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Surface-initiated atom transfer radical polymerization (SI-ATRP) of *n*-butyl acrylate from starch granules

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Abstract

Poly(*n*-butyl acrylate) grafted starch (PBA-*g*-Starch) were successfully by the surface-initiated atom transfer radical polymerization (SI-ATRP) of *n*-butyl acrylate (BA) using starch bromo-acetic ester as macroinitiator in presence of 1,10-phenanthroline and Cu(I)Br as catalyst in toluene system for the first time. The graft parameters calculated from the elemental analyses (EA) results, conversion of monomer (C%) and percentage of grafting (PG%) of 9.9 and 21.3% were achieved, respectively, after a polymerizing time of 5 h. The graft polymerizations exhibited the characteristics of a controlled/'living' polymerization. A glass transition temperature (Tg) of the PBA-*g*-Starch after a polymerizing time of 5 h was found at −48.6 °C by the differential scanning calorimetry (DSC) analysis. The product was also characterized by Fourier transform infrared (FTIR) and X-ray diffraction (XRD) techniques.

Keywords: Poly(n-butyl acrylate) grafted starch; Surface-initiated; Atom transfer radical polymerization

1. Introduction

Starch is one of the world's most abundant organic raw materials. This expensive, biodegradable, and renewable resource has been widely studied during the past decades. Starch has many useful properties, but for some applications, it lacks properties of synthetic polymers. Modification of starch by graft copolymerization provides a significant route to alter the physical and chemical properties (Gupta & Sahoo, 2001). Chemically modified starches with improved properties are gaining increasing importance in industry not only because they are low in cost, but also mainly because the polysaccharide portion of the product is biodegradable. For the last few decades, graft polymerization of monomers is one of the universal, effective and accessible methods of chemical modification of high molecular weight compounds, and natural polymers in particular (Lutfor, et al., 2000). Grafting can be carried out in such a way that the properties of the side chains can be added to those of the substrate polymers without greatly changing the latter. Chemical modification of starch via vinyl graft copolymerization constitutes a powerful means of improving starch properties, thereby enlarging the range of its utilization (Mostafa, 1995).

Starches have been graft copolymerized using various techniques in the past. Most of the them are based on a 'grafting from' process, where radicals are formed along the polymer backbone either by chemical initiators such as ceric ammonium nitrate (CAN) (Chen, Gordon, & Imam, 2004; Choi, Jung, Kwon, Ha, & Cho, 1998; Fanta, Felker, & Shogren, 2004), potassium persulfate (PPS) (Beliakova, Aly, & Abdel-Mohdy, 2004), PPS under microwave irradiation (Zheng, Wang, Zhang, & Zhao, 2005), and ammonium persulfate (APS) by reactive extrusion (Willett & Finkenstadt, 2003), or by irradiation without any radical initiator, such as microwave irradiation (Singh, Tiwari, Tripathi, & Sanghi, 2004) and γ-ray irradiation (Kiatkamjornwong, Mongkolsawat, & Sonsuk, 2002), followed by a free radical polymerization of vinyl monomers. Those methods are highly uncontrolled, and it is impossible to predetermine the lengths of the grafts from starch, and molecular weights are usually high and distributions broad.

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Atom transfer radical polymerization (ATRP) technique, the most used and studied one of the 'living'/controlled radical polymerization (LCRP), is a versatile tool to yield polymers with low polydispersity and controlled molecular weight (Matyjaszewski & Xia, 2001). In recent years, much attention has been paid to the use of surface-initiated atom transfer radical polymerization (SI-ATRP) from various surfaces, such as gold (Edmondson, Osborne, & Huck, 2004), silica (Granville, Boyes, Akqun, Foster, & Brittain, 2004; Perruchot, et al., 2001; Xiao & Wirth, 2002), silicon (von Werne et al., 2003; Wang, et al., 2002; Zhu, Yu, Kang, & Neoh, 2003), polymers (Jones & Huck, 2001) and nanosurfaces (Liu, in press).

To our knowledgements, there is no report about the graft polymerization from starch via the LCRP techniques. In the present paper, we described the SI-ATRP of *n*-butyl acrylate using starch bromo-acetic ester as macroinitiator in presence of 1,10-phenanthroline and Cu(I)Br as catalyst in toluene system.

2. Materials and methods

2.1. Materials

Normal, unmodified food grade potato starch was used after being dried at 100 °C for 24 h. Bromoacetylbromide is analytical reagent grade from ACROS ORGANICS. Both 1, 10-phenanthroline and Cu(I)Br are analytical reagent grade and re-crystallization from ethanol before using. *n*-Butyl acrylate (BA) (Tianjin Chemical Reagent Co., Tianjin, China) is analytical reagent grade and washed twice with an aqueous solution of sodium hydroxide (5%) and twice with distilled water, dried with anhydrous magnesium sulfate overnight, and then distilled over calcium hydride under vacuum. Triethylamine (TEA) used is analytical reagent grade. Ethanol, toluene, tetrahydrofuran (THF), and all other solvents used are all analytical reagent grade.

2.2. Preparation of the macroinitiators

The macroinitiator, starch bromo-acetic ester, was prepared by the followed procedure: the hydroxyl groups on the surface of the dried starch was esterified by immersing the starch granules (6.0 g) in a solution containing bromoacetylbromide (20.2 mg, 1.0 mmol), and triethylamine (111 mg, 1.1 mmol) in THF (100 mL) for 8 h with ultrasonic irradiation at room temperature. Then, the starch ester was thereafter thoroughly washed with dichloromethane and ethanol. It was also ultrasonicated for 3 min each time in both solvents.

2.3. SI-ATRP of BA

A mixture of 5.0 g macroinitiator, 172.1 mg (1.2 mmol) Cu(I)Br, 432 mg (2.4 mmol) 1,10-phenanthroline, 10 mL BA and 80 mL toluene were reflused with electromagnetic stirring. N_2 was bubbled throughout the polymerizing period. Parts of the mixture were taken out after a certain polymerizing time. The products were washed thoroughly with ethanol and water and then dried in vacuum at 40 °C. The esterification of starch and the SI-ATRP of BA procedures could be schematically shown as Scheme 1.

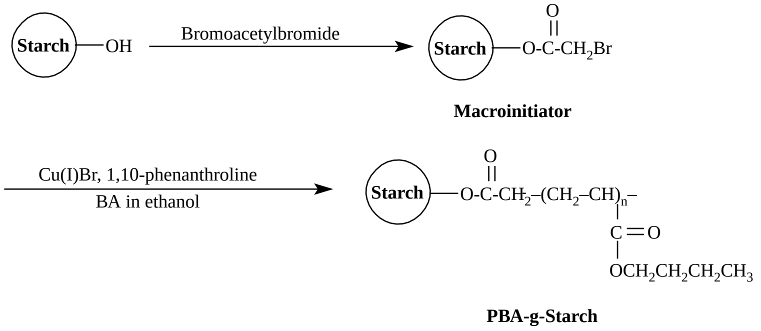
2.4. Analyses and characterizations

Elemental analysis (EA) of C and H was performed on Elementar vario EL instrument. Fourier transform infrared (FTIR) was performed using a Bio-RAD FTS-165 spectrometer by KBr disk. The glass transition temperature (Tg) of the product was conducted by the differential scanning calorimetry (DSC) analysis with a Perkin-Elmer TGA-7 system under liquid nitrogen. The X-ray diffraction (XRD) patterns were recorded in the range of $2\theta = 10$–$80°$ by step scanning with a Shimadzu XRD-6000 X-ray diffractometer. Nickel-filter Cu Kα radiation ($\lambda = 0.15418$ nm) was used with a generator voltage of 40 kV and a current of 30 mA.

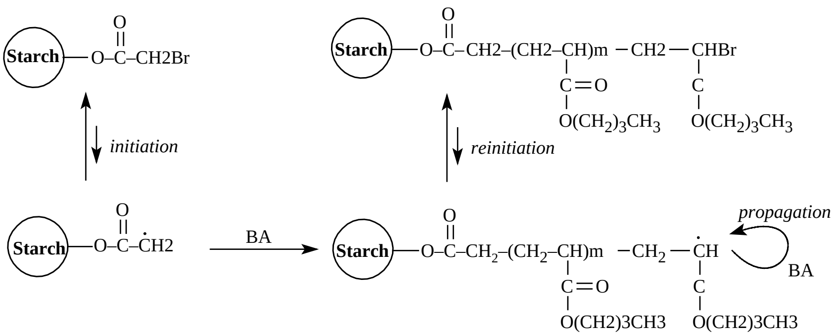
2.5. Grafting parameters

The grafting parameters were estimated from the results of elemental analyses. The conversion of the monomer (C%) and the percentage of grafting (PG%) were calculated according to the following relationships:

$$C\% = \text{PBA grafted (g)/Monomer used (g)} \times 100\%$$



Scheme 1. Preparation route to the PBA-*g*-Starch.



Scheme 2. The mechanism of the SI-ATRP of BA.

PG% = PBA grafted (g)/Starch charged (g) × 100%.

3. Results and discussion

3.1. Preparation of the macroinitiators

The macroinitiator, starch bromo-acetic ester, was prepared by the esterification of the surface hydroxyl groups of the starch with bromoacetylbromide (Scheme 1). The broad peak around 3400 cm^{-1}, originating from the hydroxyl groups of starch, was weakened after the reaction with bromoacetylbromide. The macroinitiator showed a peak around 1730 cm^{-1} which is not present in the starch. This peak was originated from the carbonyl in the bromoester groups. The yield was low because that the starch is not soluble in THF and only the surface hydroxyl groups had been esterified.

3.2. SI-ATRP of BA

The bromoester groups on the surfaces of the macro-initiators are known to be effective initiators for ATRP of acrylates. The mechanism of the SI-ATRP of BA from the surfaces of starch could be schematically shown as Scheme 2.

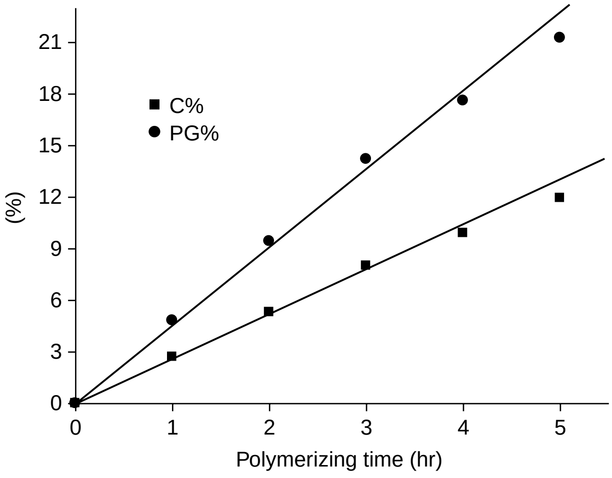


Fig. 1. The effect of the polymerizing time on the C% and PG%.

The product was washed by being dipped in dichloromethane and no non-grafted PBA was found in the solution.

Because of the distinct difference of carbon element contents between the starch (44.44%) and PBA (61.54%), it is possible to calculate the grafting parameters such as C and PG% from the elemental analyses. It was found that the C and PG% increased to 9.9 and 21.3%, respectively, with the increasing of the polymerizing time, as shown in Fig. 1. As can be seen, there is a linear increase in the C and PG% with the increasing of the polymerizing time. This exhibited the characteristics of a controlled/‘living‘ polymerization. At higher C%, the results start to spread. This might resulted from the wrapping of some initiator groups.

3.3. Structural characterizations of the PBA-*g*-Starch

The FTIR spectrum of the PBA-*g*-Starch (Fig. 2) showed a broad absorption band characteristic of the OH stretch of starch, from 3450 to 3200 cm^{-1}. Other bands, such as those at about 2958 cm^{-1} (C–H stretching), and 1426 cm^{-1} (CH_2 bending), can also be seen. Moreover, a band at 1734 cm^{-1} (ester C=O stretching), much stronger than that in the FTIR spectrum of the macroinitiators, new bands at 1249 and 1161 cm^{-1} (ester C–O stretching) were found. And the characteristic absorption peak at 940 cm^{-1} of the poly(*n*-butyl acrylate) and those at 848, 759 cm^{-1} of starch were also found.

The differential scanning calorimetry (DSC) analysis had been conducted for the PBA-*g*-Starch after a polymerizing

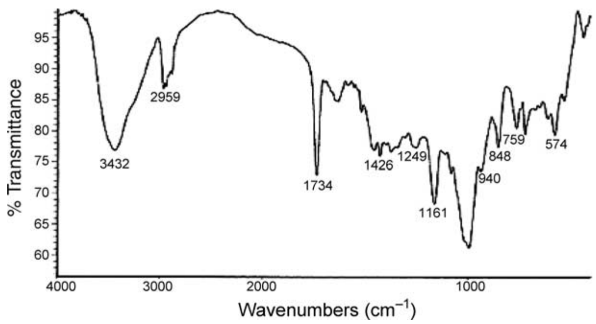


Fig. 2. FTIR spectrum of the PBA-*g*-Starch.

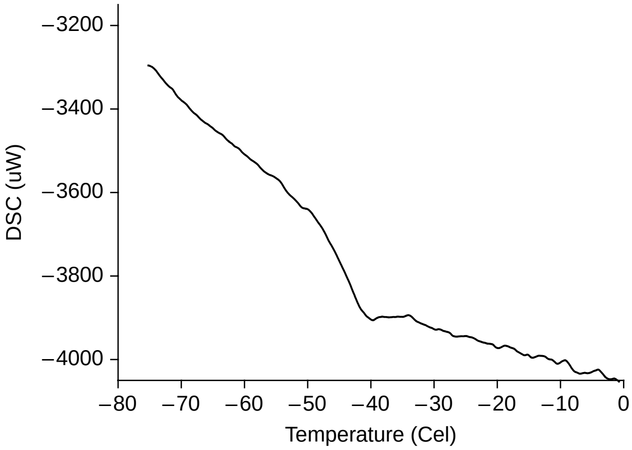


Fig. 3. DSC curve of the PBA-*g*-Starch.

time of 5 h and a glass transition temperature (Tg) of poly(*n*-butyl acrylate) at −48.6 °C was found (Fig. 3).

All these evidences showed that PBA had been successfully grafted onto the potato starch by the proposed SI-ATRP technique with the mechanism shown in Scheme 2.

3.4. XRD characterizations

Starch granules are semi-crystalline in nature. The crystallinity is essentially owing to the amylopectin fraction. The areas of crystallinity comprise about 20–25% of the total volume of the starch granules (Swinkles, 1985). X-ray powder diffraction scans for the potato starch and the PBA-*g*-Starch from the proposed method are shown in Fig. 4. For the potato starch granules prior to grafting, the major reflections at 14.02, 17.09 and 22.29, 2θ were found and the low counts (only up to 200) indicated that the potato starch has very low crystallinity. After the SI-ATRP of BA, only a main diffraction pattern of starch at around 21 2θ was found and the count rate of pure granular starch was further reduced. It can, therefore, be inferred that along with the amorphous region, the crystalline region of the granular starch maybe also involved in grafting (Gao, Tian, Yu, & Duan, 1994) or the dehydration during vacuum drying at 40 °C.

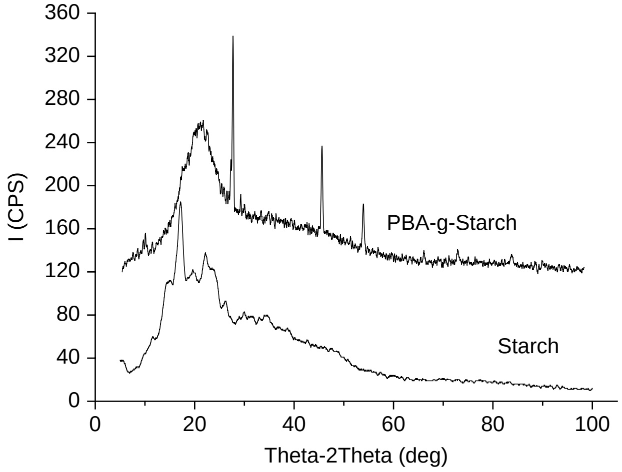


Fig. 4. X-ray powder diffraction scans of bare starch and PBA-*g*-Starch.

4. Summary and conclusions

We described the preparation of poly(*n*-butyl acrylate) grafted starch (PBA-*g*-Starch) via a surface-initiated atom transfer radical polymerization (SI-ATRP) of *n*-butyl acrylate (BA) from the surfaces of the starch bromo-acetic ester as macroinitiator in presence of 1,10-phenanthroline and Cu(I)Br as catalyst in toluene system for the first time. The SI-ATRP was confirmed by the elemental analyses (EA), FTIR and DSC analyses. The products or those with longer carbon chains from the proposed method are expected to be used for the preparation of the biodegradable plastics by being mixed with polyolefin such polyethylene without compatilizer such as EVA.

Acknowledgements

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