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Graft copolymers prepared by atom transfer radical polymerization (ATRP) from cellulose

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ABSTRACT

A cellulose-based macro-initiator, cellulose 2-bromoisobutyrylate, for atom transfer radical polymerization (ATRP) was successfully synthesized by direct homogeneous acylation of cellulose in a room temperature ionic liquid, 1-allyl-3-methylimidazolium chloride, without using any catalysts and protecting group chemistry. ATRP of methyl methacrylate and styrene from the macro-initiator was then carried out. The synthesized cellulose graft copolymers were characterized by FTIR, ^{1}H NMR and ^{13}C NMR spectroscopies. The grafted PMMA and PS chains were obtained by the hydrolysis of the cellulose backbone and analyzed by GPC. The results obtained from these analytical techniques confirm that the graft polymerization occurred from the cellulose backbone and the obtained copolymers had grafted polymer chains with well-controlled molecular weight and polydispersity. Through static and dynamic laser light scattering and TEM measurements, it was found that the cellulose graft copolymer in solution could aggregate and self-assembly into sphere-like polymeric structure.

1. Introduction

The most abundant biomacromolecule, cellulose has attracted considerable attention in recent years due to its biodegradable, biocompatible and renewable characters [1]. Graft modification of cellulose and its derivatives has been widely studied to give new materials for drug delivery, sorption agents, coatings, and membranes [2]. Many techniques for graft copolymerization of various monomers on the cellulose backbone have been developed, such as free radical polymerization [3–14], ring-opening polymerization [15,16], nitroxide-mediated polymerization (NMP) [17], reversible addition–fragmentation chain transfer (RAFT) polymerization [18,19] and atom transfer radical polymerization (ATRP) [20–33]. Among the above techniques, ATRP was extensively studied for graft copolymerization of vinyl monomers onto cellulose and cellulose derivatives in a living/controllable way. In previous studies, synthesis of cellulose-based graft copolymers by ATRP has been carried out in either heterogeneous or homogenous reaction medium. The heterogeneous ATRP was mainly used for surface modification of solid cellulose materials, such as paper or film [20–23], fiber [21,24,25], and particles [21,26]. In the homogenous case, the graft polymerization via ATRP was performed limitedly on cellulose derivatives [27–34], such as cellulose acetates (CA) [27–29], ethyl cellulose (EC) [30–33], and hydroxypropyl cellulose (HPC) [34]. So far there have been no reports about the homogeneous graft polymerization on underivatized cellulose backbone through ATRP without any protecting group chemistry. Directly grafting polymers on the underivatized cellulose backbone in a homogenous reaction medium is expected to create a new kind of materials combining the advantage of natural polymer and synthetic polymer properties simultaneously. To this end, synthesis of macro-initiator based on cellulose for ATRP in homogenous reaction media is prerequisite, but this has been restricted by the lack of effective solvents for underivatized cellulose. Recently, Bontempo et al. [35] have reported a versatile ATRP method for polysaccharide grafting in homogeneous conditions without using protecting group chemistry, in which *N*,*N*-dimethylformamide (DMF) was used as reaction medium for the synthesis of polysaccharide-based macro-initiators and water/DMF mixtures with different compositions were used as the polymerization medium for ATRP. However, this method cannot be directly used for underivatized cellulose as it is insoluble in this solvent system and other common solvents.

In our previous works [36,37], a room temperature ionic liquid, 1-allyl-3-methylimidazolium chloride (AMIMCl) was found to be

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a powerful nonderivatizing solvent for cellulose and considered as a desirable medium for the cellulose acylation.

In present work, a macro-initiator, cellulose 2-bromoisobutyrylate, was synthesized through homogeneous acylation of underivatized cellulose with 2-bromoisobutyryl bromide in ionic liquid AMIMCl. Then, the cellulose-based macro-initiators were used for graft copolymerization of methyl methacrylate (MMA) and styrene. The preliminary studies on the morphology of the graft copolymer in solution were also presented.

2. Experimental

2.1. Materials

The cellulose (Microcrystalline cellulose, Vivapur 101) with a degree of polymerization (DP) of 200 was used. Ionic liquid AMIMCl was synthesized according to the method our group reported elsewhere [37]. Both cellulose and AMIMCl were dried before use. Methyl methacrylate (MMA) and styrene were purchased from Beijing Chemical Engineering Plant (Beijing, China) and were dried over anhydrous $MgSO_4$ and then distilled from CaH_2 under reduced pressure. To remove copper(II), CuCl (Shanghai Zhenxing Chemical Regent Factory) was stirred in glacial acetic acid, filtered, and washed with acetone for three times and then dried under vacuum at room temperature for 12 h. 2,2′-dipyridine (Shiying Chemical Regent Factory, Beijing) and 2-bromoisobutyryl bromide (BrB*i*B) (Aldrich, 98%) were used as-received. Other solvents, such as *N*,*N*′-dimethyl formamide (DMF), butanone, toluene and 1,4-dioxane, produced by Beijing Chemical Engineering Plant, were dried and then distilled under reduced pressure.

2.2. Synthesis of macro-initiator cellulose 2-bromoisobutyrylate (Cell-B*i*B)

The preparation of the cellulose-based macro-initiator Cell-B*i*B was carried out according to the procedure shown in Scheme 1. Cellulose (1.0 g, 6.2 mmol) was dissolved in AMIMCl (20.0 g AMIMCl, 10.0 ml DMF as dilute) under 80 °C to form a clear yellow solution, then the mixture was cooled to room temperature. To obtain Cell-B*i*B with a degree of substitution (DS) of 0.72, for example, a total of 7.1 g (31.0 mmol) of BrB*i*B was added dropwise into the ice-cold cellulose/AMIMCl solution and stirred in a flask under nitrogen. Then the mixture was left to warm up to room temperature and stirred for 8 h. The resulting solution was poured into excessive deionized water and precipitated out the white floccules. The white floccules, that is Cell-B*i*B, was washed thoroughly with water, then filtered and dried under vacuum at 50 °C for 12 h before characterization. The DS of B*i*B was calculated from the ^{1}H NMR spectrum.

2.3. ATRP of MMA or/and styrene using Cell-B*i*B as the initiator

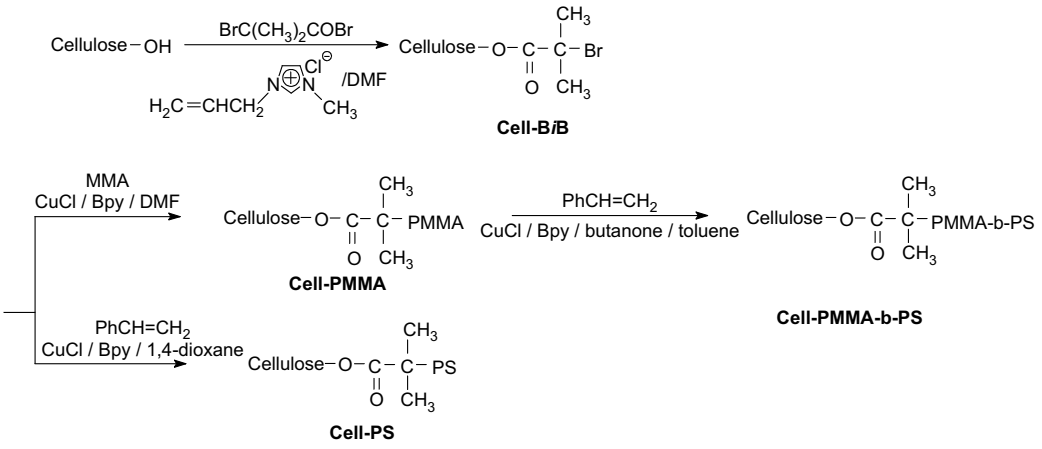
The macro-initiator Cell-B*i*B was used to initiate the polymerization of MMA or/and sytrene on the cellulose backbone by ATRP with CuCl/2,2′-bypyridine (Bpy) as a catalyst system. General procedure for the synthesis of PMMA grafted cellulose (Cell–PMMA) is as follows: Cell-B*i*B (135 mg, 0.36 mmol of Br) was added to a flask containing a reaction mixture of MMA (7.200 g, 72 mmol), Bpy (169 mg, 1.08 mmol) and DMF (15.0 g). When the initiator was completely dissolved, Cu(I)Cl (36 mg, 0.36 mmol) was added, and the flask was sealed with a rubber septum. The flask was evacuated and back-filled with nitrogen for 3 times and thereafter immersed into an oil bath set to 60 °C. At a certain interval time, an amount of reaction mixture was withdrawn from the flask with degassed syringes and poured into excessive methanol to precipitate out the solid products. After filtered and washed, the white solid products were collected and dried at 50 °C under vacuum for 12 h before characterization. The synthesis of polystyrene grated cellulose (Cell–PS) was carried out with the similar procedure. Some experimental conditions are listed in Table 2.

100 mg of the copolymer was then dissolved in the mixture of 1.5 ml acetone and 2.5 ml THF and hydrolysed with 0.4 ml 70% sulfuric acid. The solution was refluxed for 12 h. The residue polymer was precipitated into methanol, washed and dried in vacuum at 50 °C for further GPC characterization.

The Cell–PMMA copolymer with active terminal groups was further used to initiate polymerization of styrene to give a block copolymer of Cell–PMMA-*b*-PS by ATRP with the same catalyst system as mentioned above. Cell–PMMA (145.1 mg, containing 0.1 mmol Br) was dissolved in the mixture of 10.0 ml butanone and 8.0 ml toluene. CuCl (10.0 mg, 0.1 mmol) and Bpy (31.2 mg, 0.2 mmol) were added and lead to a brown solution. Then styrene (5.208 g, 50 mmol) was added and stirred for 4 h at 110 °C. The resulting product was precipitated in the mixture of methanol/water (v/v = 1/1) and dried under vacuum at 50 °C.

2.4. Characterization

The chemical structure of the macro-initiator Cell-B*i*B was characterized by FTIR (Perkin Elmer 2000 FTIR), ^{1}H and ^{13}C NMR (Bruker DMX 400 NMR spectrometer). The ^{1}H NMR data of cellulose graft copolymers were collected at 100 °C in DMSO-d_6 or



Scheme 1. Synthesis procedure of macro-initiator Cell-B*i*B and cellulose graft copolymers.

benzene-d_6. The molecular weight and molecular weight distributions of PMMA and PS obtained by hydrolysis of Cell–PMMA and Cell–PS were measured on a gel permeation chromatography (GPC) (equipped with a Waters 515 pump, three columns Styragel H T3, Styragel HT4, and Styragel HT5, and a 2414 differential refractometer detector) with THF as the eluent, the flow rate was 1 ml/min. A series of monodispersed polystyrene were used as the standard to generate the calibration curve.

The conformation of Cell–PMMA in DMF solution was studied by static and dynamic laser light scattering (SLS and DLS). A modified commercial light-scattering spectrometer equipped with a ALV 5000 multi-τ digital time correlator and a solid-state laser ($\lambda = 632.8$ nm) as the light source was used. The primary beam is vertically polarized with respect to the scattering plane. The details of the SLS and DLS instrumentation and theory can be found elsewhere [38,39]. In SLS, the angular dependence of the excess absolute time-averaged scattering light intensity, known as the excess Rayleigh ratio $R(q)$, of dilute polymer solutions was measured. $R(q)$ is related to the weight-average molar mass (M_w), polymer concentration (C), and the scattering angle (θ) as [40]

$$\frac{KC}{R(q)} \approx \frac{1}{M_w}\left(1 + \frac{1}{3}\left\langle R_g^2 \right\rangle_z q^2\right) + 2A_2C$$

where $K = 4\pi^2 n^2 (dn/dC)^2/(N_A\lambda_0^4)$ and $q = (4\pi n/\lambda_0)\sin(\theta/2)$ with N_A, dn/dC, n, and λ_0 being the Avogadro number, the specific refractive index of increment, the solvent refractive index, and the wavelength of the light in vacuum, respectively; A_2 is the second virial coefficient; and $\langle R_g \rangle$ is the root-mean square z-average radius of gyration of the polymer chain in solution. For the Cell–PMMA in DMF at 20 °C and $\lambda = 632.8$ nm, the respective value of $dn/dC = 0.045$ ml/g was determined by using a novel and high precision differential refractometer [41]. In DLS, the intensity–intensity time correlation function $G^{(2)}(t,q)$ in the self-beating mode was measured. The Laplace inversion of $G^{(2)}(t,q)$ can lead to a line-width distribution $G(\Gamma)$, which can be further converted to a translational diffusive coefficient distribution $G(D)$ by $\Gamma = Dq^2$ and a hydrodynamic radius distribution by the Stokes–Einstein equation: $R_h = k_B T/6\pi\eta D$, where η, k_B, and T are the solvent viscosity, the Boltzmann constant, and the absolute temperature, respectively. In this article, the R_h of the graft copolymer Cell–PMMA was measured with DLS at 30° and all the measurements were carried out at 20 ± 0.1 °C.

The aggregated and self-assembly morphology of Cell–PMMA were examined by transmission electron microscopy (TEM) (Hitachi H-800). In order to observe the aggregated morphology of Cell–PMMA in good solvent, samples were prepared as follows: one drop of Cell–PMMA solution in DMF (w/v = 1/100) was placed onto a copper grid coated with carbon film and was self-dried at room temperature. In order to observe the aggregated morphology of Cell–PMMA in selected solvent, 5 ml Cell–PMMA solution in DMF (w/v = 1/100) was slowly dropped into 95 ml acetone under stirring to obtain the solution of Cell–PMMA in acetone. Then one drop of this solution was taken to prepare samples in the same procedure described above. The samples were directly observed by TEM without any staining.

3. Results and discussion

3.1. Synthesis of macro-initiator Cell-BiB

The homogeneous acetylation of cellulose with acetic anhydride was readily carried out in ionic liquid AMIMCl [36]. The macro-initiator Cell-B*i*B was synthesized by homogeneous acylation of cellulose with BrB*i*B in AMIMCl as shown in Scheme 1. Fig. 1 displays the FTIR spectra for the underivatized cellulose and Cell-B*i*B. The stretching vibration of C=O at 1741 cm^{-1} in the FTIR spectrum of Cell-B*i*B indicates that 2-bromoisobutyryloxyl was bonded with cellulose. Moreover, the broad stretching band of hydroxyl groups at ca. 3500 cm^{-1} for Cell-B*i*B is significantly reduced comparing with that of cellulose, also indicating the partial substitution of hydroxyl groups by acylation.

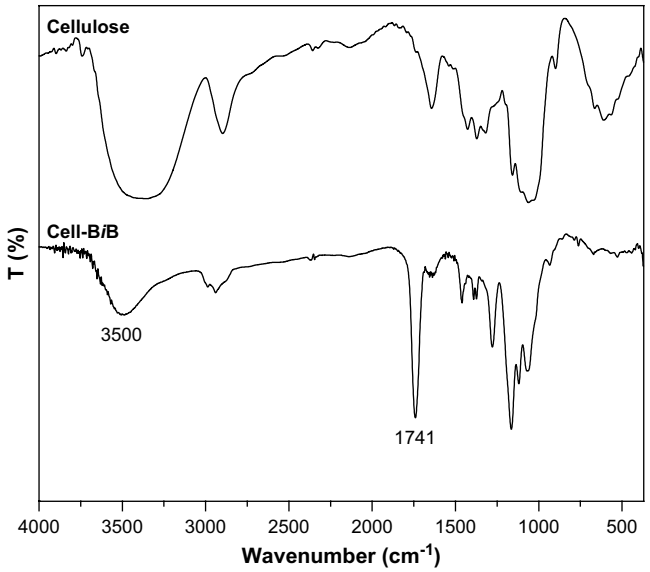


Fig. 1. FTIR spectra of underivatized cellulose and macro-initiator Cell-B*i*B (DS = 0.93).

The introduction of the B*i*B groups on cellulose chains was further confirmed by NMR measurement. The ^{1}H NMR and ^{13}C NMR spectra of Cell-B*i*B are shown in Fig. 2. The chemical shift of proton in the range of 1.6–2.0 ppm in the ^{1}H NMR spectrum of Cell-B*i*B should be attributed to methyl protons of bromoisobutyryl group. In the ^{13}C NMR spectrum, the signals for carbon atoms in the cellulose backbone, for example, C-1 (d_4), present multiple peaks instead of singlets, indicating the substitution on different hydroxyl groups of cellulose.

The effect of reaction parameters, such as reaction time and the molar ratio of B*i*B/AGU, on the DS of B*i*B was investigated and shown in Table 1. It can be seen that the DS of the Cell-B*i*B increases with the increase of reaction time and B*i*B/AGU ratio. The highest DS value achieved was 0.98. It should be noticed that, in previous studies using cellulose derivatives as the starting materials, the higher DS of B*i*B was very difficult to obtain and its values were often less than 0.5 [21,22,31], this is mainly due to the occupation on hydroxyl groups of cellulose by ester or ether groups. Obviously, homogeneous acylation of underivatized cellulose with BrB*i*B may give a relatively higher DS of B*i*B.

Comparing with the underivatized cellulose, the incorporation of relatively bulky B*i*B groups would lead to the suppression of hydrogen-bonding interactions between cellulose chains and therefore significantly alter its solubility in solvents. The solubility of Cell-B*i*B in some solvents is also listed in Table 1. The acylated product, Cell-B*i*B, was soluble in butanone and partially soluble in the mixture of THF/H_2O. The Cell-B*i*B samples with relatively high DS are also soluble in DMF (DS > 0.72) and 1,4-dioxane (DS > 0.93). Therefore, the relatively high DS and good solubility of macro-initiator Cell-B*i*B provide feasibility for subsequent graft polymerization via ATRP, and the residual hydroxyl groups in Cell-B*i*B might provide unexpected characters for the new materials and active sites for further functionalization.

3.2. Graft copolymerization

The Cell-B*i*B macro-initiator was used for ATRP of MMA and styrene in a CuCl/Bpy catalytic system. The polymerization

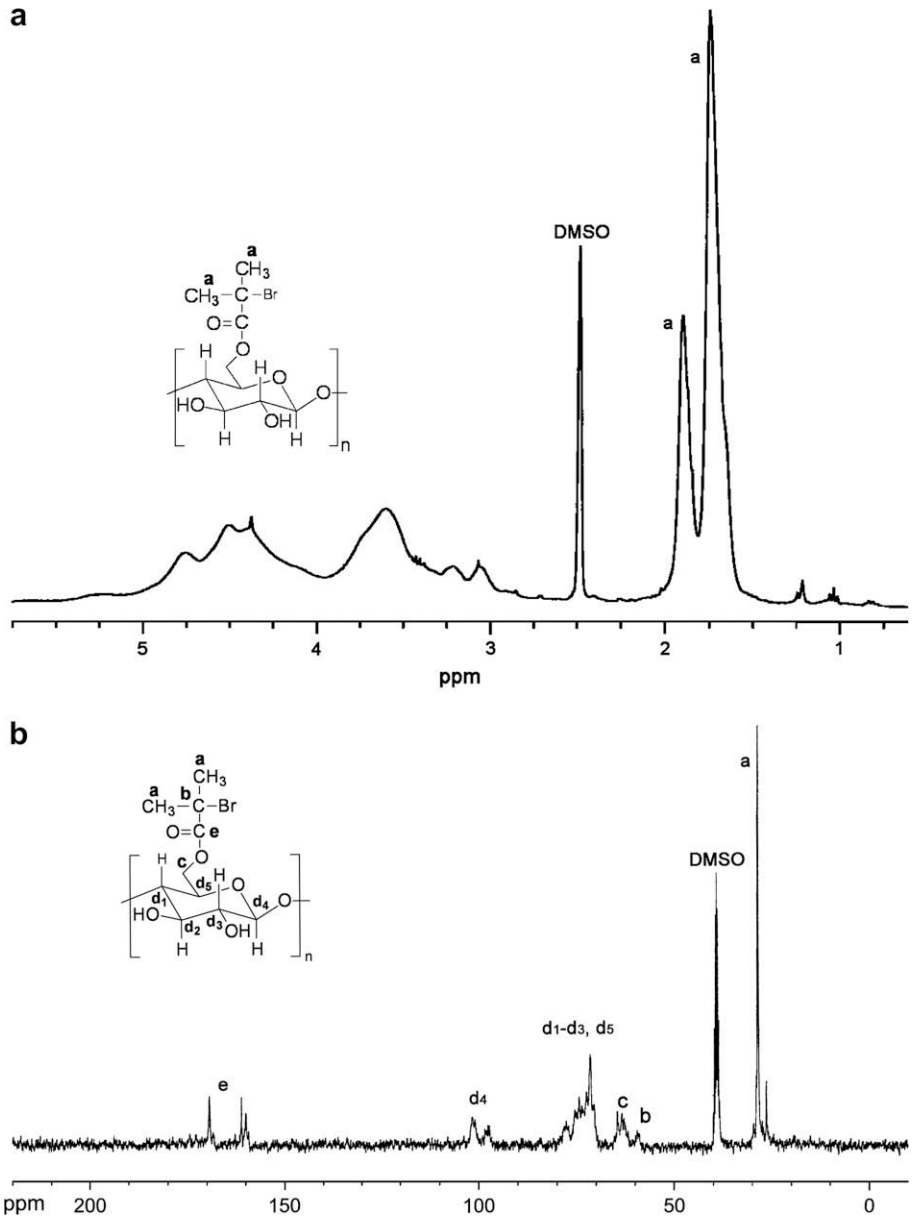


Fig. 2. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of Cell-B*i*B (DS = 0.93) in DMSO-d_6.

procedures are shown in Scheme 1. The graft copolymers Cell–PMMA and Cell–PS and graft block copolymer Cell–PMMA-*b*-PS were characterized by ^{1}H NMR analysis (Fig. 3). The chemical shift of proton at 3.6 ppm can be observed in Fig. 3a, which is attributed to protons of $-OCH_3$ in PMMA. The signal in the range of 6.5–7.0 ppm (Fig. 3b) is ascribed to the proton of $-C_6H_5$ in styrene. The chemical shift of protons at 3.6 and 6.5–7.0 ppm (Fig. 3c) for $-OCH_3$ and $-C_6H_5$, respectively, is shown for the graft block copolymer Cell–PMMA-*b*-PS. The signal of the cellulose backbone hydrogen is very weak, even under high temperature and higher concentration, as a result, the integration of the hydrogen is inaccurate. So the molecular weight of the grafting copolymer was carried out by GPC method.

Table 1
Results and experiment conditions of the homogenous acylation of cellulose by BrB*i*B in AMIMCl.

No.	Molar ratio[a]	Time (h)	DS[b]	Solubility		
				DMF	1,4-Dioxane	Butanone
1	1:2.5	20	0.62	−	−	+
2	1:5	8	0.72	+	−	+
3	1:5	20	0.93	+	+	+
4	1:5	48	0.98	+	+	+

[a] Molar ratio of anhydroglucose units(AGU)/B*i*B.
[b] DS is calculated from ^{1}H NMR.

The polymerization kinetics of MMA and styrene grafted on cellulose was studied. The monomer conversion was determined by weighing the samples. Semilogarithmic plot of the monomer conversion of MMA versus the reaction time is shown in Fig. 4a. At the initiating stage, a curvature was observed which shows the termination due to the impact of the close proximity of the initiators. The variation of $\ln([M]_0/[M]_t)$ of MMA is linear with time in the period of 25 to ca. 200 min, where $[M]_0$ is the initial monomer concentration and $[M]_t$ is the monomer concentration at time t. Therefore, within this period the polymerization was suggested to be first order, and the concentration of the growing radical species in the system was constant with respect to relatively low monomer

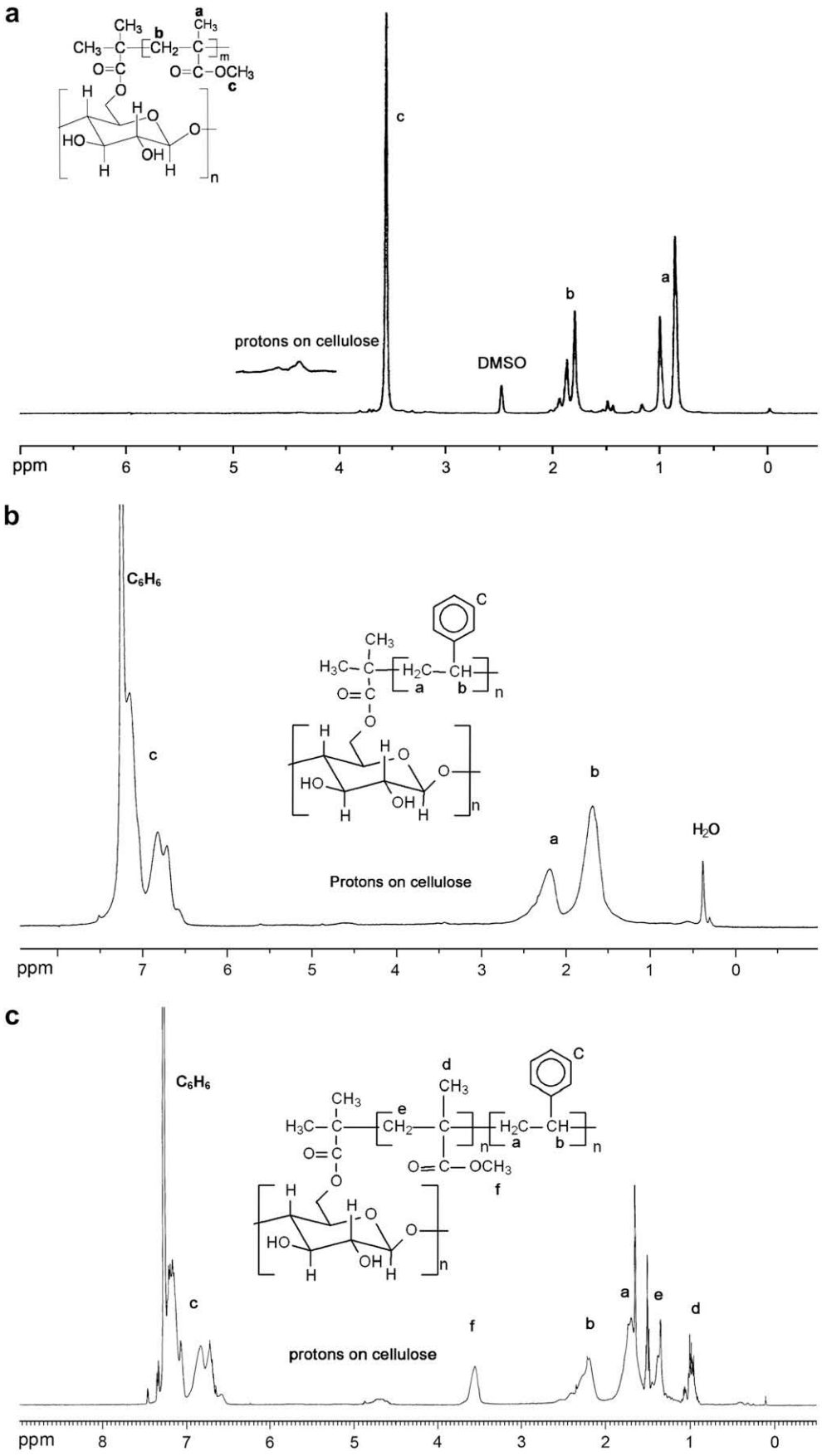


Fig. 3. ^{1}H NMR of Cell–PMMA in DMSO-d_6 (a), Cell–PS (b) and Cell–PMMA-*b*-PS (c) benzene-d_6.

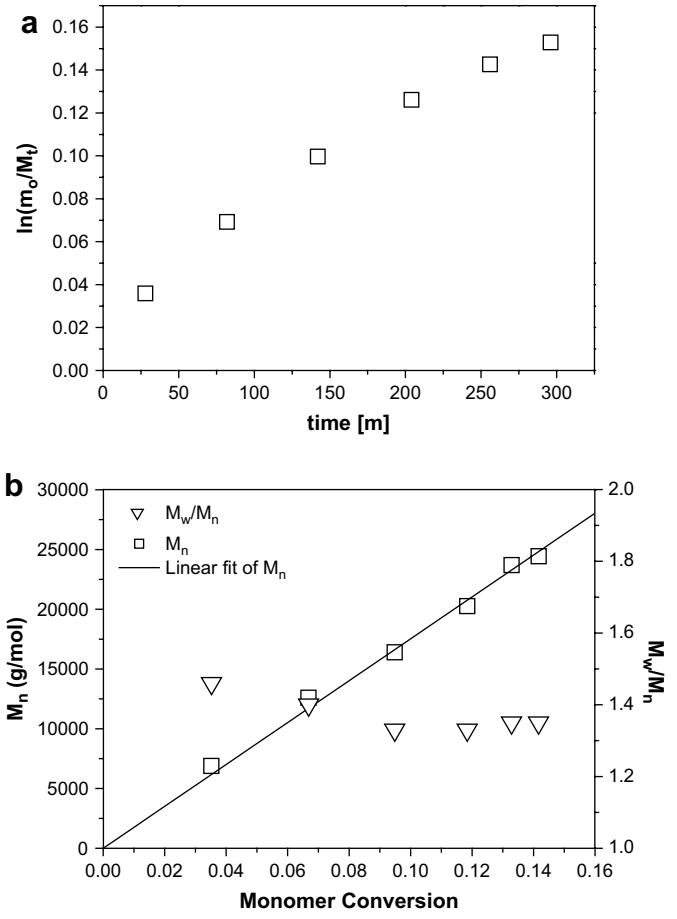


Fig. 4. Semilogarithmic plot of monomer consumption versus time for MMA polymerizing in DMF initiated by Cell-*Bi*B (a). Dependence of the number-average molecular weight and polydispersities (M_w/M_n) of side chain PMMA (b) on monomer conversion. [Cell-*Bi*B (DS = 0.72)]/[CuCl]/[Bpy]/[MMA] = 1:1:3:200, polymerization temperature is 60 °C.

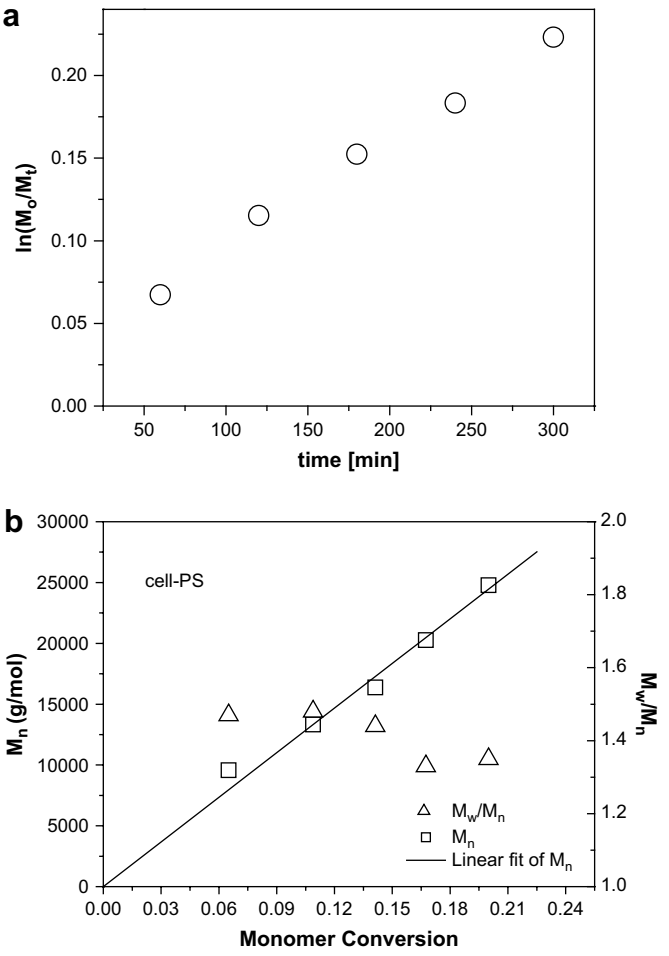


Fig. 5. Semilogarithmic plot of monomer consumption versus time for styrene polymerizing in 1,4-dioxane initiated by Cell-*Bi*B(a). Dependence of the number-average molecular weight and polydispersities (M_w/M_n) of side chain PS on monomer conversion (b). [Cell-*Bi*B (DS = 0.93)]/[CuCl]/[Bpy]/[styrene] = 1:1:3:100, polymerization temperature is 110 °C.

conversion. After 200 min, a slight curving occurred. The possible reason might be the polar solvent used and the decrease of radical concentration is due to partial termination of living free radicals. Fig. 4b 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 PMMA increases linearly with the consumption of the monomer, and the M_w/M_n is about 1.4, suggesting that the above polymerization can be regarded as a controlled living polymerization.

The similar polymerization results of cellulose with styrene were also obtained, as shown in Fig. 5. It also suggests the impact of the high DS of the initiator at the initiating stage, but unlike the grafting of PMMA, the deviation from the linear first order was not obvious even the monomer conversion reached 20%. Thus it may be explained by the difference of DMF and 1,4-dioxane. DMF has been recognized to cause possible competing complexation of the metal catalyst or ligand exchange [34], while 1,4-dioxane is more suitable for ATRP reactions.

Above discussion indicates that the graft copolymerization of MMA and styrene onto the cellulose backbone by ATRP was accomplished successfully. Furthermore, graft block copolymer of cellulose with PMMA and PS was also obtained by ATRP of styrene with Cell–PMMA containing active terminal bromine. Different reaction conditions were attempted to obtain well-defined cellulose graft copolymers. Table 2 shows the experimental results obtained by changing the reaction conditions.

3.3. The morphology of cellulose grafted copolymer Cell–PMMA

The solution of Cell–PMMA in DMF was studied firstly by SLS with the sample listed in row 3 of Table 2. Fig. 6 is a typical Zimm plot of Cell–PMMA in DMF with the concentration of Cell–PMMA in the range of $1–6 \times 10^{-4}$ g/ml. It was obtained that $M_w = 2.5 \times 10^7$ g/mol; $A_2 = 1.9 \times 10^{-8}$ mol dm^3/g^2; $\langle R_g \rangle = 158$ nm. Increasing the concentration of Cell–PMMA to $1–5 \times 10^{-3}$ g/ml, the obtained M_w (3.1×10^7 g/mol) and $\langle R_g \rangle$ (170 nm) are increased and A_2 (1.0×10^{-9} mol dm^3/g^2) is decreased, implying the existence of the inter-chain associations of Cell–PMMA under the experiment conditions. However, it should be noted that A_2 is positive for this solution, indicating that DMF is a good solvent for this graft copolymer Cell–PMMA.

The same sample was further measured by DLS. Table 3 shows the R_h and R_g/R_h of Cell–PMMA graft copolymer in DMF. It shows that R_h increased dramatically from about 110 to 250 nm with increasing the concentration of Cell–PMMA. The R_h increases with raising the concentration of Cell–PMMA in solution, also indicating the inter-chain association of Cell–PMMA in DMF. The increase in the R_h is more than in the R_g with increasing the concentration of Cell–PMMA in DMF, which is due to that the increase in density of copolymer association caused solvent molecules to immobilize or not drain in the dense packed copolymer coils. The immobilized solvent may be taken as a measure of the R_h of copolymer and so

Table 2
Results and experiment conditions of ATRP of MMA and styrene onto cellulose.

No.	[M]/[I][a]/[Cu(I)]/[Pby]	M	Solvent (wt%)	Temp. (°C)	Time (min)	M_n^c (g/mol)	M_w/M_n[c]	Conversion (%)
1	200:1:1:3	MMA	DMF (70.9)	40	25	3800	1.19	4.9
2	240:1:1:3	MMA	DMF (40.9)	50	90	16000	1.49	11.9
3	500:1:1:3	MMA	DMF (66.7)	50	480	96300	1.34	18.6
4	200:1:1:3	MMA	DMF (66.7)	60	60	6900	1.46	3.5
5	240:1:1:2	MMA	Butanone (40.5)	60	60	10500	1.51	4.0
6	100:1:1:2	MMA	Butanone (59.9)	70	180	30700	1.44	28.4
7	200:1:1:2	MMA	Butanone (75.0)	60	360	20300	1.33	11.9
8	200:1:1:3	Styrene	DMF/H_2O[b] (66.7)	60	20	5100	1.48	11.6
9	100:1:1:3	Styrene	1,4-Dioxane (80.8)	110	120	13300	1.48	14.1
10	500:1[d]:1:2	Styrene	Butanone/toluene	110	240	–	–	8.6

[a] [I] = mole of bromine, calculated from ^{1}H NMR of Cell-B*i*B.
[b] DMF/H_2O mass ratio = 95:5.
[c] Obtained from GPC for the grafted chains by hydrolysis of Cell–PMMA and Cell–PS.
[d] [I] = mole of bromine in Cell–PMMA.

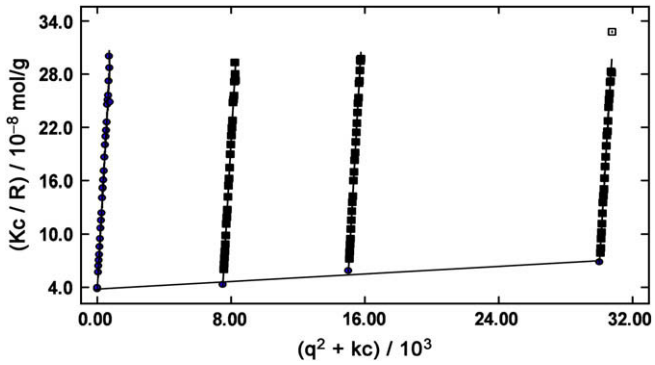


Fig. 6. Typical Zimm plot of Cell–PMMA in DMF at 20 °C, where C ranges from 2×10^{-4} to 6×10^{-4} g/ml. [Cell-B*i*B (DS = 0.93)]/[CuCl]/[Bpy]/[MMA] = 1:1:3:500, polymerization temperature is 50 °C, and reaction time is 48 h.

the defined R_h of Cell–PMMA in DMF became larger when the copolymer segment density is increased. It is also found that the value of R_g/R_h is between 0.7 and 1.4. It is well known that the ratio of R_g/R_h is related to the spatial density distribution and the degree of draining of the scattering object in solution or dispersion. That is, R_g/R_h 0.774 means a uniform and nondraining hard sphere, and R_g/R_h 1.54 means a linear, random-coil chain in a good solvent, when R_g/R_h in the range of 0.7–1.4 means a branching chain, or star-like, or porous sphere-like polymeric structures [42–47].

It is reasonable that the morphology of the comb graft copolymer Cell–PMMA in diluted solution was a branching chain or star-like structures while in the concentrated solution it was associated into sphere-like polymeric structure. The morphology of Cell–PMMA graft copolymer was also studied by TEM. TEM shows the images of Cell–PMMA particulates after solvent evaporation (Fig. 7). The average diameters of sphere-like particulates derived from the solution of good solvent DMF and selective solvent acetone are roughly 50 and 200 nm, respectively. To some extent, it indicates stronger tendency of aggregation of Cell–PMMA copolymers in selective solvent acetone than in good solvent DMF.

Table 3
R_h and R_g/R_h of Cell–PMMA derived from laser light scatting in DMF.

Concentration (10^{-4} g/ml)	R_h (nm)	R_g/R_h
2	114	1.38
4	120	1.32
5	138	1.14
10	163	1.04
30	199	0.85
50	245	0.70

In conclusion, a new and convenient method for graft modification of cellulose directly onto its backbone under a homogeneous condition has been successfully carried out. The macro-initiator for ATRP was synthesized by direct homogenous acylation of cellulose in an ionic liquid AMIMCl. The hydroxyl groups on the cellulose were partially converted into tertiary bromoester groups by reaction with BrB*i*B in the absence of any catalysts and protecting group

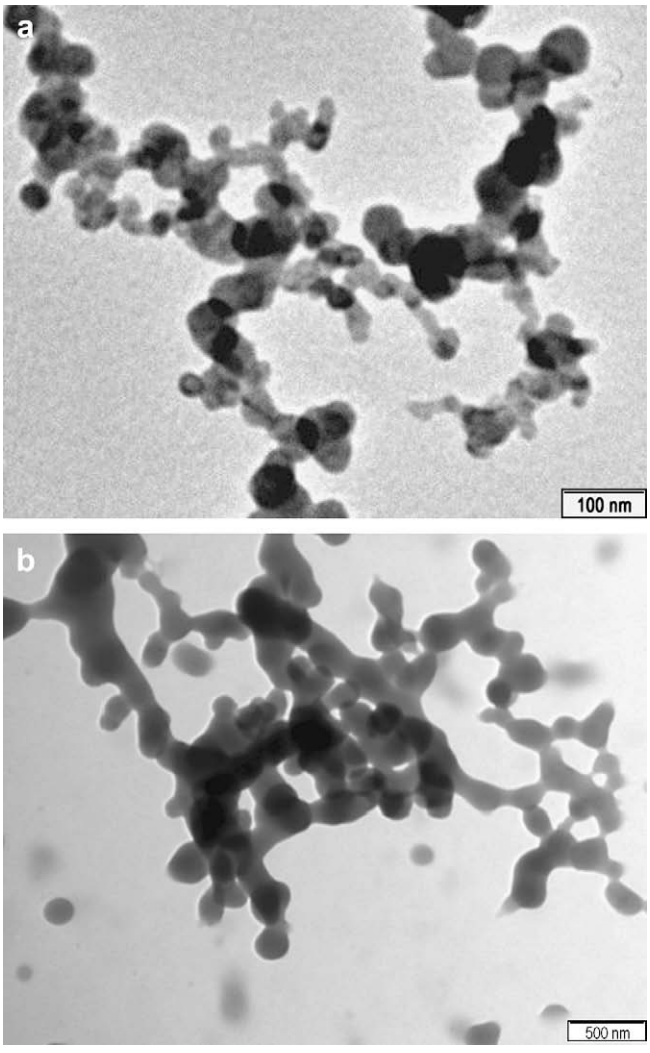


Fig. 7. TEM pictures for Cell–PMMA in DMF (a) and in the selected solvent acetone (b), after solvent evaporation.

chemistry. The DS of B*i*B could be controlled by varying the reacting time and molar ratio of acylation reagent to cellulose. The tertiary bromoester groups on the cellulose are efficient for "graft from" copolymerization. Graft copolymers of cellulose have obtained by ATRP of MMA or/and styrene under mild controllable conditions. The obtained comb graft copolymer Cell–PMMA could aggregate and self-assemble in solution. It is expected that some other monomers with special functional groups, such as *N*-isopropylacrylamide (NIPAAM), 2-hydroxyethyl methacrylate (HEMA), also can graft copolymerization on the cellulose backbone in mild conditions to create new functional materials. Further studies are in progress.

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