), *N,N*-dimethyl formamide (DMF), and triethylamine (TEA) were all of analytical grade. Nitrogen was obtained from Jinan Deyang Special Gas Co., Ltd.

Methods

Dissolution of cellulose in DMAc/LiCl

An amount of 0.68 g cellulose was weighed and put into a 250 ml three-necked round-bottom flask, and then 100 ml of DMAc was added to it. The mixture was heated at 160 ℃ for 0.5 h under magnetic stirring. Then, the mixture was filtrated and the residue was dried in a vacuum drying oven at 60 ℃ overnight to obtain activated cellulose. An amount of 20 g DMAc was added into a 250 ml three-necked round-bottom flask, and then 2 g LiCl was dissolved completely in the DMAc to obtain the DMAc/LiCl solution. The activated cellulose was added into the DMAc/LiCl solution and was heated at 100 ℃ for 4 h. The cellulose/DMAc/LiCl solution was allowed to stay at room temperature for 24 h to obtain a clear, slightly viscous solution.

Acylation of cellulose with BrBiB in DMAc/LiCl

The cellulose solution obtained above was cooled down to 0 ℃ using an ice-water bath. A defined amount of BrBiB was slowly dropped into the solution via a constant pressure drop funnel under a nitrogen atmosphere. Then the triethylamine with the same mole as BrBiB was added into the mixture. After the flask was sealed, the reaction mixture was heated to a predetermined temperature in an oil bath and allowed to proceed for scheduled time under magnetic stirring. Then the resulting mixture was slowly poured into deionized water with vigorous stirring. The precipitated acylation product, namely cellulose-BiB, was redissolved in DMF. After re-precipitating in deionized water and re-dissolving in DMF for three times, the cellulose-BiB was dialyzed for three days in deionized water and was dried in a vacuum freeze-drying oven for 48 h.

X-ray diffraction analysis

The X-ray diffraction profiles of native cellulose, regenerated cellulose, and cellulose-BiB were recorded using an X-ray diffractometer (D8-Advance, Germany Bruker AXS Corporation).[22] Ni-filtered Cu Kα radiation (λ = 0.1542 nm) generated at a voltage of 40 kV and a current of 40 mA was utilised, as well as a scan speed of 1-2°/min from 5° to 50°.

FT IR analysis

FT IR spectra of native cellulose, regenerated cellulose, and cellulose-BiB were recorded using an IR Prestige-21 FT IR spectrophotometer. The samples were pressed into pellets with KBr before measuring. The spectra were collected at a resolution of 2 cm^{-1}, in the range of 500 and 4,000 cm^{-1}.

^{1}H NMR and ^{13}C NMR analyses

^{1}H NMR spectra of the cellulose-BiB were recorded on an AVANCE Ⅱ 400 spectrometer at room temperature in DMSO-*d6*. The substitution degree (DS) value of the cellulose-BiB [1] was calculated from the integration ratios of proton resonances of the methyl of the BrBiB to those of the backbone hydrogens (Eq. (1)) according to the method of Goodlett *et al*.:[23]

$$DS = \frac{7 \times S_1}{6 \times S_2} \quad (1)$$

where S_1 is the integral of the resonances in the range of 1.6-2.0 ppm of the protons of the methyl of the BrBiB, S_2 is the integral of the resonances in the range of 3.0-5.8 ppm of the protons of the cellulose backbone. The water peak at 3.3 ppm was subtracted manually by integration of the respective peak.[24]

The ^{13}C NMR spectrum of the cellulose-BiB was recorded on the AVANCE Ⅱ 400 spectrometer with a minimum of 5000 scans, a sample concentration of 40 $g \cdot L^{-1}$, a sweep width of 80 KHz, and a delay time of 3 s in DMSO-*d6*. The distribution of 2-bromoisobutyryl moiety among the three hydroxyl groups of the AGU was determined according to the method of Kamide and Okajima.[25] The DS_{C6}, DS_{C3}, and DS_{C2} of the cellulose-BiB were calculated using the following formulas:

$$DS_{C6} = \frac{DS_{Total} \times S_{C6}}{S} \qquad DS_{C3} = \frac{DS_{Total} \times S_{C3}}{S}$$

$$DS_{C2} = \frac{DS_{Total} \times S_{C2}}{S} \qquad S = S_{C6} + S_{C3} + S_{C2} \quad (2)$$

where DS_{C6}, DS_{C3}, and DS_{C2} are the DS of corresponding carbon atoms, DS_{Total} is the DS of the cellulose-BiB calculated via ^{1}H NMR spectroscopy, and S_{C6}, S_{C3}, and S_{C3} are the integral of the resonances of the peak at 170.23 ppm, 169.49 ppm, and 169.13 ppm, respectively.

Thermogravimetric analysis

A thermogravimetric analyzer (TGA Q50, TA Instruments, USA) was employed for the

thermogravimetric analysis of native cellulose, regenerated cellulose, and cellulose-BiB. The samples were heated from room temperature to 600 ºC at a heating rate of 10 ºC/min under a nitrogen atmosphere. The TA universal analysis software was used for dealing with the TG curves. The samples were all dried at room temperature for 24 h in a vacuum drying oven prior to TGA measurements.

RESULTS AND DISCUSSION

The cellulose-based macroinitiator, cellulose-BiB, can be synthesized by the reaction of the hydroxyl groups of cellulose with BrBiB.[1] The reaction scheme is shown in Figure 1. Due to the extensive intra- and inter- molecular hydrogen bonding, crystallinity, and resulting poor solubility of the dissolving pulp,[26] it is necessary to use a powerful solvent system to achieve a high level of substitution and create the possibility of a far more selective reaction of cellulose.[27] DMAc/LiCl, DMSO/TBAF, and ionic liquid are three important classes of cellulose reaction solvents for homogeneous modification.[28] The mixed solvent DMAc with LiCl has been used as an efficient cellulose solvent for over a quarter century to dissolve, derivatize and analyze the cellulose.[29] In this work, we chose the DMAc/LiCl system, which is a true solvent for cellulose to ensure that the cellulosic hydroxyl groups are readily accessible. It is necessary to mention that the aggressive hydrochloric acid as a by-product of the acylation reaction will be generated when the hydroxyl groups of AGU react with BrBiB. To promote the acylation reaction and limit the cellulose acidic degradation, the acid-binding agent triethylamine was added to neutralize HCl as it is formed.

Dissolution of cellulose in DMAc/LiCl

In order to dissolve the cotton dissolving pulp into the DMAc/LiCl system completely, a pretreatment (activation) procedure is needed. The activation treatments can be performed in various ways, such as swelling and solvent exchange, enhancing the accessibility and the solubility of the pulp. Here, three activation procedures are chosen and their effects on the dissolution of the pulp are shown in Table 1. As can be seen, without activation treatment, the cotton dissolving pulp cannot dissolve in the DMAc/LiCl.

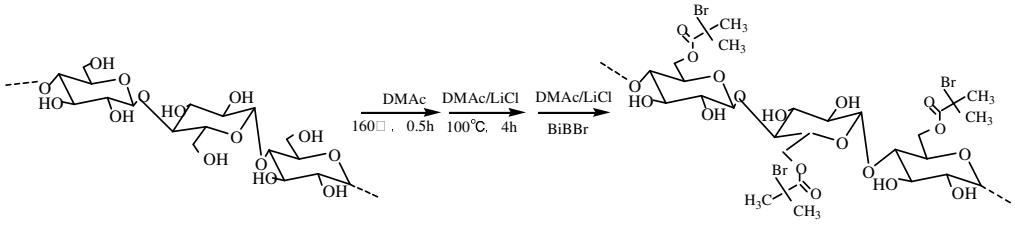

Figure 1: Reaction scheme for the synthesis of cellulose-BiB in DMAc/LiCl

Table 1
Effects of activation treatments on the dissolution of cotton dissolving pulp in DMAc/LiCl

Treatment method	Crystallization index (%)	Dissolution concentration (%)	Transmittance of solution (%)	Colour of solution
Untreated	86.1	3	insoluble	-
75% EDA, 40 ºC, 4 h	69.7	3	91.6	light yellow
DMAc, 160 ºC, 0.5 h	84.5	3	89.1	colourless
DMAc+0.2%$KMnO_4$, 160 ºC, 0.5 h	83.7	3	89.8	yellowish-brown

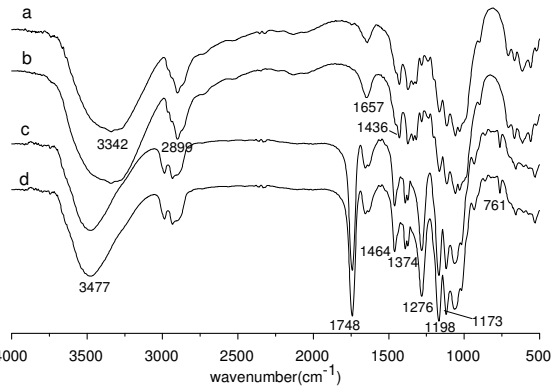

Figure 2: FT-IR spectra of native cellulose (a), regenerated cellulose obtained after dissolution in DMAc/LiCl (b), cellulose-BiB with DS of 0.795 (c), and cellulose-BiB with DS of 1.012 (d)

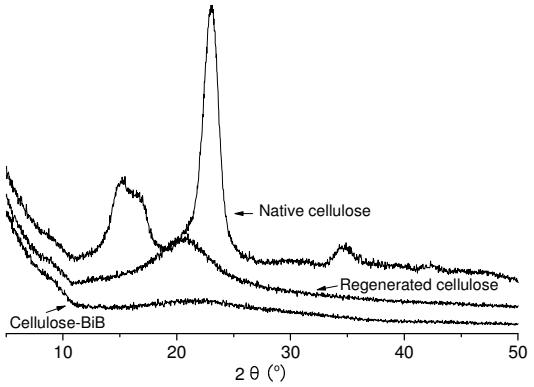

Figure 3: XRD spectra of native cellulose, regenerated cellulose, and cellulose-BiB (DS = 1.012)

A pretreatment with 75% ethylene diamine (EDA) at 40 ºC for 4 h or with DMAc at 160 ºC for 0.5 h could facilitate subsequent dissolution of the pulp. The swelling agents can generally penetrate into the highly ordered regions and split the bonds between chains and fibrils of cellulose, improving the solubility of the pulp. The changes of the crystallinity index after pretreatment indicated lower destructivity of the DMAc activation method than that of the EDA activation. Moreover, the cellulose solution activated by EDA is light yellow and the activation procedure is not convenient. If 0.2% $KMnO_4$ was added during the DMAc activation treatment, the cellulose solution became yellowish-brown and the dissolution efficiency did not improve, meaning that an oxidation reaction of cellulose happened during the pretreatment process. It can be concluded that pretreating cellulose in the solution of DMAc, which is convenient and easy to operate, is the optimum activation method for the cotton dissolving pulp.

FT IR is used to determine the changes of the structure of the cellulose regenerated after dissolution in DMAc/LiCl solution. Figure 2 illustrates the FT IR spectra of native cellulose (a) and regenerated cellulose (b). The absorption peaks in the two spectra were quite similar, indicating a similar structure of native cellulose and regenerated cellulose. This means that the chemical structure of cellulose has not changed during the dissolving process, suggesting that DMAc/LiCl is a direct solvent of cellulose and no derivatization reaction occurred.

Figure 3 shows the X-ray diffraction curves of native cellulose, regenerated cellulose, and cellulose-BiB. The diffraction curve of native cellulose had strong characteristic peaks at around 15°, 17°, and 22.5° corresponding to the (110), (1$\bar{1}$0), and (002) planes of crystals, and a weak characteristic peak at about 34.7° corresponding to the (004) plane, which was coincident with the structure of cellulose I.[30] After dissolution in DMAc/LiCl and regeneration, the diffraction curve of regenerated cellulose only had a broad characteristic peak at around 19.8°,

being typical of the diffraction pattern of cellulose II.[31] The results revealed that the crystal form of cellulose I in native cellulose has been converted to cellulose II during the dissolution and regeneration process. As shown in Figure 3, the degree of crystallinity of regenerated cellulose almost fades away, meaning that most crystalline structure of cellulose has completely been destroyed during the dissolving process of cellulose in DMAc/LiCl. This means that DMAc/LiCl can provide the possibility to functionalize cellulose in a homogeneous solution, and that breaking intra- and inter-molecular hydrogen bonds can dramatically improve the accessibility of the acylation reagent with OH of AGU subsequently.

Effects of reaction conditions on DS of cellulose-BiB

Table 2 shows the results of cellulose acylation in the DMAc/LiCl solvent systems. As can be seen from the table, the DS values of the cellulose-BiB depended on the reaction conditions, including the molar equivalents of BrBiB per AGU, reaction temperature, and reaction time.

At a ratio of 3.0 equivalents BrBiB per AGU, a low DS of 0.521 was obtained with a reaction time of 24 h at 35 ºC. If the ratio increased to 4.0, 5.0, and 6.0 equivalents BrBiB per AGU respectively, the DSs of 0.677, 0.852 and 1.012 were achieved, respectively. This means that the DS of the cellulose-BiB increased with the molar ratio of BrBiB/AGU. The reason for the increase of the reaction efficiency with the molar ratio was that the collision probability of BrBiB with OH in AGU increased with increasing the amount of BrBiB, resulting in higher DS of the cellulose-BiB. However, when the molar ratio of BrBiB/AGU reached 8.0:1, the DS of the resulting cellulose-BiB was only 0.838, much lower than that of 6.0:1. The presence of the excess BrBiB increased the collision probability of the moleculars of BrBiB and BrBiB, reducing the availability of BrBiB with OH of AGU. Therefore, in order to prepare the cellulose-based macroinitiator with a high DS value, the appropriate molar ratio of BrBiB/AGU is quite important.

The influence of the reaction temperature on the DS value of the cellulose-BiB, applying a molar ratio of 6.0:1 (BrBiB/AGU) and a reaction time of 24 h, is shown in Table 2. The DS values of 0.846, 1.012 and 0.804 were obtained when the reaction temperature was 25 ºC, 35 ºC, and 45 ºC, respectively. It means that improving the reaction temperature properly could quicken the molecular motion of reactants and accelerate the acylation reaction rate, and consequently increase the DS value of the cellulose-BiB. However, when the reaction temperature elevated to 45 ºC, the DS of the cellulose-BiB decreased.

Table 2
Conditions and results of the homogeneous reaction of cellulose with BrBiB in DMAc/LiCl

Sample	Temperature (ºC)	Time (h)	Molar ratio[a]	DS[b]
S_1	35	24	3.0: 1	0.521
S_2	35	24	4.0: 1	0.677
S_3	35	24	5.0: 1	0.852
S_4	35	24	6.0: 1	1.012
S_5	35	24	8.0: 1	0.838
S_6	25	24	6.0: 1	0.846
S_7	45	24	6.0: 1	0.804
S_8	35	0.5	6.0: 1	0.391
S_9	35	1	6.0: 1	0.479
S_{10}	35	2	6.0: 1	0.688
S_{11}	35	4	6.0: 1	0.768
S_{12}	35	6	6.0: 1	0.795
S_{13}	35	8	6.0: 1	0.806
S_{14}	35	12	6.0: 1	0.925
S_{15}	35	36	6.0: 1	0.931
S_{16}	35	48	6.0: 1	0.870

[a] Mol BrBiB per mol AGU
[b] Degree of substitution determined by ^{1}H NMR spectroscopy

The acylation reaction was an exothermic reaction and was more rapid at relatively low temperature. On the other hand, some side effects might occur at higher temperature, leading to a lower DS value. A relatively appropriate reaction temperature is preferred to obtain cellulose-BiB with a high DS value. The DS of the cellulose-based macroinitiator *versus* reaction time is also illustrated in Table 2. When the reaction was conducted at 35 ºC with a molar ratio of 6.0:1 (BrBiB/AGU), the DS of the cellulose-BiB increased with the reaction time, indicating that the extent of acylation increased appreciably with the reaction time. This increment could be due to the increase rate and time of collision of BrBiB with cellulosic molecules.[32] However, the DS value of 1.012 of cellulose-BiB was obtained at 24 h, of 0.931 at 36 h, and 0.870 at 48 h, showing a declining trend. This may be due to the fact that an increasing amount of HCl would be generated and the concentration of acid-binding agent would become insufficient with an extended reaction time, probably leading to the hydrolysis of a fraction of ester groups[29] and decreasing the DS of the resulted cellulose-BiB.

Characterization of cellulose-BiB

Figure 2 gives the FT IR spectra of the cellulose acetylation products, the cellulose-BiBs, with different DS (c and d). Compared with the spectrum of the regenerated cellulose (b), the intensity of peaks at 3,477 cm^{-1} (OH stretching) and 1,374 cm^{-1} (OH bending) of the spectra of the cellulose-BiBs (c and d) decreased obviously, and that the spectra of cellulose-BiBs (c and d) had strong absorption bands at 1,748 cm^{-1} corresponded to the stretching vibration of C=O in BiB,[1,6] indicating that the BiB has been grafted onto the cellulose backbone successfully after the acylation modification. The absorption bands at 1,198 cm^{-1} and 1,173 cm^{-1} proved that the carbonyl groups in the cellulose-BiBs existed by the form of ester groups. The band at 1276 cm^{-1} is assigned to the skeletal C-C stretching vibrations in the $C(CH_3)_2Br$ groups.[12] The introduction of the stretching vibration absorption peak of $-CH_3$ near 1,464 cm^{-1}, which is the characteristic absorption peak of BiB, and the stretching vibration absorption peak of C-Br at 761 cm^{-1} in the spectra of cellulose-BiB further demonstrated the successful formation of the cellulose-BiB.[12]

The structure of the cellulose-BiBs is further confirmed by their ^1H NMR spectra, a representative one being shown in Figure 4. The chemical shift in the range of 3.0-5.8 ppm (sign of b) is attributed to the protons of the AGU. The chemical shift around 1.6-1.9 ppm (sign of a) is ascribed to the methyl protons of bromoisobutyryl group.[1,6] This further demonstrated that the acylation reagent BrBiB has been grafted onto the cellulose backbone successfully. Figure 5 (A) shows the full-range ^{13}C NMR spectrum of the cellulose-BiB. The shift δ 169-170.5 ppm (e) is assigned to the signal of the carbonyl carbon region. The peak at 102.5 ppm (b1) is assigned to C1 adjacent to C2 bearing an unsubstituted hydroxyl group, and the peak around 98.9 ppm (b1'), which belongs to C1 adjacent to C2 bearing a substituted hydroxyl group, is very weak. The peak at 78 ppm (b4) is attributed to C4 adjacent to C3 bearing an unsubstituted hydroxyl group, and the peak around 76 ppm (b4') is attributed to C4 adjacent to C3 bearing a substituted hydroxyl group. The resonance peaks of C2, C3 and C5 heavily overlap as they give only a strong cluster around 72-76 ppm.[18] The chemical shift at 64.5 ppm (b6') is assigned to C6 carbons bearing a substituted acetyl group. The peak around 60 ppm assigned to the unmodified C6[33] is not observed, indicating an almost complete substitution of the hydroxyl group at the C6 position. δ 65.9 ppm (c) and δ 30 ppm (a) are the typical chemical shifts of quaternary carbon atoms and carbon atoms of methyl in the BiB,[1,12] respectively. There are not only the resonance peaks of carbon atoms in the cellulose, but also the resonance peaks of carbon atoms in BiB in the ^{13}C NMR spectrum, also demonstrating the successful substitution of OH groups on the cellulose backbone by BrBiB.

The cellulose-based macroinitiator, cellulose-BiB, was soluble in a range of organic solvents, such as dimethylsulfoxide (DMSO), DMF, *N*-methyl-2-pyrrolidone (NMP), and tetrahydrofuran (THF), displaying good solubility. The degree of crystallinity of cellulose-BiB completely disappeared after the acylation reaction of cellulose with BrBiB shown in Figure 3, further indicating that the supramolecular structure of cellulose is completely destroyed. Therefore, the cellulose-BiB can be used to produce cellulose-based graft copolymers with well-defined structure in homogeneous systems

by ATRP.

Regioselectivity of homogeneous acylation

The regioselective synthesis of cellulose-based macroinitiator is crucial to prepare cellulose-based graft copolymers by ATRP. The reactivity differences between the C6-, C3-, and C2-OH groups during acylation of cellulose with BrBiB in DMAc/LiCl were evaluated by the carbonyl carbon region of ^{13}C NMR. The expanded carbonyl region spectra of cellulose-BiB are shown in Figure 5 (B) and (C). The absorption peaks at 170.23 ppm, 169.49 ppm, and 169.13 ppm are attributed to the carbonyl carbon linked to C6, C3, and C2, respectively. The partial DS values of the bromoisobutyryl moiety among the three OH groups are calculated from the integration of carbonyl carbon area of the ^{13}C NMR spectrum, and the results are presented in Table 3.

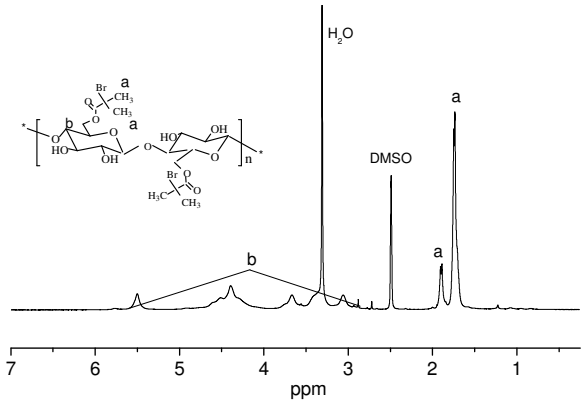

Figure 4: ^{1}H NMR spectrum of cellulose-BiB (DS = 0.795) in DMSO-*d6*

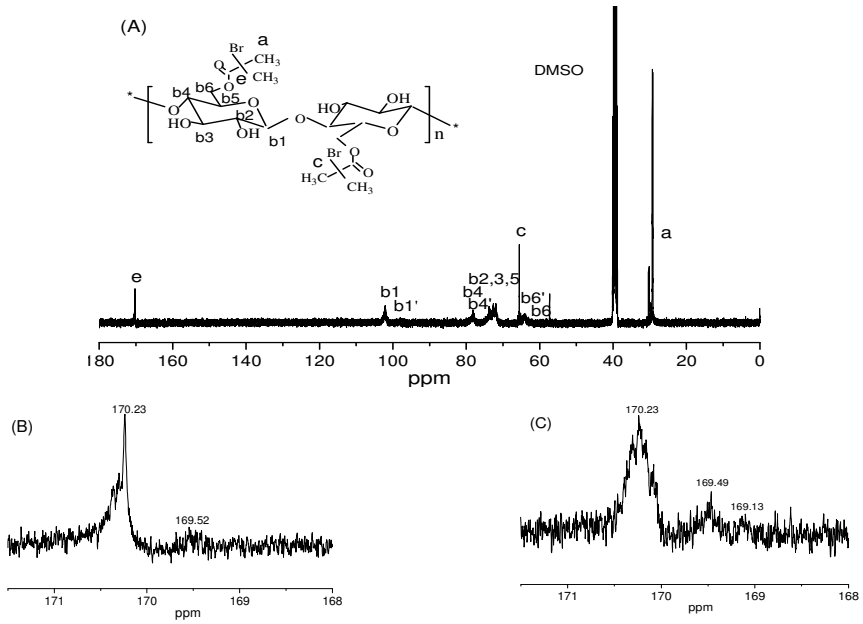

Figure 5: ^{13}C NMR spectrum of cellulose-BiB with DS of 0.795 (A), the carbonyl carbon region of cellulose-BiB ((B), DS = 0.688 and (C), DS = 1.012)

After the reaction of cellulose with BrBiB for 0.5 h under the molar ratio of 6.0:1 of BrBiB/AGU and the reaction temperature of 35 ºC, the partial DS at C6 of the resulted

cellulose-BiB (sample S_8, DS_{Total} = 0.391) was equal to the DS_{Total}, revealing that the BrBiB was selectively introduced into the C6-OH of the AGU. When the reaction time extended to 1 h, the partial DS at C6 of the resulted cellulose-BiB, sample S_9 with the DS_{Total} equal to 0.479 was 0.452, while the DS at C3 was 0.027, meaning that the C3-OH began to be substituted. For the sample S_{11} with the DS_{Total} of 0.768 obtained at 4 h, the partial DS at C6, C3, and C2 was 0.640, 0.096, and 0.032, respectively, revealing that the C2-OH was also substituted. This trend indicated that at the beginning of the acylation, the reaction occurred almost exclusively at the C6-OH. Only when the majority of primary hydroxyl groups have been substituted, the C3-OH and C2-OH began to be substituted by BrBiB. The absence of the peaks around 60 ppm, assigned to the unmodified primary hydroxyl carbons in cellulose[33] in the ^{13}C NMR spectroscopy (Fig. 5 (A)) also indicated that the C6-OH was almost completely substituted.

The substitution distribution of bromoisobutyryl groups along the cellulose backbone of the other sample in Table 3 satisfied the same order of $P_{C6}>>P_{C3}>P_{C2}$. Most of the substituents were found at the C6 position, whereas a small proportion of the secondary hydroxyls at C3 and C2 were also acylated. It may be concluded that the acylation reaction occurs preferably at the primary than at the secondary alcohols, and the reaction activity of the C2 hydroxyl groups is somewhat lower than that of the C3 hydroxyl groups. The result was similar to that observed by Regiani *et al*.[34] BrBiB is a voluminous reagent molecule. The higher steric hindrance of the bulky 2-bromoisobutyryl substituents makes it easier for them to substitute the primary OH at C6 with lower steric hindrance, but more difficult to reach the secondary OH groups with more steric hindrance. Moreover, the great majority of the initiator groups situated at position C6 of the cellulose-based macroinitiator will promote the synthesis of cellulose graft copolymer fairly regioselectively by ATRP.

Table 3
Distribution of acyl groups among C6, C3, and C2 of cellulose-BiB

Sample	DS_{Total} [a]	DS_{C6} [b]	P_{C6} (%) [c]	DS_{C3} [b]	P_{C3} (%) [c]	DS_{C2} [b]	P_{C2} (%) [c]
S_8 (0.5 h)	0.391	0.391	100	0	0	0	0
S_9 (1 h)	0.479	0.452	94.36	0.027	5.64	0	0
S_{10} (2 h)	0.688	0.625	90.84	0.063	9.16	0	0
S_{11} (4 h)	0.768	0.640	83.33	0.096	12.50	0.032	4.17
S_{12} (6 h)	0.795	0.641	80.62	0.096	12.08	0.058	7.30
S_{13} (8 h)	0.806	0.643	79.78	0.102	12.65	0.061	7.57
S_{14} (12 h)	0.925	0.701	75.78	0.140	15.14	0.084	9.08
S_4 (24 h)	1.012	0.728	71.94	0.182	17.98	0.102	10.08
S_{15} (36 h)	0.931	0.716	76.91	0.152	16.32	0.063	6.77
S_2 (4.0:1)	0.677	0.597	88.19	0.059	8.71	0.021	3.10

[a] DS_{Total} refers to the DS of cellulose-BiB determined by ^1H NMR spectroscopy
[b] DS_{C6}, DS_{C3} and DS_{C2} refer to the DS of the corresponding carbon atom
[c] P_{C6}, P_{C3}, P_{C2} refer to the percentage of DS of the corresponding carbon atom

Table 4
Thermostability of native cellulose, regenerated cellulose and cellulose-BiB

Sample	*T*di (ºC)	*T*dm (ºC)	*T*df (ºC)	Residual mass (wt%)
Native cellulose	276	359	391	8.56
Regenerated cellulose	183	251	299	31.14
Cellulose-BiB	253	307	357	12.34

T_{di}, the initial decomposition temperature, is the temperature at which the decomposition rate results in a significant weight loss; T_{dm}, the maximum decomposition temperature, is the temperature at which the highest decomposition

rate is observed for the corresponding pattern; T_{df}, the final decomposition temperatures, corresponds to maximal decomposition of the sample

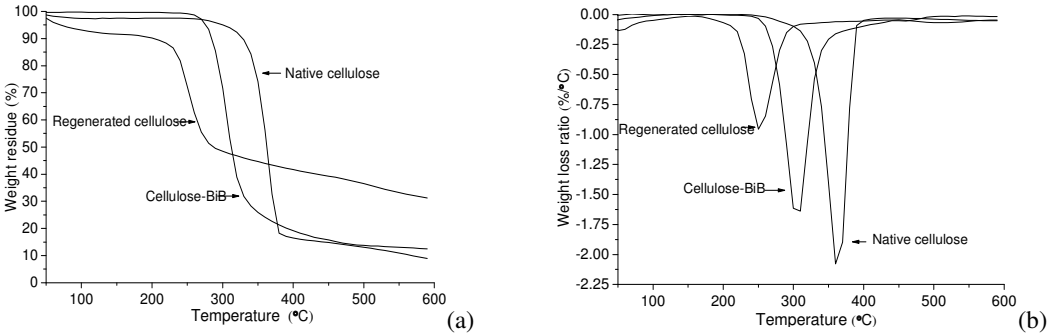

Figure 6: Thermogravimetry curves (a) and derivative thermogravimetry curves (b) of native cellulose, regenerated cellulose, and cellulose-BiB

Thermal analysis of the cellulose-BiB

Figure 6 shows the thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of the native cellulose, regenerated cellulose, and cellulose-BiB and their data of thermostability are summarized in Table 4. The native cellulose starts to decompose at 276 ºC, whereas the regenerated cellulose begins to decompose at 183 ºC. The decomposition temperature with the largest weight loss rate is 391 ºC for the native cellulose and 299 ºC for the regenerated cellulose. The initial decomposition temperature (*T*di), maximum decomposition temperatures (*T*dm), and final decomposition temperatures (*T*df) of the regenerated cellulose all significantly decreased compared with the native cellulose, implying that the thermal stability of cellulose markedly declined after been activated and dissolved. The reason of the decrement was probably due to partial hydrolysis and degradation of the cellulose macromolecule during dissolution, especially during activation of cellulose at high temperature. On the other hand, the breaking of intra- and inter-molecular hydrogen bonds in the cellulose chain during the activating and dissolving process gave the chains more mobility under the thermal condition.[18] The *T*di, *T*dm, and *T*df of the cellulose-BiB are also lower than that of the native cellulose, but much higher than that of the regenerated cellulose. These trends of the decomposition temperature indicated that the thermal stability of the regenerated cellulose increased due to the introduction of the bromoisobutyryl group. However, the thermal stability of cellulose-BiB was still lower than that of the native cellulose. This is attributed to the introduced bromoisobutyryl groups breaking the hydrogen bonds in the cellulose chain, which gave the chains more mobility under the thermal condition.[18]

The residual mass above 600 ºC was 8.56% for the native cellulose, 31.14% for the regenerated cellulose, and 12.34% for the cellulose-BiB. The pyrolysis residues are primarily indecomposable inorganic salts.[30] The highest pyrolysis residues of the regenerated cellulose indicated that more inorganic salts were involved into cellulose after dissolution in DMAc/LiCl. It should be noted that the pyrolysis residue of the cellulose-BiB was also higher than that of the native cellulose. The involvement of inorganic salts in the regenerated cellulose, which partly remained in the cellulose after acylation, was the main reason.

CONCLUSION

The DMAc/LiCl is an appropriate medium for homogeneous acylation of cellulose with BrBiB in the presence of TEA. The DS of the acylated product, cellulose-BiB, increased with the increase of the molar ratio of BrBiB/AGU and the reaction time. Moreover, in order to prepare cellulose-BiB with different substitution patterns, the reaction time should be controlled. Under the reaction conditions of 6.0:1 molar ratio of BrBiB/AGU, 35 ºC of reaction temperature, and 24 h of reaction time, the cellulose-BiB with a high DS of 1.012 was achieved. The acylation was in most cases selective for the primary hydroxyl groups and the distribution of the acyl

groups among the three hydroxyl groups followed the order of C6-OH>>C3-OH>C2-OH. Moreover, the acylation at the secondary alcohols, C2-OH and C3-OH, was still observed indicating that the regioselectivity is not complete. The acylation of cellulose with BrBiB decreased the thermal stability of cellulose.

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