Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Polymer Chemistry

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ARTICLE TYPE

Corn starch-based graft copolymers prepared via ATRP at the molecular level

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Abstract: Ionic liquid was employed as a reaction media to prepare starch-based graft copolymers via atom transfer radical polymerization (ATRP) due to its high dissolubility for starch and chemical inertness. Starch macro-initiators with varying degree of substitution (DS) were successfully synthesized
10 in ionic liquid 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) by homogeneous esterification with 2-bromoisobutyryl bromide at room temperature without use of any additional catalysts. Starch-based copolymers (Starch-*g*-PS and Starch-*g*-PMMA) were prepared at the molecular level via homogeneous ATRP using CuBr/PMDETA and CuBr/BPY as catalysts. Compared with heterogeneous surface-initiated polymerization, the graft density and graft ratio were significantly improved. The structure and thermo
15 behaviour of the graft copolymers were characterized by ^{1}H NMR, FTIR and TGA. The molecular weights of the grafted polymer chains were analyzed by gel permeation chromatography (GPC) after hydrolyzing of the starch backbone from the copolymer. The effects of molar ratio of monomer to initiator, solvent, ligand and temperature on the graft polymerization were investigated as well.

Introduction

20 As the rapid development of economy society, fuel and resource problems become a hot topic attracting growing attention, which put renewable materials, such as starch, cellulose and other polysaccharides, at a crucial position in the forthcoming decades[1]. Starch, as one of biodegradable natural polymer materials with
25 large abundance and low cost, is playing an important role for both industry usage and fundamental research[2-7]. To enlarge the application scope of starch in industry, starch was modified with different methods, such as esterification, oxidation, graft reaction and etc.[8-10] Among them, starch graft copolymers, with properties
30 of both natural polymer and synthetic polymer, have attracted most attentions because of their potential applications in industry, etc. Many starch graft copolymers have been synthesized by ring-opening polymerization (ROP)[11-13], reversible addition fragmentation chain transfer (RAFT) polymerization[14, 15], and
35 atom transfer radical polymerization (ATRP)[16-19].

ATRP, one of the most researched living/controlled radical polymerization, has gained extensive interests due to its good control over copolymer architecture[20]. In recent decades, diverse modified starch and other glycopolymer[21, 22] were prepared
40 through ATRP, enlarging their structure library. Liu[16] and coworkers prepared starch-*g*-poly(butyl methacrylate) (Starch-*g*-PBA) by surface-initiated ATRP. Nurmi[17] and coworkers grafted methyl methacrylate (MMA) from starch acetate. Moghaddam[18] and coworkers modified the surface of starch with polystyrene
45 and polyacrylamide by ATRP. Carboxymethyl starch graft polyacrylamide (CMS-g-PAA) or polyhydroxyethylacrylate (CMS-g-PHEA) were prepared by ATRP as well[19]. However, due to high molecular weight, complex structure, and poor solubility of natural starch, graft polymerizations from natural starch are
50 almost surface-initiated and heterogeneous, greatly limiting the graft density and graft ratio.

Ionic liquids (ILs), employed as a novel and environmentally benign solvents, instead of classical organic ones, have shown great improvements in chemical process, such as organic
55 synthesis, polymer preparation and modification. Due to their distinctive physicochemical properties of low volatility, thermal and chemical stability, ability to dissolve organic/inorganic solutes and gases, and tunability of cations and anions, ionic liquids have been widely applied in many fields[23-30]. Former
60 researches already demonstrated that ionic liquids had a great ability on dissolving biomass[31-40], based on which to invent a new route for preparation of biomass-based materials[27, 41-49]. Some ionic liquids, such as [AMIM]Cl[50], [EMIM]Ac[51], [BMIM]Ac[33, 52, 53], [BMIM]C[51, 52, 54-57], [EMIM][Me$_2$PO$_4$][47] and [BMIM]dca[33, 52,
65 58] have been used as solvents for esterification of natural starch, and the acylated starch could be well dissolved in common organic solvents such as DMF, which is a good solvent for carrying out ATRP reaction. Furthermore, synthesized soluble ATRP macroinitiator in ionic liquid has already been applied to
70 the graft polymerization of cellulose[59-65].

Recently, we synthesized Starch-*g*-PS in ionic liquid [EMIM]Ac using traditional free radical polymerization with potassium persulfate as initiator.[66] But the grafted PS length could not be controlled and with relatively low grafting ratio. To
75 improve these, herein, starch based macroinitiator with good solubility was synthesized in [AMIM]Cl and used for ATRP of

styrene and MMA at the molecular level. The graft ratio and graft density were both improved greatly compared to surface-initiated ATRP and traditional free radical grafting polymerization. The thermostability behaviour of grafted copolymers was characterized by TGA.

Experimental Section

Materials

Corn starch from Beijing Shuangxuan Microbe Culture Medium Products Factory was purchased from Aladdin and dried under vacuum at 60 °C for 48 h before use. Ionic liquid [AMIM] Cl was prepared according to the literature procedures[60] and dried under vacuum at 80 °C for 24 h before usage. Styrene and MMA from Beijing Chemical Plant were dried over CaH_2 and then distilled under reduced pressure. CuBr was stirred in glacial acetic acid overnight, then filtered, washed with ethanol three times and dried under vacuum at room temperature for 24 h, and followed by storing in the glove box. 2-bromoisobutyryl bromide (BrBiB) and N,N,N',N'N'-Pentamethyldiethyliamine (PMDETA) were purchased from Aladdin and used as received. Other reagents such as N,N-dimethyl formamide (DMF), 1,4-dioxane, anhydrous methanol, and tetrahydrofuran (THF) from Beijing Chemical Plant were used as received.

Synthesis of macroinitiator Starch-Br

[AMIM] Cl (10.00 g) and corn starch (1.00 g, 6.20 mmol) were added to a 100 mL three-necked flask and mechanically stirred at 80 °C for about 2 h under N_2 flow to form a transparent solution. After cooling the mixture to room temperature, 21.1 g (92.6 mmol) BrBiB was added with N_2 flow under an ice-cold bathing and mechanically stirred. Then the mixture was warmed up to room temperature and mechanically stirred for 1 h. The final products were precipitated in excessive deionized water and washed thoroughly, followed by filtered, washed and dried under vacuum at 60 °C for 24 h. (Yield 75%)

ATRP of styrene or MMA onto starch

A certain amount of Starch-Br, monomer, ligand and solvent were added to a 25 mL Schlenk flask, and then stirred until dissolved completely. The mixture was degassed with three freeze-evacuate-thaw cycles, flushing with argon after thawing, and then transferred into the glove box. An appropriate amount of CuBr was added to the mixture in the glove box. The flask was immersed into an oil bath at a certain temperature for a prescribed time period. The polymerization was stopped by cooling the mixture with ice water and exposing it to air. Then the mixture was dropped into 150 mL anhydrous methanol, filtered, washed with anhydrous methanol three times and dried at 50 °C under vacuum for 24 h.

Cleave of graft polymer chains from starch backbone

Starch graft copolymers (0.2 g), THF (10 mL) and 70% (v/v) H_2SO_4 (1 mL) were added into a 25 mL round-bottomed flask. The mixture was stirred and refluxed at 90 °C for 24 h. The resulting mixture solution was precipitated with 100 mL anhydrous methanol, filtered and washed thoroughly with anhydrous methanol three times. The product was dried under vacuum at 50 °C for 24 h.

Calculation of monomer conversion, grafting ratio and initiation efficiency

Monomer conversion, grafting ratio and initiation efficiency were calculated according to eq 1, eq 2 and eq 3, respectively. W_1 (g), W_2 (g) and W_{mon} (g) are the dry weight of Starch-Br, starch graft copolymers and the monomer at the beginning of the polymerization, respectively. M_n and M_n(th) are number average molecular weight and theoretical value of polymer chains, respectively.

$$Conversion = \frac{W_2 - W_1}{W_{mon}} \times 100\% \qquad (1)$$

$$Grafting\ Ratio = \frac{W_2 - W_1}{W_1} \times 100\% \qquad (2)$$

$$Initiation\ Efficiency = \frac{M_n(th)}{M_n} \times 100\% = \frac{[M] \bullet Conversion / [Initiator]}{M_n} \times 100\% \qquad (3)$$

Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 MHz spectrometer with DMSO-d_6 or $CDCl_3$ as solvent. Fourier Transform Infrared (FTIR) spectra were recorded with the samples/KBr pressed pellets on an Omnic Avatar 360. The number average molecular weight and molecular weight distribution of graft chains were measured on a Polymer Laboratories gel permeation chromatograph (PL-GPC 50) equipped with a RI detector using chloroform as eluent at a flow rate of 1 mL min⁻¹ at 40 °C. The number average molecular weight and molecular weight distribution of Starch-Br and starch graft copolymers were measured on a system comprised of a Waters 515 HPLC pump equipped with a Waters 2414 RI detector using DMF with 0.01 M LiBr as eluent. Monodisperse polystyrene was used as calibration standards. Thermogravimetric Analysis (TGA) was performed in Al_2O_3 pan with a METTLER STRAE SW 9.30 thermogravimetric analyzer with a heating rate of 10 °C min⁻¹ from 25 to 600 °C under nitrogen atmosphere. All samples were dried prior to TGA measurements.

## Results and discussion

Synthesis of macroinitiator Starch-Br

The starch macroinitiator (Starch-Br) was prepared in one step via a esterification reaction with α-bromoisobutyroyl bromide in [AMIM]Cl as depicted in Scheme 1. ¹H NMR (Figure 1a), ¹³C NMR (Figure 1b) and FTIR (Figure 2b) spectra were employed to demonstrate the successful synthesis of the starch-based macroinitiator. The absorption peak at 1740 cm⁻¹ (Figure 2b) was assigned to stretch of C=O group from initiator, and compared with corn starch (Figure 2a), the broad and asymmetric featured peak of starch at 3381 cm⁻¹ significantly shifted to 3433 cm⁻¹ due to O-H vibrations and diminished after esterification, which also demonstrated that macroinitiator was prepared successfully. The chemical shifts in the range of 3.7-6.2 ppm and 1.7-2.2 ppm (Figure 1a) should be attributed to protons of anhydroglucose unit (AGU) and the methyl protons of bromoisobutyryl group, respectively, which can quantify the degree of esterification (DS). In the ¹³C NMR spectrum (Figure 1b), the C1 resonance of starch shifted from 100 ppm to 96 ppm, and the C6 resonance varied from 60 ppm to 65 ppm after esterification.

We studied the influences of solvent, molar ratio of BiB/AGU

Table 1 Experiment data of esterification of starch at various molar ratios of anhydroglucose/BiB and reaction time.

Entry	[AMIM]Cl (wt %)	DMF (wt %)	Malor ratio[a]	Time (h)	DS[b]
1	60	40	1:1	1	0.56
2	60	40	1:3	1	0.72
3	60	40	1:5	1	0.83
4	60	40	1:7	1	1.11
5	60	40	1:9	1	1.22
6	100	0	1:5	1	1.06
7	100	0	1:5	6	1.20
8	100	0	1:5	24	1.53
9	60	40	1:5	0.15	0.12
10	60	40	1:5	1	0.83
11	60	40	1:5	2.5	0.93
12	60	40	1:5	24	1.36

[a] Molar ratio of anhydroglucose (AGU)/BiB.

[b] DS is calculated from ^{1}H NMR.
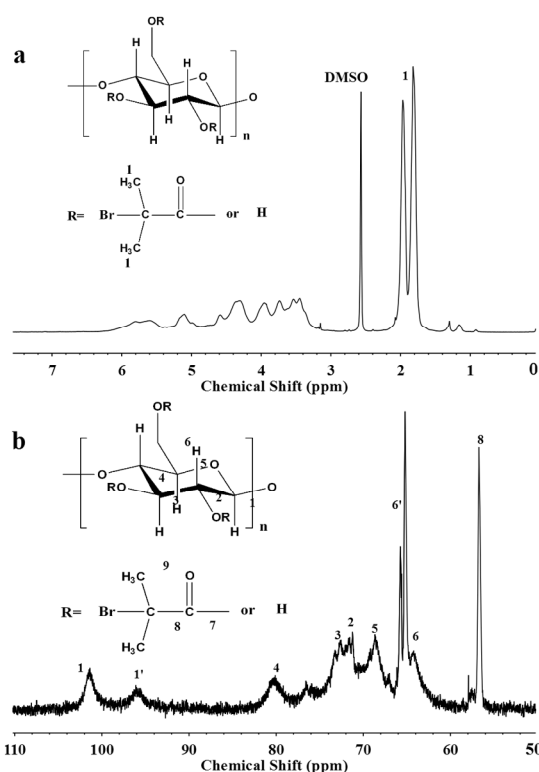
Figure 1 (a) ^{1}H NMR and (b) ^{13}C NMR spectra of starch-Br (DS=1.2) in DMSO-d$_6$.
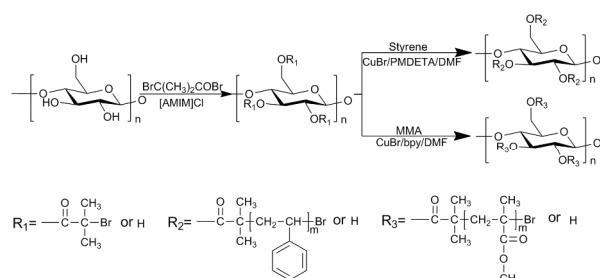
Scheme 1 Synthesis of corn starch-based ATRP macroinitiator and starch graft copolymers.
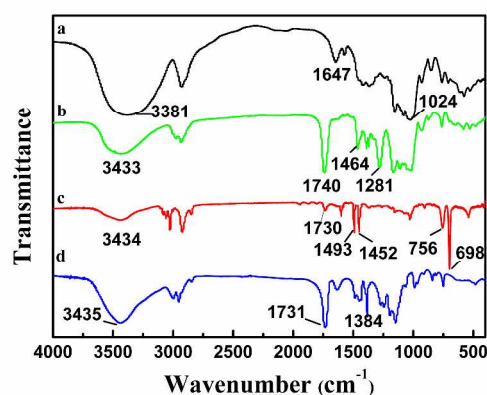

Figure 2 FTIR spectra of (a) corn starch, (b) Starch-Br, (c) Starch-*g*-PS and (d) Starch-*g*-PMMA.
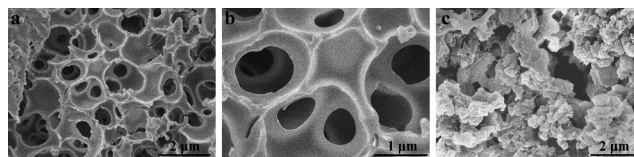

Figure 3 SEM images of starch-Br (a,b) and regenerated starch from [Amim]Cl (c).

and reaction time on esterification of starch, and the results are summarized in Table 1. It shows that the DS of macroinitiator increases with the enhancing BiB and the extension of reaction time in both pure [AMIM]Cl and a mixture with 40 wt% of DMF. The results also present that the cosolvent DMF slowed down the reaction rate and reduced the DS. The highest DS (1.53) was achieved when the molar ratio of BiB/AGU was 5 and reacted for 24 h in pure ionic liquid. The morphology of dry state starch macroinitiator was investigated by SEM as shown in Figure 3a, 3b. Starch macroinitiator exhibited macroporous structure with an average pore size of about 700 nm. We speculated this porous structure would accelerate its dissolving speed, and also could be used as a porous template for graft reaction in poor solvent, like THF. Before esterification reaction, regenerated starch exhibited a bulk structure (Figure 3c), indicating that the porous structure was induced from the change of starch chemical structure.

Graft copolymerization of styrene and MMA onto starch via ATRP

Macroinitiator with DS of 1.20 was selected as the initiator of ATRP for both styrene and MMA. The reaction process is
5 described in Scheme 1.

ATRP of styrene was carried out using Starch-Br as macroinitiator and CuBr/PMDETA as catalytic system. Macroinitiator can dissolve better in DMF than in dioxane. But due to strong polarity, DMF would accelerate the reaction rate of
10 ATRP, making the polymerization of styrene out of control. Therefore, mixed solvent of dioxane/DMF was selected to coordinate between solubility of macroinitiator and controllability of polymerization. The whole reaction process was homogeneous at the molecular level, which was critical for
15 improving the graft density and ensuring the uniform distribution of graft polymer chains.

Various influence factors of the graft reaction including molar ratios of monomer to initiator, solvents, and ligand were investigated in this study, and the results are shown in Table 2.
20 The number average molecular weights of polystyrene chains varied from 2700 to 13200 g mol^{-1}, and polydispersity (PDI) values were relative narrow, which demonstrated that the graft reactions are living polymerization. It is apparent from Table 2 that the length of graft chains could be regulated by changing
25 molar ratio, temperature, solvent and reaction time. Because the polymerizations were conducted at the molecular level, it could reach relatively higher graft ratios (94-1795 %) as compared with

that in traditional free radical polymerization as well as surface-initiated ATRP on starch.
30 The effect of molar ratios of [St]/[Starch-Br] on graft polymerization, which was carried out at 70 °C, is displayed in Table 2. As shown in Table 2 (entries 9, 13 and 14), reaction rates, as well as the number average molecular weights, were proportional with the molar ratios of [St]/[Starch-Br]. Monomer
35 conversions increased from 7.46% to 9.84% and 10.48% with increasing molar ratio of [St]/[Starch-Br] from 100:1 to 150:1 and 200:1, respectively, while keeping other reaction variables constant in the whole study. A gradual increase of [St] also resulted in an increase of number average molecular weights
40 from 2900 to 4500 g mol^{-1}. It was observed simultaneously that changes of PDI of polystyrene were obvious. As shown in Table 2, when the molar ratio of [St]/[Starch-Br] was 100:1, PDI was as narrow as 1.27. But when molar ratios changed into 150:1 and 200:1, PDI became quite wide (even larger than 1.50). Similar
45 results were observed while the graft polymerization was conduct at 80 °C.

The graft polymerization was performed in a series of solvents: DMF, dioxane and dioxane/DMF (v/v=3:1). From Table 2 (entries 5, 7), one can see that graft chains with higher M_n were
50 obtained in dioxane, while that was lower in DMF. In addition, when using dioxane/DMF (v/v=3:1) as mixed solvents (entry 3), M_n of graft chains were between that obtained in the two single solvents mentioned above. The probable reason is the solubility difference of macroinitiator in different solvents, resulting in

55 Table 2 Experiment data of ATRP of St onto starch.

Entry	[St]:[Starch-Br][a]: [Cu^{I}Br]:[PMDETA]	Solvent	Temp. (°C)	Time (h)	Conv. (%)[b]	M_n (10^3 g/mol)[c]	M_w/ M_n[c]	Graft Ratio (%)	Initiation Efficiency (%)	DS of Starch-g-PS
1	100:1:1:1	Dioxane/DMF (v/v=3:1)	80	1	5.67	2.7	1.39	166	22	0.264
2	100:1:1:1	Dioxane/DMF (v/v=3:1)	80	1.5	8.49	3.3	1.38	249	27	0.324
3	100:1:1:1	Dioxane/DMF (v/v=3:1)	80	2	10.19	4.2	1.49	299	27	0.324
4	150:1:1:1	Dioxane/DMF (v/v=3:1)	80	2	13.25	4.4	1.46	583	47	0.564
5	100:1:1:1	Dioxane	80	2	12.84	5.5	1.49	376	23	0.276
6	200:1:1:1	Dioxane	80	3	13.32	7.3	1.34	781	38	0.456
7	100:1:1:1	DMF	80	2	9.12	3.1	1.45	267	31	0.372
8	100:1:1:1	Dioxane/DMF (v/v=3:1)	70	2	3.20	1.8	1.35	94	18	0.216
9	100:1:1:1	Dioxane/DMF (v/v=3:1)	70	3	7.46	2.9	1.27	218	27	0.324
10	100:1:1:1	Dioxane/DMF (v/v=3:1)	70	6	9.11	3.3	1.35	267	29	0.348
11	100:1:1:1	Dioxane/DMF (v/v=3:1)	70	8	11.20	4.7	1.33	328	25	0.300
12	100:1:1:1	Dioxane/DMF (v/v=3:1)	70	24	61.22	13.2	2.13	1795	48	0.576
13	150:1:1:1	Dioxane/DMF (v/v=3:1)	70	3	9.84	3.5	1.62	433	44	0.528
14	200:1:1:1	Dioxane/DMF (v/v=3:1)	70	3	10.48	4.5	1.55	614	48	0.576
15	100:1:1:1	DMF	70	2	12.43	3.4	1.54	364	38	0.456
16	100:1:1:1	DMF	70	2.5	16.60	5.5	1.54	486	31	0.372

[a] [Starch-Br]=mole of bromine, DS=1.20, calculated from ^{1}H NMR.

[b] The monomer conversion was determined by weighing the samples.

[c] GPC analysis was used to characterize number average molecular weight (M_n) and PDI of graft chains after hydrolysis
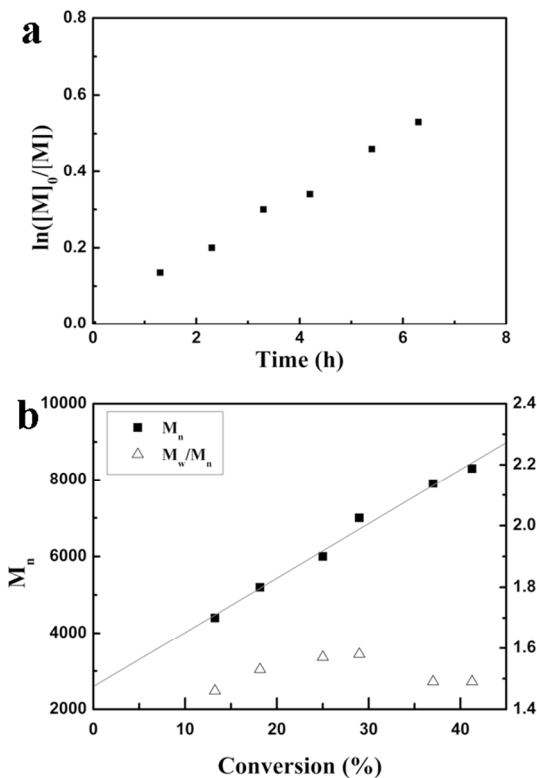
Figure 4 (a) Kinetic and (b) molecular weight/dispersity data of the polymerization of styrene onto starch at 80 °C in dioxane/DMF (v/v=3:1). The molar ratio of $[St]_0/[starchBr]_0/[Cu^IBr]_0/[PMDETA]_0=150/1/1/1$.

different initiation efficiency, which can significantly affect M_n. Nevertheless, it didn't affect the PDI significantly when polymerization was performed in different solvents.

Ligand is another important influencing factor of polymerization. In order to search optimum polymerization condition, the influence of ligand on polymerization was examined by using 2,2-dipyridyl (BPY) and PMDETA. No polymer was formed in the presence of BPY. However, when PMDETA, a ligand with stronger coordination ability, was employed, graft polymerization proceeded successfully.

A simple kinetic study of grafting styrene onto starch was performed in order to confirm the livingness of the graft process. The temporal evolution of $\ln([M]_0/[M])$ is shown in Figures 4 and
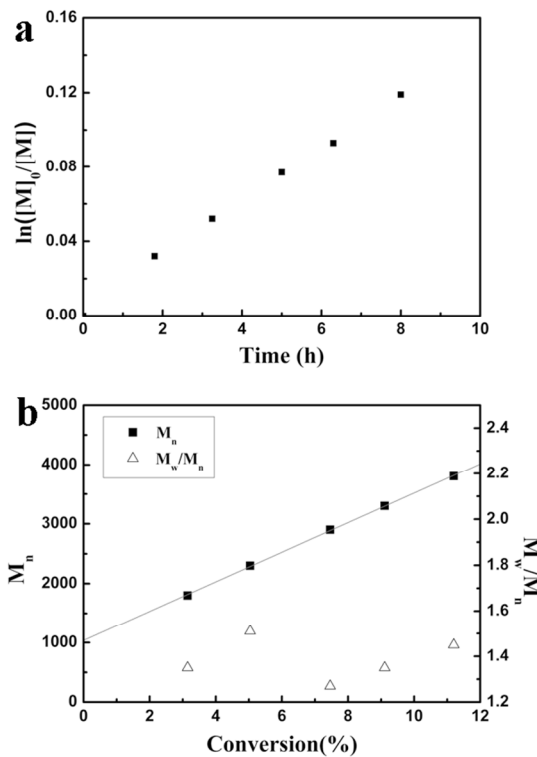

Figure 5 (a) Kinetic and (b) molecular weight/dispersity data of the polymerization of styrene onto starch at 70 °C in dioxane/DMF (v/v=3:1). The molar ratio of $[St]_0/[starchBr]_0/[Cu^IBr]_0/[PMDETA]_0=100/1/1/1$.

5 where $[M]_0$ and $[M]$ are the monomer concentration at the beginning of polymerization and at time t, respectively. The plots present a linear dependence of $\ln([M]_0/[M])$ on time, as well as rectilinear evolution of M_n with monomer conversion, which demonstrated that the polymerization was first order. Additionally, the PDI remained narrow during the polymerization process, which suggested that the graft polymerization of styrene onto corn starch was a controllable living radical polymerization. Similarly, MMA was also used as monomer for ATRP, in which CuBr/BPY and DMF was employed as catalyst and solvent, respectively, to prepare Starch-*g*-PMMA copolymers, and obtained results are tabulated in Table 3. In contrast, using BPY as ligand led to well-controlled polymerization in grafting

Table 3 Experiment data of ATRP of MMA onto starch in DMF.

Entry	[MMA]:[Starch-Br][a]:[Cu^IBr]:[BPY]	Temp. (°C)	Time (min)	Conv. (%)[b]	M_n (10^4 g/mol)[c]	M_w/M_n[c]	Graft Ratio (%)	Initiation Efficiency (%)	DS of Starch-*g*-PMMA
1	100:1:0.5:1.5	25	30	12.36	1.59	1.25	336	7.78	0.093
2	100:1:0.5:1.5	25	39	16.04	1.96	1.34	465	8.19	0.098
3	100:1:0.5:1.5	25	120	30.34	2.19	1.28	969	13.87	0.166
4	100:1:1:3	25	60	16.42	1.94	1.49	479	8.47	0.102
5	100:1:0.5:1.5	30	180	33.20	2.30	1.41	1070	14.45	0.173
6	100:1:0.5:1.5	40	180	40.66	2.49	1.30	1333	16.35	0.196
7	50:1:0.5:1.5	50	120	12.38	1.30	1.40	118	4.77	0.057
8	100:1:0.5:1.5	50	180	50.79	2.44	1.37	1690	20.84	0.250
9	200:1:0.5:1.5	50	120	46.06	2.70	1.41	3147	34.16	0.410
10	100:1:0.5:1.5	50	150	25.96	1.29	1.26	815	20.15	0.242

[a] [Starch-Br]=mole of bromine, DS=1.20, calculated from ^{1}H NMR.

[b] The monomer conversion was determined by weighing the samples.

[c] GPC analysis was used to characterize number average molecular weight (M_n) and PDI of graft chains after hydrolysis.
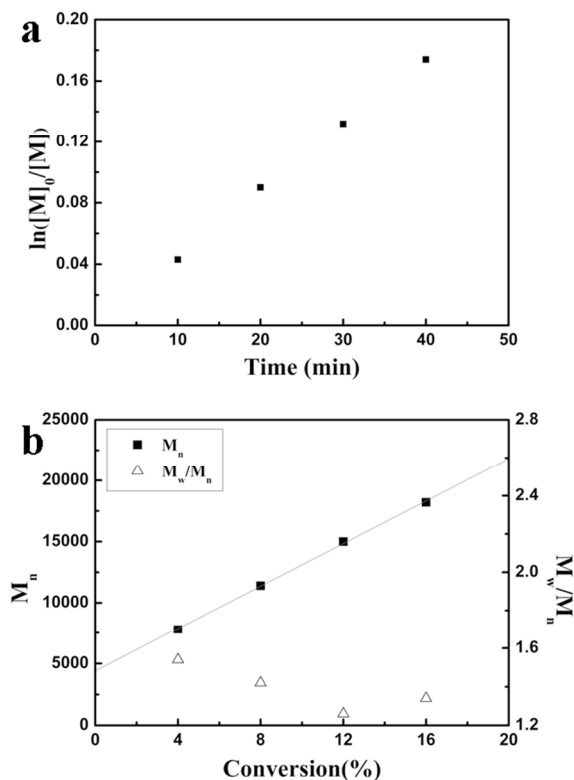
Figure 6 (a) Kinetic and (b) molecular weight/dispersity data of the polymerization of MMA onto starch at 25 °C in DMF. The molar ratio of $[MMA]_0/[starch-Br]_0/[Cu^IBr]_0/[BPY]_0=100/1/0.5/1.5$.

MMA onto starch, which was different from St. Similarly, the molecular weight of PMMA side chains could be tuned by altering molar ratio of [MMA]/[Starch-Br], temperature and reaction time as well.

A linear dependence of $\ln([M]_0/[M])$ vs time and linear evolution of M_n with monomer conversion were observed again in the kinetic plots as shown in Figure 6. The controllability of polymerization was demonstrated by sustained low PDI values, which decreased during the whole reaction process. However, unlike the styrene, initiation efficiencies of MMA were remarkably lower, usually below 20%. These values could also be regulated by varying molar ratio of [MMA]/[Starch-Br], temperature and reaction time.

Graft copolymers of Starch-*g*-PS and Starch-*g*-PMMA were characterized by ^{1}H NMR (Figure 7). The chemical shifts at δ =6.3-7.2 ppm and at δ =1.2-2.1 ppm (Figure 7a) were ascribed to protons of $–C_6H_5$ and $–CH_2–CH–$ in polystyrene chains, respectively. The standard signals in the range of 0.6-1.0 ppm, 1.6-2.1ppm and 3.4-3.8 ppm (Figure 7b) should be assigned to $–CH_3$, $–CH_2–$ and $–OCH_3$ in PMMA chains, respectively. No signals of monomers were observed in both Figures 7a and 7b, which proved that there were no residual monomers in the final products. The signals of starch backbone were too weak to be observed even at high concentrations because of the high molar ratio of monomer to Starch-Br. So the DS of Starch-*g*-PS and Starch-*g*-PMMA cannot be calculated based on ^{1}H NMR spectra. It was calculated by the multiplication of the DS of macro-initiations and the initiation efficiency.
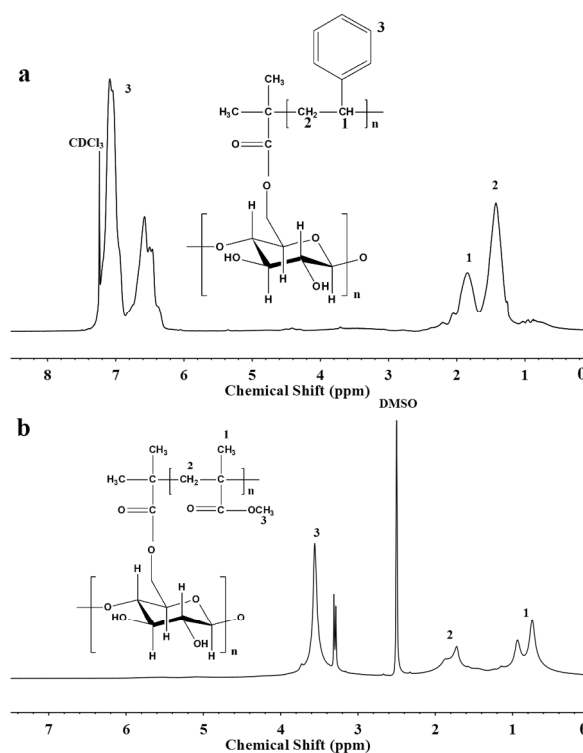

Figure 7 ^{1}H NMR spectra of (a) Starch-*g*-PS in CDCl$_3$ and (b) Starch-*g*-PMMA in DMSO-d$_6$.
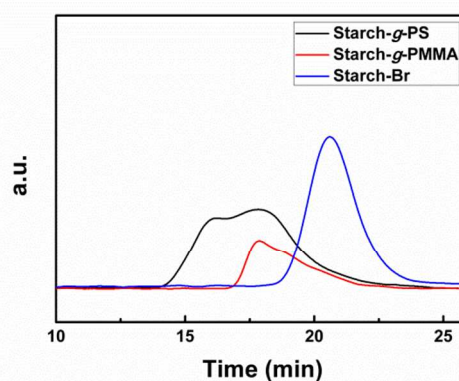

Figure 8 GPC traces of Starch-Br, Starch-g-PS and Starch-g-PMMA.

Table 4 GPC results of Starch-Br, Starch-g-PS and Starch-g-PMMA.

sample	M_n^a	PDI
Starch-Br	2.75×10^5	1.82
Starch-g-PS	6.14×10^6	4.09
Starch-g-PMMA	1.03×10^6	2.63

[a] GPC analysis was used to characterize number average molecular weight (M_n) and PDI of starch graft copolymers.

In order to further confirm PS and PMMA was truly grafted on the starch, the graft polymers regarding starch have been identified by using infrared. Figure 2 shows representative infrared spectra of corn starch, Starch-Br, Starch-*g*-PS and Starch-*g*-PMMA. Vibrations at 698 cm^{-1}, 756 cm^{-1}, 1452 cm^{-1} and 1493 cm^{-1} (Figure 2c) represented the characteristic absorption bands of polystyrene, which further demonstrated that

PS was successfully grafted onto starch. And the presence of PMMA gave rise to a resonance at 1731 cm⁻¹ and 1384 cm⁻¹ as shown in Figure 2d.

In order to prove the purity of starch-g-PS and Starch-g-PMMA, we should certify that there are no monomers, homopolymers and non-grafted starch-Br residue. As displayed in Figure 7 of ^{1}H NMR spectra of Starch-*g*-PS and Starch-*g*-PMMA, there were no signals in the range of 5.0-6.0 ppm, confirming that there were no residual monomers in the products. Figure 8 shows the GPC traces of Starch-Br, Starch-g-PS and Starch-g-PMMA. Compared with Starch-Br, the peaks of Starch-g-PS and Starch-g-PMMA shifted to high molecular weight, confirming the success of graft polymerization. The peak of non-grafted starch-Br was vanished in the GPC traces of Starch-*g*-PS and Starch-*g*-PMMA, which indicated that there was no residual non-grafted Starch-Br in the products. Table 4 lists M_n and PDI of Starch-Br and starch graft copolymers. The only way to form homopolymer in this system is thermal polymerization. According to our previous experiments, M_n of PS synthesized by thermal polymerization without using any initiators at 80 °C for 3 h (under the same experimental condition as entry 6, Table 2) was 19800, which was much lower than that of starch-*g*-PS (6.14×10^6 as shown in Table 4). No products were obtained in thermal polymerization of MMA without using any initiators at 50 °C for 3 h (under the same experimental condition as entry 8, Table 3). In Figure 8, it can be clear seen that there were no signals at higher flow time as compared with that of Starch-Br in the trace of starch-g-PS and starch-g-PMMA, demonstrating no homopolymers in the final products. All of the above illustrated that the products synthesized by this method were of high purity.
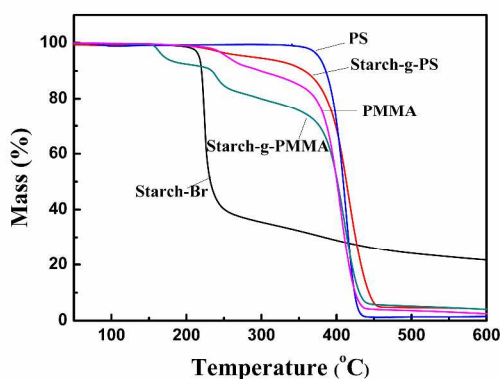

Figure 9 Thermogravimetric analysis of Starch-Br, PS, Starch-*g*-PS, PMMA and Starch-*g*-PMMA.

TGA has been proved to be a suitable method to investigate the thermal stability and polymer grafting content of polymeric systems. The threshold decomposition temperature gives an indication of the highest processing temperature that can be used. Figure 9 depicts the thermogravimetric curves of Starch-Br, PS, Starch-*g*-PS, PMMA and Starch-*g*-PMMA. The weight loss of Starch-Br and homo PS occurred at about 220 °C and 370 °C, and finally lost 80 % and almost 100 % of weight, respectively. Starch-*g*-PS showed two-step weight loss progress: about 230 °C and above 370 °C. The process about 230 °C was attributed to the degradation of the starch-Br component. Starch-based

macroinitiator showed only one degradation step and the starch-*g*-PS copolymers also presented this process, at a slightly lower temperature. This shift in the temperature axis could be a result of the more complex nature of starch in the copolymer, probably forming diverse networks structures with the synthetic polymer. The second degradation temperature was a little higher than that of PS, because higher molecular weight PS was grafted on starch. Three decomposition steps could be observed in the thermal degradation curves of Starch-*g*-PMMA. The first one occurred at 150 °C, corresponding to the decomposition of Starch-Br, which was much lower than that of Starch-*g*-PS, while the rest two steps were the same as those of homo PMMA.

Conclusions

To our best knowledge, it is the first time that ionic liquid was used as solvent to prepare starch-based macroinitiator for ATRP. In the present study, two kinds of copolymers, Starch-*g*-PS and Starch-*g*-PMMA, were prepared by ATRP. The polymerizations were carried out at the molecular level, significantly improving graft density and graft ratio as compared with heterogeneous surface-initiated polymerization. The graft copolymers were characterized by ^{1}H NMR, FTIR and TGA. The grafted chains were cleaved from starch backbone by hydrolysis and analyzed by gel permeation chromatography (GPC), which demonstrated that the grafted chains with well-controlled molecular weight and polydispersity had been covalently grafted onto starch backbone. The effects of molar ratio of monomer to initiator, solvent, ligand and temperature on the polymerization were investigated. The optimal reaction condition for polymerization of styrene was at 70 °C in Dioxane/DMF(v/v=3/1) with CuBr/PMDETA as catalyst and molar ratio of [St]/[Starch-Br] of 100:1. The present methodology could be applied to a wide range of monomers to afford other new starch-based materials.

Acknowledgment

Notes and references

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