Controlled Grafting of Poly(vinyl acetate) onto Starch via RAFT Polymerization

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ABSTRACT: A structure-exact starch-based xanthate agent was prepared and used as chain transfer agent to mediate RAFT polymerization of vinyl acetate, which offered a convenient way to well control the structure and composition of starch-*g*-poly(vinyl acetate). The structures of the intermediate and the polymer were verified with FTIR and ^{1}H-NMR. Gel permeation chromatography measurement results indicated that the polymerization was performed as expected. It was found that the relationship between number average molecular weight and monomer conversion was linear. The polydispersity index of grafted side-chain ranged from 1.19 to 1.53 and most of them were around 1.2. There was one more degradation stage appeared on the thermogravimetric analysis profile of starch-*g*-poly(vinyl acetate) than that of starch. TEM observation exhibited that the product was able to self-assemble into micelles in aqueous solution, which suggested the copolymer was amphiphilic. Both the thermal and amphiphilic properties demonstrated the starch-*g*-poly(vinyl acetate) was successfully synthesized as well. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3450–3455, 2012

Key words: starch; vinyl acetate; RAFT agent; controlled grafting

INTRODUCTION

Starch possesses the remarkable characters such as biodegradability, low cost, and renewability, which makes it a promising candidate for developing various materials. Many efforts have been exerted to develop starch-based polymers as alternatives of petroleum-based polymers.[1–3] However, the mechanical and processing properties of starch are poor. Usually, this is improved with physical means including plasticizing and blending.[4,5] Besides, chemical modification is another effective strategy to enhance the properties of starch. In fact, it is a way to incorporate some special polymers onto the backbone of this polysaccharide. As a result, starch is functionalized and its application ranges is broadened subsequently.

Polyvinyl alcohol (PVA) aqueous solution is able to form physically cross-linked hydrogel. Such a hydrogel is an attractive matrix for biomedical and pharmaceutical applications.[6,7] In view of this, common radical copolymerization has been adopted to incorporate poly(vinyl acetate) (PVAc) onto starch and the copolymer has been converted into starch-*g*-PVA subsequently in our laboratory.[8] The molecular weight of the side-chains was simply adjusted by using methanol or ethyl alcohol as the chain transfer agent. To control precisely, the side-chain length of starch-*g*-PVAc (SVAc), we have synthesized a starch-based RAFT agent through a route including esterification, addition, and substitution reactions, and then used it to conduct the starch-based xanthate-mediated living radical polymerization of VAc.[9] However, the way to prepare starch-based RAFT agent involves so many steps and the obtained agent may exist two forms. To simplify the synthesis procedure and generate a structure-exact starch-based chain transfer agent (SCTA), we design a new route and present it in this article. Subsequently, SCTA-mediated RAFT polymerization of VAc is performed to control the grafting of PVAc onto starch backbone. The structures of the intermediate and final product are well characterized to reveal the feasibility of our goal, that is, to precisely control the RAFT polymerization of VAc with a structure-exact SCTA.

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EXPERIMENTAL

Materials

Water-soluble starch was dried before use. Vinyl acetate (VAc) was purified by distillation. N, N′-azobisisobutyronitrile (AIBN) was purified by recrystallization

from anhydrous ethanol. Ninety-five percent ethanol, potassium ethyl xanthogenate, dimethyl sulfoxide (DMSO), and N, N-dimethylacetamide (DMAc) were all analytical grade reagents and used as received. All the aforementioned reagents were purchased from Shanghai Chemical Agents, China. Bromoacetyl bromide (99%), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide (EDC·HCl), and 4-dimethylaminopyridine (DMAP) were purchased from Alfa Aesar and used as received. Tetrahydrofuran (THF, TEIDA) was used as received.

Synthesis of starch-based bromide

To prepare SCTA, an intermediate, that is, starch-based bromide was synthesized according to the literature[10] with some improvements. In brief, 4 g dry starch was dissolved in 80 mL DMAc at 100°C. After the solution was cooled down to room temperature, 0.98 g (7.41×10^{-3} mol) DMAP and 1.4 g (7.41×10^{-3} mol) EDC·HCl were added. The solution was placed into an ice bath, a mixture of bromoacetyl bromide and DMAc (v/v = 1 : 2) was added in droplet subsequently, and was allowed to react at room temperature for 24 h with agitation. The crude product was precipitated from 95% ethanol and purified by extracting with anhydrous ethanol in a Soxhlet apparatus for 24 h. A white powder was obtained after being dried at 60°C to constant weight. Yield: 65%.

Synthesis of SCTA

SCTA, that is, a kind of starch-based xanthate agent, was prepared according to the literature.[11] Briefly, 5 g starch-based bromide was dissolved in 30 mL DMSO. Four grams of potassium ethyl xanthogenate and another 20 mL DMSO were added and the mixture was allowed to react at 60°C for 24 h under stirring. Another 10 g potassium ethyl xanthogenate was added into the solution, and kept at room temperature with agitation to continue reaction for 24 h. After removing the by-product KBr by filtration, the crude product was precipitated from 300 mL anhydrous ethanol and purified by extracting with ethanol in a Soxhlet apparatus for 24 h. The dried light yellow powder was pure SCTA. Yield: 55%.

Controlled synthesis of starch-*g*-PVAc

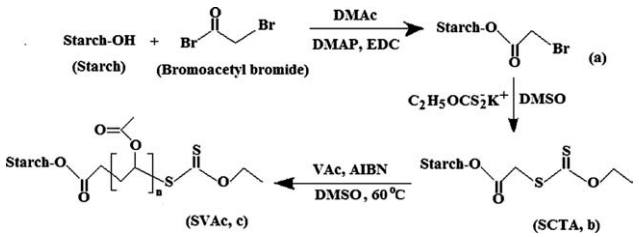
To obtain SVAc with well-defined PVAc chains, the RAFT polymerization of VAc mediated via SCTA was conducted.[12,13] Briefly, 4 mL VAc (4.33 mol L^{-1}), 0.1 g SCTA, and 0.02 g AIBN (1.22×10^{-2} mol L^{-1}) were dissolved in 6 mL DMSO. The mixture was transferred into Schlenk tube, which was thoroughly deoxygenated by three consecutive freeze-pump-thaw cycles. The other reaction samples were prepared in the same way. The tubes were placed in 60°C water bath and removed at regular time intervals. The reaction was ended by plunging the tubes into iced water. SVAc was precipitated from plenty of water, filtered, washed with water for three times, and dried in vacuum at 50°C to constant weight. To remove the free homopolymer, the products were extracted with anhydrous ethanol in a Soxhlet apparatus for 48 h. The conversion of monomer was determined by gravimetric method.

Characterizations

The powdered starch-based bromide, SCTA and SVAc were mixed with dry KBr and compressed into disk, respectively. Fourier transform infrared spectra (FTIR) of these samples were recorded using a Nexus 470 FTIR spectrometer. The element analysis (EA) was performed with EA3000 CHNS/O Element Analyzer. ^{1}H-NMR spectra of SCTA and SVAc were recorded on a Bruke AV400 NMR spectrometer using DMSO-d_6 as solvent. Thermogravimetric analysis (TGA) was performed with a TA V2.4F thermoanalyzer, which was conducted over the temperature range from 25 to 800°C with a programmed temperature increment of 20°C/min under N_2 atmosphere.

To measure the molecular weight and polydispersity index (PDI) of PVAc chain on SVAc backbone, 2 g RAFT polymerization product was dispersed in 20 mL THF, then mixed with 30 mL 1*M* HCl and kept refluxing for 6 h.[14] The residual polymer was washed with distilled water for three times and dried in vacuum at 50°C to constant weight. The starch component of SVAc was thoroughly removed with such a acidic hydrolysis and the remainder was PVAc chains.[9] Then the apparent molecular weight and PDI of PVAc, which attached on SVAc, were measured on a Waters gel permeation chromatography (GPC) with three linear Styragel columns, Waters 1515 pump, and Waters 2414 differential refractive index detector at 30°C. THF was used as eluent at a flow rate of 1.0 mL/min and polystyrene standards were employed for calibration.

Self-assembly behavior of SVAc in aqueous solution was observed with TEM.[15] One milliliter 0.004 g/mL SVAc/THF solution was added into a beaker containing 10 mL water slowly under vigorous stirring and kept at room temperature for 12 h to remove THF thoroughly. The formed SVAc micellar solution was deposited on a carbon-coated electron microscopy copper grid. Water was evaporated at ambient temperature and atmospheric pressure. The morphology of the micelles was determined with Hitach H-7650 TEM at an acceleration voltage of 80 KV.



Scheme 1 Controlled synthesis of well-defined starch-*g*-PVAc via RAFT polymerization.

RESULTS AND DISCUSSION

Synthesis of SCTA

RAFT polymerization is an effective way to carry out the living/controlled radical polymerization of VAc monomer.[16,17] Cellulose-based xanthate agent is capable of mediating the controlled graft polymerization of VAc onto cellulosic materials.[13] However, few attentions have been paid to using abundant chitosan and starch as substrate of RAFT polymerization.[18] To our best knowledge, only one polysaccharides-based RAFT agent that has been reported for mediating controlled radical polymerization of VAc. No starch-based RAFT agent for this target has been reported yet. Herein, we adopt this strategy to control the graft polymerization of VAc onto starch to obtain the precursor of starch-*g*-PVA. In this way, the advantages of starch are retained, and the structure and composition of the copolymer are controllable. SCTA is such a macro-RAFT agent to conduct the RAFT polymerization of VAc onto starch.

As shown in Scheme 1, SCTA is prepared via two steps. First, the starch-based bromide is synthesized via the esterification of starch with bromoacetyl bromide by using DMAP and EDC·HCl as catalysts. Then, the bromide atom on the intermediate (**a**) is substituted with xanthate group to generate SCTA (**b**).

The structure of (**a**) and (**b**) are confirmed with FTIR spectra (Fig. 1). Compared to the spectra of starch, a strong adsorption band for typical stretching vibration of —C=O appears at 1735 cm^{-1} on that of (**a**), which indicates the bromoacetyl bromide group has bonded onto starch backbone. After the bromide atom on (**a**) has been substituted with xanthate group, the characteristic absorption peak of —C=S and C—S group appears at 1020 and 852 cm^{-1}, respectively. These results suggest the two reactions have been successfully carried out.

The ^{1}H-NMR spectra of SCTA (Fig. 2) are also measured to verify further its structure. The chemical shifts at 3.46–3. 81, 5.11, 5.38, and 5.49 ppm are related to the modified starch backbone. The signals at 1.06, 4.56, and 4.88 ppm are attributed to the

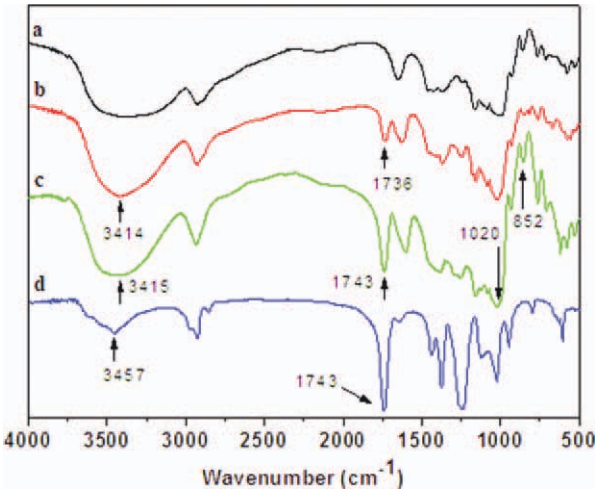


Figure 1 FTIR spectra of starch (a), starch-based bromide (b), starch-based chain transfer agent (c), and starch-*g*-PVAc (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

methyl and methylene groups on xanthate moiety, respectively.

In addition, the EA shows the percentage contents of S element (S%) in SCTA are 7.09 and 11.61% when the feeding ratio of bromoacetyl bromide/anhydroglucose unit (AGU) is 1 : 1 and 2 : 1 (mol : mol), respectively. This suggests that the S% of SCTA depends on the feeding ratio of reactants, and confirms the existence of xanthate group on SCTA as well. Furthermore, the degree of substitution (DS), which reflects the amount of —OH groups on AGU has been converted into RAFT moiety and restricts the density of PVAc chain grafting onto starch backbone, can be calculated from *S*%. The degrees of substitution of SCTA, which are calculated according to the formula DS = 162 × S%/(32

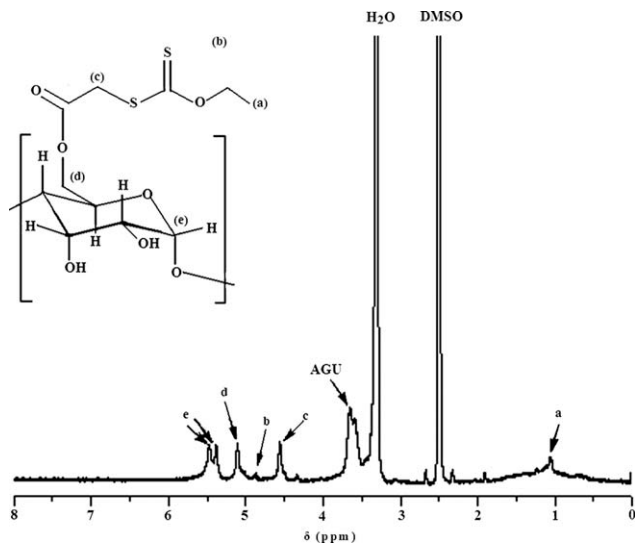


Figure 2 ^{1}H-NMR spectra of starch-based chain transfer agent.

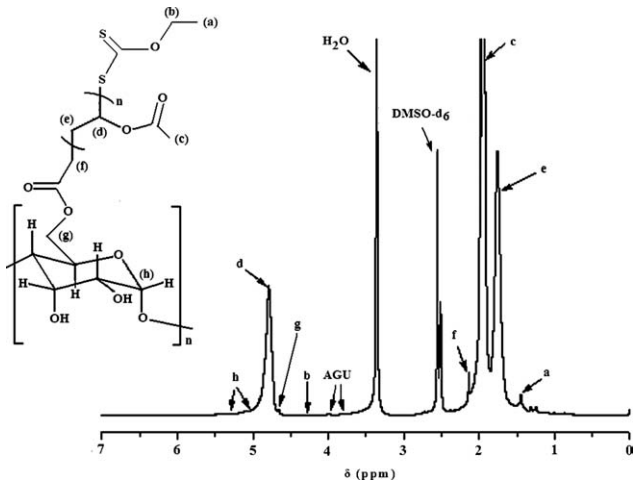


Figure 3 ^{1}H-NMR spectra of starch-*g*-PVAc.

$- 135 \times S\%$), are 0.53 and 1.15 for the samples that contain 7.09 and 11.61% sulfur element, respectively. Evidently, the target product is synthesized successfully, and the structure of SCTA is exact. Both are just as what we expected.

Controlled grafting of VAc onto starch

SCTA-mediated RAFT polymerization of VAc is performed to produce SVAc containing well-defined PVAc side chains. The structure of the graft polymer is examined with FTIR and ^{1}H-NMR analyses. As shown in Figure 1, the absorption peaks appeared at 1735 and 3449 cm^{-1} are attributed to the —C=O and —OH groups, respectively. The hydroxyl group belongs to starch segment, whereas carbonyl group may exist in PVAc segment and the remained moiety of SCTA. Compared to the FTIR spectra of SCTA, the intensity of the absorption band at 1735 cm^{-1} is much higher in the case of the graft copolymer. These suggest that PVAc chain has been grafted onto the starch backbone. On the ^{1}H-NMR spectra (Fig. 3) of the final product, the signals that exhibited at 1.67–1.86, 1.89–1.99, and 4.73–4.87 ppm are related to the protons on PVAc chain. Whereas the peaks appeared at 2.13, 3.71–3.94, 4.65, 5.09, and 5.37 ppm belong to that on the modified starch segment. As for the protons of xanthogenate group, their chemical shifts show at 1.45 and 4.31 ppm. In other words, the FTIR and ^{1}H-NMR analysis results have demonstrated the product is the targeted SVAc.

GPC analysis results reveal that the SCTA-mediated RAFT polymerization of VAc is controllable. The weight average molecular weight and the PDI of one SVAc sample are 2.63×10^5 and 2.72, respectively. To acquire the information about molecular weight and its distribution of the grafted PVAc, the acidic hydrolysis is executed to thoroughly remove starch moieties from SVAc and GPC measurement of the residues is performed subsequently. It is found that the PDI of the grafted PVAc chain is rather low. PDI ranges from 1.19 to 1.53 and most of them are around 1.2 (Table I). The number-average molecular weight (M_n) of the side chain increases almost linearly with monomer conversions (Fig. 4). The kinetic curve of the RAFT polymerization is almost linear (Fig. 5) too. These are consistent with the main features of living/controlled radical polymerization[19] and indicate that SCTA is an effective macro-RAFT agent to conduct the RAFT polymerization of VAc monomer. In addition, the S% of SCTA, which reflects the content of xanthate group, increases with increasing the feeding ratio of bromoacetyl bromide/AGU. This means the effective concentration of CTA on SCTA chains, which greatly affect the RAFT polymerization of VAc, is able to be adjusted in a certain range. As a result, the

TABLE I
GPC Analysis Results of Starch-*g*-PVAc Side Chain (1.22×10^{-2}mol L^{-1} AIBN; 4.33 mol L^{-1} VAc; 0.1 g SCTA; 6 mL DMSO; 60°C)

Sample[a]	S (%)[b]	Time (h)	Conversion (%)[c]	Yield (%)[d]	M_n (g/mol)	PDI[e]
PVAc-1	11.61	6	21.6	6.1	17,996	1.24
PVAc-2	11.61	8	37.4	8.1	52,045	1.29
PVAc-3	7.09	8	62.8	9.2	79,847	1.43
PVAc-4	11.61	9	41.3	8.5	56,592	1.53
PVAc-5	11.61	13	60.9	9.1	79,603	1.21
PVAc-6	11.61	14	70.3	9.4	104,837	1.19

[a] The sample is cleaved from starch-*g*-PVAc.
[b] The percentage content of S element in the SCTA used for polymerization.
[c] Conversion of monomer is determined by gravimetric method and calculated as Conversion (%) = $(W_h + W_{SVAc} - W_{SCTA})/W_m \times 100$, where W_h, W_{SVAc}, W_{SCTA}, and W_m are the amount of the formed homopolymer, purified starch-*g*-PVAc, SCTA, and the monomer, respectively.
[d] Yield of SVAc is calculated as Yield (%) = $W_{SVAc}/(W_{SCTA} + W_m) \times 100$, where W_{SVAc}, W_{SCTA}, and W_m represent the same variables mentioned above, respectively.
[e] PDI = M_w/M_n.

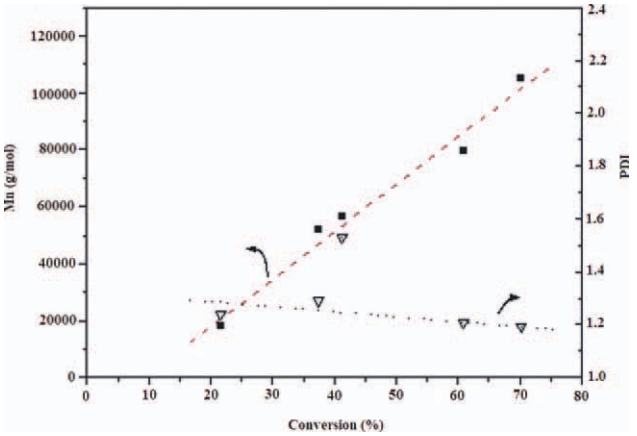


Figure 4 Dependence of molecular weight and molecular distribution on monomer conversion for SCTA-mediated RAFT polymerization of vinyl acetate (1.22×10^{-2} mol L^{-1} AIBN; 4.33 mol L^{-1} VAc; 0.1 g SCTA; 6 mL DMSO; 60°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

molecular weight of the grafted PVAc decreases with increasing the S% of SCTA (Table I; PVAc-2 vs. PVAc-3). In addition, the maximum density of the grafting chains is approximately equal to the S% of SCTA according to the polymerization mechanism (Scheme 1).

Figure 6 shows that the thermal degradation profiles of starch, PVAc and SVAc are distinct. The profile of starch exhibits only one decomposition stage (267–383°C) due to its single component. Owing to two moieties existing in the same macromolecular chain, SVAc shows two degradation stages. The first degradation stage is attributed to both degradation of starch and PVAc, whereas the second stage (≥417°C) belongs the degradation of PVAc moiety.[20]

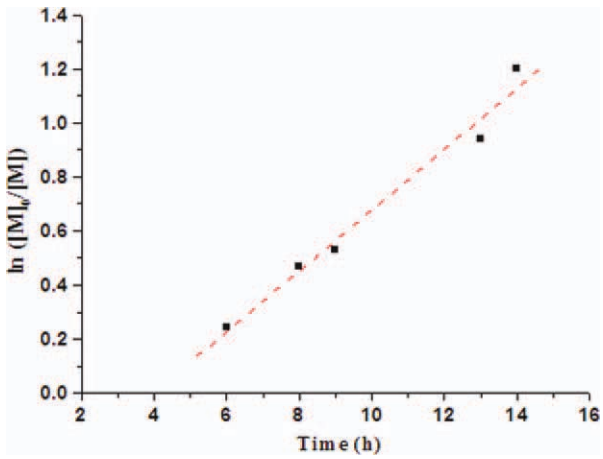


Figure 5 Kinetic curve of SCTA-mediated RAFT polymerization of vinyl acetate (1.22×10^{-2} mol L^{-1} AIBN; 4.33 mol L^{-1} VAc; 0.1 g SCTA; 6 mL DMSO; 60°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

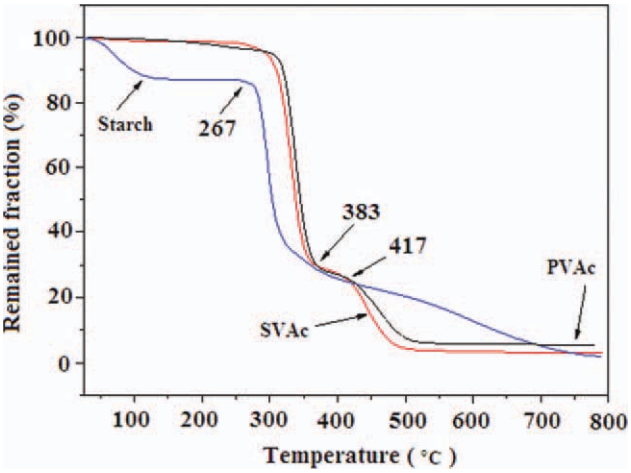


Figure 6 Thermogravimetric analysis profiles of Starch, PVAc, and starch-*g*-PVAc. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TGA results also prove grafting polymerization of VAc onto starch is carried out successfully.

RAFT polymerization is a powerful tool for constructing the well-defined polymers, and is a versatile tool to obtain functional micelles as well.[21] As starch and PVAc are hydrophilic and hydrophobic, respectively, the copolymer SVAc is amphiphilic and can self-assemble in aqueous to form micelle. Moreover, the aforementioned DS values indicate that the density of grafted PVAc side-chains is appropriate for the copolymers to exhibit amphiphilic nature. Therefore, SVAc obtained from SCTA-mediated RAFT polymerization of VAc is able to self-assemble into micelles in aqueous solution too. Figure 7 shows the formed micelles are regularly nanospheres. The self-assembly behavior of SVAc reveals its amphiphilicity and verifies the structure of the graft polymer once more. In addition, as shown in the previous work,[9] the controllable size of the side chain

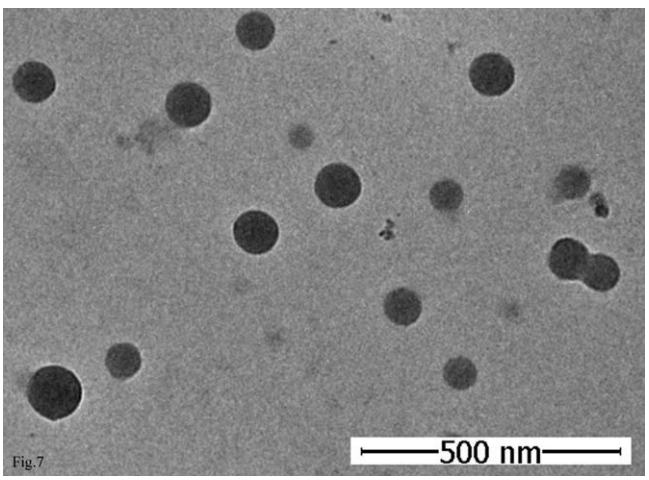


Figure 7 TEM image of starch-*g*-PVAc micelle (the concentration of the solution is 4×10^{-4} g/mL).

leads to the properties of starch-*g*-PVAc is tunable as well. The target of this article focuses on simplifying the synthesis procedure to generate a structure-exact SCTA and confirming that the obtained SCTA is able to control the grafting of PVAc onto starch. Therefore, the effect of PVAc chain-length on the properties of the copolymer is no longer repeated in this article.

CONCLUSIONS

A novel SCTA that possesses exact structure is synthesized via esterification and substitution reactions. Starch is directly applied as initial reactant and the reaction conditions of these two steps are facile. Evidently, such a route to prepare SCTA is practicable.

The obtained SCTA is used to conduct the controlled grafting of PVAc onto starch. The experimental results reveal that starch-*g*-PVAc with well-defined structure and composition is successfully prepared. Both the reaction conditions for preparing SCTA and RAFT polymerization such as the ratio of bromoacetyl bromide/AGU and polymerization time can be used to control the molecular weight of grafted side chain as well as the composition of SVAc. Notwithstanding SVAc is easily transferred into starch-*g*-PVA via saponification reaction,[8,22] the method present in this article is effective for combining the individual good properties of starch and PVA. This provides a convenient and useful way to develop starch-based materials for biomedical and other applications.

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