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Synthesis of amphiphilic ethyl cellulose grafting poly(acrylic acid) copolymers and their self-assembly morphologies in water

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Abstract

Amphiphilic ethyl cellulose (EC)-*g*-poly(acrylic acid) (PAA) copolymers were synthesized by atom transfer radical polymerization (ATRP). Firstly, ethyl cellulose macro-initiators with the degree of the 2-bromoisobutyryl substitution of 0.04 and 0.25 synthesized by the esterification of the hydroxyl groups remained in EC macromolecular chains and the 2-bromoisobutyryl bromides. Secondly, *tert*-butyl acrylate was polymerized by ATRP with the ethyl cellulose macro-initiator and EC-*g*-P*t*BA copolymers were prepared. Finally, the EC-*g*-PAA copolymers were prepared by hydrolyzing *tert*-butyl group of the EC-*g*-P*t*BA copolymers. The grafting copolymers were characterized by means of GPC, ^{1}H NMR and FTIR spectroscopies. The molecular weight of graft copolymers increased during the polymerization and the polydispersity was low. A kinetic study showed that the polymerization was first-order. Meanwhile, EC-*g*-PAA copolymers were self-assembled to micelles or particles with diameters of 5 nm and 100 nm in water (pH = 10) when the concentration was 1.0 mg/ml.

Keywords: Ethyl cellulose-*g*-poly(acrylic acid); ATRP; Self-assembly

1. Introduction

Cellulose is one of the inexpensive, biodegradable, renewable and the most abundant organic raw material and it has been widely studied during the past decades. Cellulose lacks some properties that synthetic polymers have in some applications although it has many useful properties. Modification of cellulose by graft copolymerization provides a significant route to alter the physical and chemical properties of cellulose materials.

Cellulose has been graft copolymerized using various techniques [1–4]. Most of them are based on a ''grafting-from'' process, where radical is formed along polymer backbone either by various chemical initiators or by irradiation, and then, the free radical polymerization of vinyl monomers occurs. In these methods, chain scission can occur and cellulose backbone is not kept intact. Also, the lengths of the grafting chains on the cellulose backbone and the distribution of the molecular weights of the side chains are unable to be controlled [5].

The controlled radical polymerization techniques developed in past decade may resolve intrinsic problems for the conventional radical polymerization. Atom transfer radical polymerization (ATRP) is one of the most broadly applied methods of

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controlled radical polymerization for its easy experimental setup, readily accessible and inexpensive catalysts (usually copper complexes of aliphatic amines, imines or pyridines), and simple initiators (alkyl halides) [6–10,36,37]. ATRP relies on the reversible reaction of low-oxidation-state metal complex with alkyl halide generating radicals and the corresponding high-oxidation-state metal complex with a coordinated halide ligand [11].

ATRP has been widely used for the synthesis of block, graft and star copolymers as well as polymers with more complex structures based on poly(methacrylate), polystyrene and their copolymers [12–19]. Carlmark [20] has applied ATRP methods to graft the cellulose fibers. Cellulose diacetate-*graft*-poly(methyl methacrylate) (CDA-*g*-PMMA), ethyl cellulose-*graft*-polystyrene (EC-*g*-PS) and ethyl cellulose-*graft*-poly(methyl methacrylate) (EC-*g*-PMMA) copolymers [21,22] have been synthesized in our laboratory.

The polymerizations of the amphiphilic copolymers are very valuable [23–25]. PAA is one of the most useful blocks in amphiphilic block polymers. It was used, for example, to prepare the shell-cross-linked (SCK) nanoparticles in an aqueous solution with amidation of the acrylic acid groups by cross-linking the polymer micelle peripheral layer [26,27]. The self-assembly morphologies of amphiphilic copolymers are also of interest in areas ranging from material science to biology.

If the hydrophilic PAA chains are grafted on the ethyl cellulose (EC) backbone, which is a hydrophobic polymer, a grafting copolymer with both hydrophobic and hydrophilic properties can be prepared. In this paper, the synthesis of amphiphilic EC-*g*-PAA copolymers by ATRP (Scheme 1) was studied. The process and kinetics of the ATRP polymerization were discussed and the aggregation of EC-*g*-PAA copolymers in water was investigated.

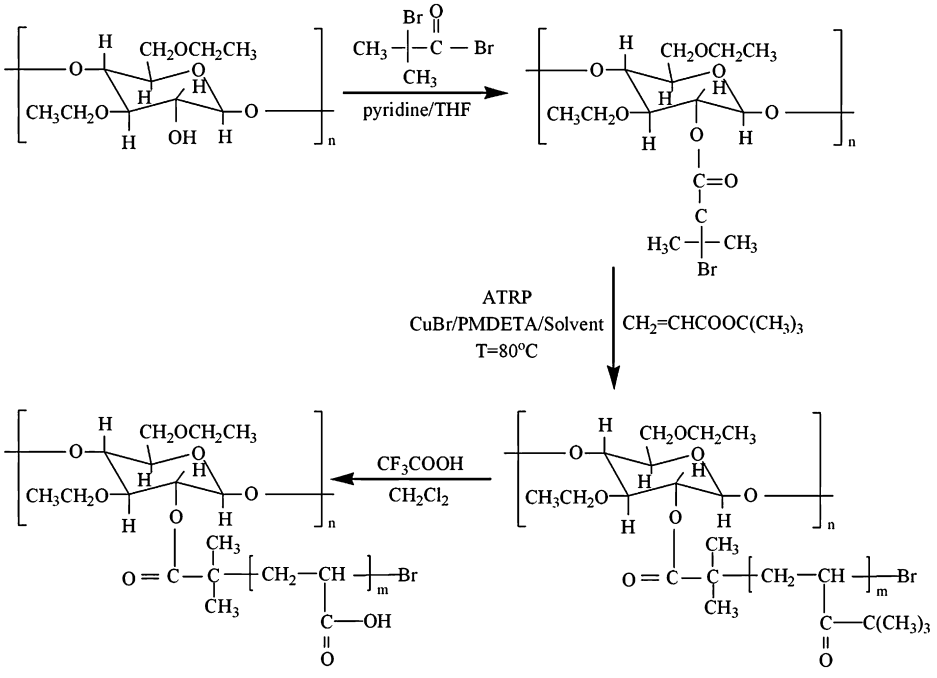
2. Experimental part

2.1. Materials

tert-Butyl acrylate (98%, Aldrich) (*t*BA) was distilled under reduced pressure before use. Ethyl cellulose (EC) (Luzhou Chemical Engineering Plant, Luzhou, China), with a degree of ethyl substitution of 2.1, was dried at 50 °C in vacuum for about two days. In order to remove copper(II), copper(I) bromide (CuBr) (Shanghai Zhenxing Chemical Regent Factory, Shanghai, China) was stirred in glacial acetic acid, filtered, and washed with acetone three times. The solid was dried in vacuum at room temperature overnight. Pyridine was dried over anhydrous magnesium sulfate and filtered prior to use. Toluene was distilled under reduced pressure. Cyclohexanone was dried with anhydrous magnesium sulfate and then filtered before use. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA) (98%, Aldrich), 2-bromoisobutyryl bromide (98%, Aldrich) and copper(II) bromide ($CuBr_2$) were used as received. All other solvents were dried by anhydrous magnesium sulfate.

2.2. Synthesis of the macro-initiator EC–Br

The preparation of the macro-initiator was carried out according to the literature [21]. Different degrees of substitution of Br for the macro-initiator were obtained by altering the ratio of 2-bromoisobutyryl bromide to EC. 2-Bromoisobutyryl bromide in 10 ml dry THF was added dropwise to a mixture of



Scheme 1. Synthesis of the EC-*g*-PAA copolymer.

EC and pyridine with 100 ml THF in a 500 ml three-necked round-bottom flask with stirring at 0 °C in an ice/water bath. When the dropping process was completed, the mixture was removed to an oil bath of 40 °C with stirring for 3 h. And then the reaction mixture was kept at room temperature for about 24 h. The bottom solution in the flask was cloudy and the upper was clear. The clear upper solution was removed and precipitated in distilled water for three times. Finally, the products were dried for seven days at 30 °C in vacuum.

2.3. Synthesis of EC-g-PtBA copolymer

The EC–Br macro-initiator (0.1111 g, 0.02 mmol of initiating sites) and PMDETA (0.0035 g, 0.02 mmol) were placed into a 100 ml three-necked round-bottom flask equipped with a magnetic stirring bar. After sealing it with a rubber septum, the flask was degassed and back-filled with nitrogen, which was repeated three times. Deoxygenated toluene (6.9 g, 75 mmol) and cyclohexanone (3 g, 30 mmol) were added to dissolve the EC–Br macro-initiator. After the EC–Br macro-initiator was dissolved, *tert*-butyl acrylate (9.6 g, 75 mmol) and CuBr (0.0030 g, 0.02 mmol) were added into the system. The mixed solution became light green. The reaction mixture was degassed by three freeze–pump–thaw cycles. After stirring for 10 min, the flask was immersed in an oil bath at 80 °C for concerned time. The polymerization was stopped by opening the mixture in air and diluted by THF. The catalysts were removed by passing the dilute polymer solution through alumina column. The polymer was precipitated by pouring the polymer solution into excess cold methanol, and the precipitate collected by filtration was dried in a vacuum at 40 °C for two days.

2.4. Hydrolysis of the EC backbone of EC-g-PtBA copolymers

EC-*g*-P*t*BA (0.2 g) copolymer was dissolved in 20 ml THF. After 1 ml 70% H_2SO_4 was added, the mixture solution was heated to boiling temperature and refluxed for 24 h. The residual polymer was participated in distilled water and dried in vacuum at 50 °C.

2.5. Preparation of EC-g-PAA copolymers

EC-*g*-P*t*BA (0.2 g) copolymer was dissolved in anhydrous THF (10 ml). Trifluoroacetic acid (TFA) (2 ml) was added and the mixture was stirred for 24 h, during which the poly(*tert*-butyl acrylate) side chains of EC-*g*-P*t*BA copolymers were hydrolyzed. The mixture was dried by evaporation and EC-*g*-PAA copolymers were obtained.

2.6. Characterization

Monomer conversion was obtained gravimetrically. Molecular weights and the molecular weight distribution of EC macro-initiators and graft copolymers were measured by gel permeation chromatography (GPC), on a system equipped with a Waters 515 pump, three columns (Styragel HR1, Styragel HR3, Styragel HT4) and a 2410 differential refractometer detector. The eluant was THF and the flow rate was 1 ml/min. Monodisperse polystyrene was used as the standard to generate the calibration curve. ^{1}H NMR analysis was carried out with a Bruker DMX 400 NMR spectrometer. FTIR spectra were recorded by a Bruker-Equinox 55 FT-TR spectrometer. Copolymers were dissolved in the solvent, and then copolymer films were obtained by casting the solution onto a NaCl plate for FTIR measurements. The copolymer film was dried in vacuum at room temperature for 24 h before measurements. Laser light scattering measurement was performed with a commercial spectrometer (AlV/SP-150 equipped with an ALV-5000 multi-τ digital time correlator) and a solid-state laser (ADLS DPY 425II, output power = 400 MW at $\lambda = 632$ nm) as the light source was used. The EC-*g*-PAA copolymers were dissolved in methanol and this was followed by the dropwise addition into distilled water (pH = 10, NaOH solution) with mild stirring until the concentration reached to 1.0 mg/ml. The solution was equilibrated for 30 min before measurements. The hydrodynamic radius (R_h) of the graft copolymers in the solution was measured with dynamic light scattering (DLS) at 90°. Atom force microscopy (AFM) images were collected with a Nanoscope III multimode atomic force microscope (Veeco Metrology Group) in the tapping mode (set point ratio = 0.7–0.9). Silicon tips on cantilevers (resonance frequency = 300 kHz) with a spring constant of 32 N m^{-1} were used. The scanning rate was in the range of 0.5–1.0 Hz. The samples of AFM measurements were prepared by 50 μl of the solution spinning coated on a cleaved freshly mica surface and the solvent was evaporated at the room temperature in vacuum.

3. Results and discussion

3.1. Synthesis of EC–Br macro-initiator

The remaining OH functionality on the ethyl cellulose (EC) chains can be used to introduce other functionality through conventional organic reactions, such as α-haloether group to initiate ATRP. Thus the hydroxyl group on EC was converted into α-bromoisobutyrate group by the reaction with 2-bromoisobutyryl bromides in the presence of pyridine in THF at 0 °C. As shown in Fig. 1, the FTIR spectrum reveals the appearance

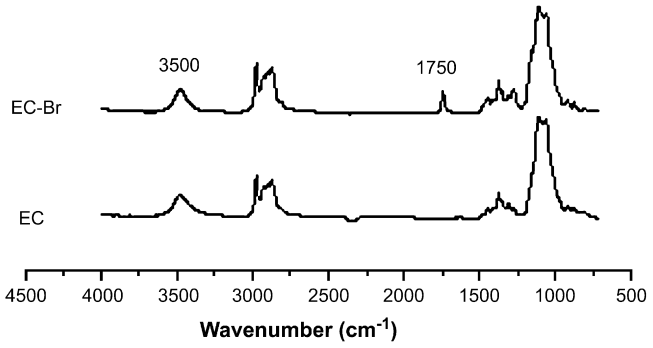


Fig. 1. FTIR spectra of EC and EC–Br macro-initiator with Ds = 0.04.

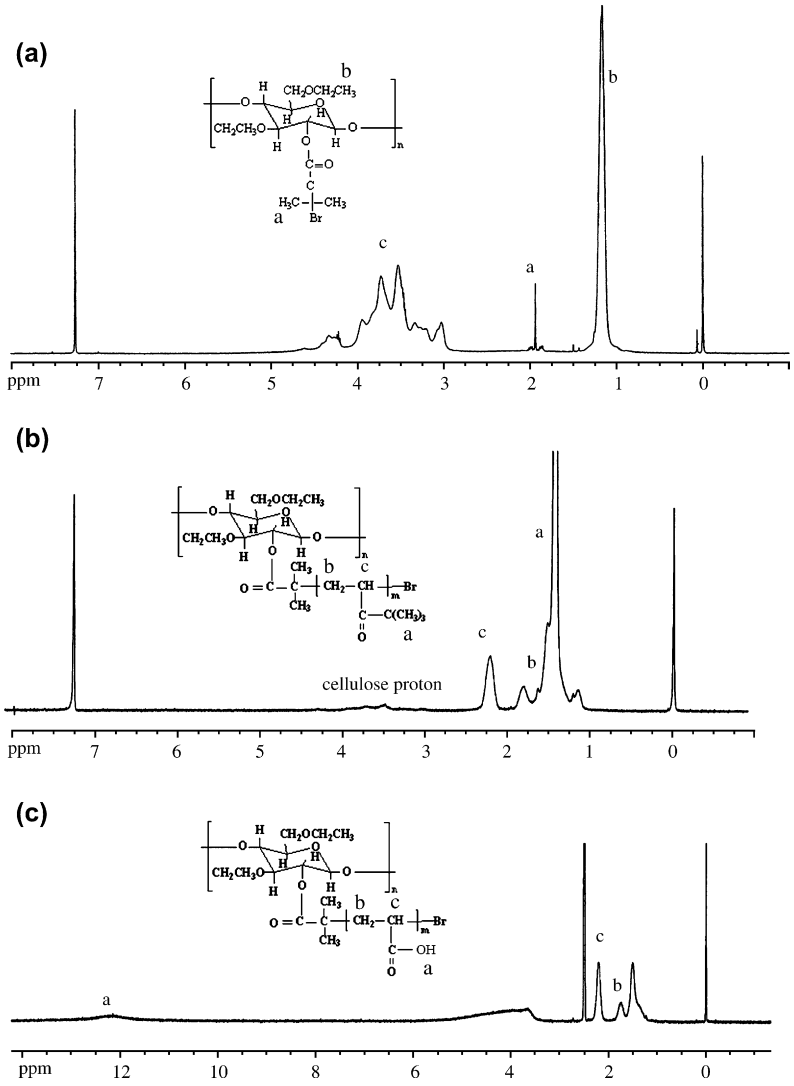


Fig. 2. ^{1}H NMR spectra of: (a) EC−Br macro-initiator with Ds = 0.04 in $CDCl_3$; (b) EC-*g*-P*t*BA in $CDCl_3$; (c) EC-*g*-PAA in DMSO-d_6 (the example of b is the product of reaction 0.5 h in G1 and the example of c is the hydrolysis product of b by hydrolyzing the *tert*-butyl group on the P*t*BA block).

of the characteristic C═O stretching vibration of the ester at 1750 cm^{-1}. This means that the 2-bromoisobutyryl group is introduced into EC chains.

The substitution of the hydroxyl groups on the EC backbone with 2-bromoisobutyryl groups is further confirmed by ^{1}H NMR (Fig. 2a). The ^{1}H NMR spectrum of the resulting product reveals the presence of a new single peak at $\delta = 1.85$ ppm (peak a) for methyl protons in the ester group ($-(CH_3)_3Br$), a single peak at $\delta = 1.28$ ppm (peak b) for methyl protons in ethyl group ($-CH_2CH_3$) and the multiple peaks at $\delta = 3.0-5.0$ ppm (peak c) for the methylene protons and hydrogen protons in the glucose. By comparing the integral area of the peak *a* with that of the peak *b*, the substitution degree of the 2-bromoisobutyryl group for the EC−Br macro-initiator can be calculated and it is 0.04 for the sample in Fig. 2a.

As reported in our previous work [22], the substitution degree of the bromoisobutyryl group can be controlled by altering the ratio of the 2-bromoisobutyryl bromide to the EC in the reaction system. The preference for substitution at C-6-OH on the glucose unit of the EC has been observed [28]. For ethyl cellulose with the degree of the substitution of 2.1, the bromoesterification should mainly occur at C-2-OH or C-3-OH position. Two EC−Br macro-initiators with different substitution degrees of the 2-bromoisobutyryl group (Ds = 0.04 and 0.25) were prepared in this work.

3.2. Synthesis of EC-g-PtBA via ATRP

tert-Butyl acrylate (*t*BA) can be polymerized using CuBr complexed by using *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as the catalyst and EC−Br macro-initiator as the initiator in toluene/cyclohexanone mixed solvent. Acidic monomers are usually unable to be polymerized by ATRP due to a side reaction of the monomer with the metal complex and quaternization of the nitrogen ligands [29] and the protected derivative of the acidic monomers, *tert*-butyl

Table 1
The ATRP of EC-*g*-P*t*BA

	EC−Br_{Ds} [a]	[Monomer][initiator]/[CuBr]/[PMDETA]	T (°C)	$M_n \times 10^5$ [b]	M_w/M_n [b]
G1	0.04	3750:1:2:2	80	3.04	1.56
G2	0.25	300:1:1:1	80	2.00	2.0

[a] EC−Br_{Ds} means the degree of the Br substitution, and 0.04 is one initiating site for every 25 glucose rings and 0.25 is one initiating site for every four glucose rings.
[b] The results of GPC of EC-*g*-P*t*BA.

acrylate can be used to prepare grafting copolymers. Toluene is usually used as the solvent to synthesize poly(*tert*-butyl acrylate) as one block in diblock or triblock polymerization [30–32,38]. PMDETA is commercially available and is much less expensive than bi-pyridine derivatives. Graft polymerization in the presence of multidentate alkyl amino ligands proceeds at faster rates and lower temperature [33]. ATRP catalysts are not easy to be dissolved in non-polar solvent systems. Increasing the polarity of the solvent can affect the solubility of the catalyst. Cyclohexanone, which is a good solvent for the EC−Br macro-initiator [34], is added into the system to increase the solubility of the EC−Br macro-initiator.

It is well known that ethyl 2-bromoisobutyrate is an excellent initiator for ATRP with a high-initiating efficiency. Therefore, the previously synthesized EC−Br macro-initiator with different degrees of the Br substitution can be used to initiate ATRP of *t*BA to prepare EC-*g*-P*t*BA copolymers. The macro-initiators with the degree of the Br substitution of 0.04 that is one initiating site for every 25 glucose rings and 0.25 that is one initiating site for every four glucose rings have been used to initiate the polymerization of *t*BA. The proper systems in Table 1 were selected. In particular, because of densely initiating site of the macro-initiator G2, the radical−radical coupling termination occurs much more than the general ATRP in this reaction [35]. Therefore, the less mole ratio of monomer to initiator should be used to keep a dilute reactive mixture. Besides the dilute reactive mixture, 5% excess of $CuBr_2$ relative to CuBr should be added into the reactive mixture to make the reaction rate moderate, which has been found to bring the best results [12]. The temperature of the polymerization was 80 °C. The GPC spectra of the EC−Br macro-initiator and the EC-*g*-P*t*BA grafting copolymer are shown in Figs. 3a and 4a. It is clearly exhibited that the molecular weight shifts to the high-molecular weight after the polymerization. The polydispersity of the copolymer is also lower than that of the EC−Br macro-initiator. Meanwhile, in order to hydrolyze the EC backbone and gain the P*t*BA graft chains, the last two examples were hydrolyzed in the mixture solution of 70% H_2SO_4 and THF at boiling point for 24 h [21]. The residual polymer was measured by GPC (Figs. 3b and 4b) and it is shown that the polydispersities of copolymers are very low.

The "livingness" of atom transfer radical polymerization process can be ascertained from a semilogarithmic plot with

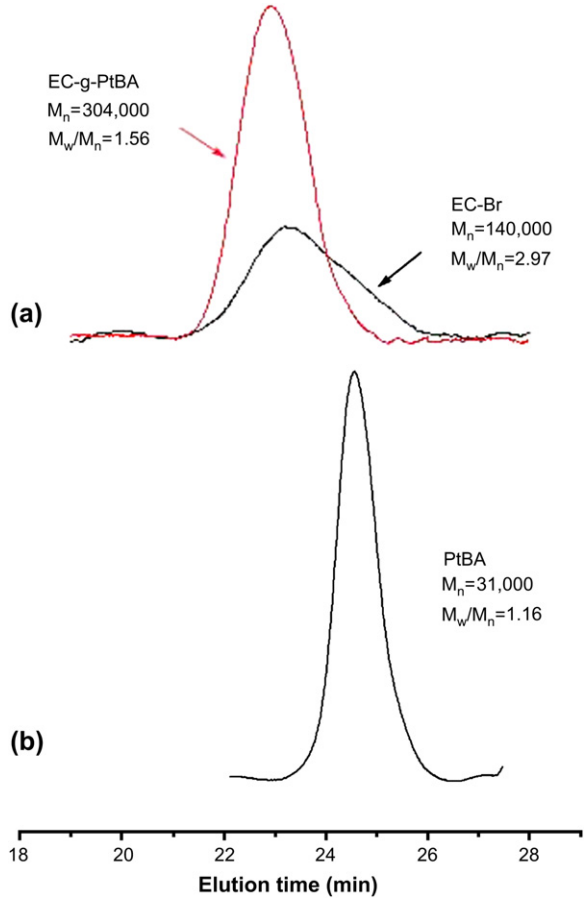


Fig. 3. GPC traces of: (a) EC−Br and EC-*g*-P*t*BA; (b) P*t*BA in G1.

the linear first-order kinetics, which reflects the constant concentration of propagating radicals. Semilogarithmic plots of the monomer conversion versus the reaction time for *t*BA copolymerization with different degrees of Br substitution

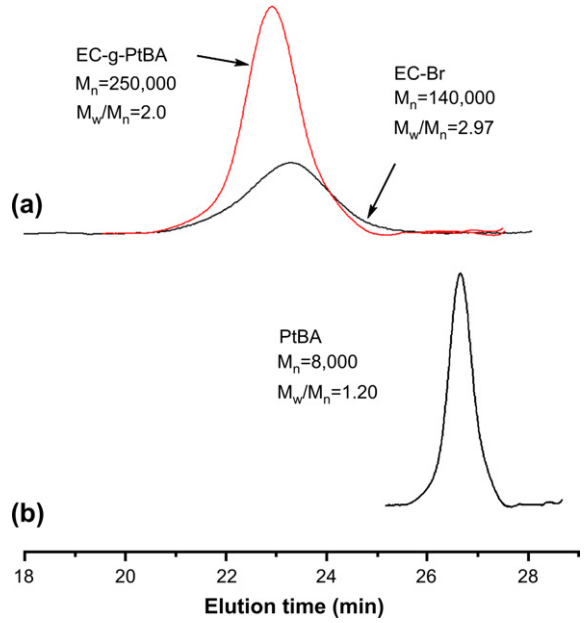


Fig. 4. GPC traces of: (a) EC−Br and EC-*g*-P*t*BA; (b) P*t*BA in G2.

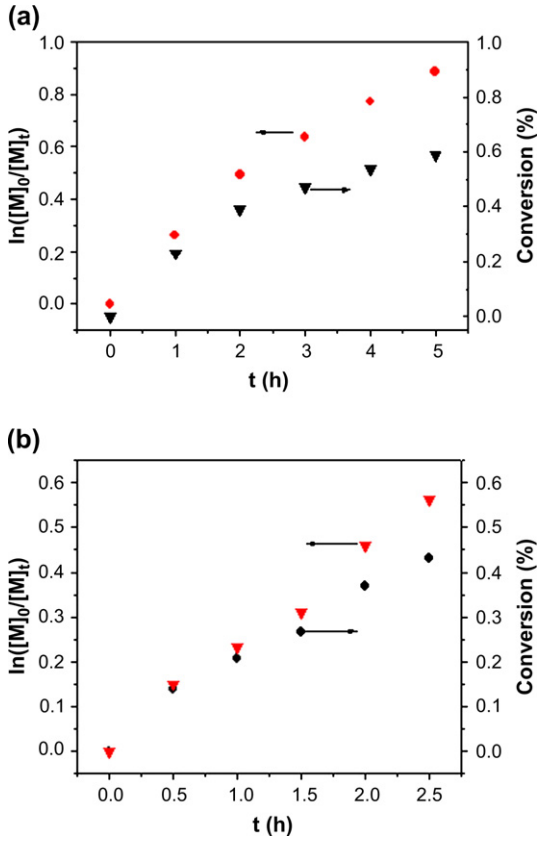


Fig. 5. The variation of $\ln([M]_0/[M]_t)$ with the time in the graft copolymerization of EC−Br with *t*BA: (a) G1 and (b) G2.

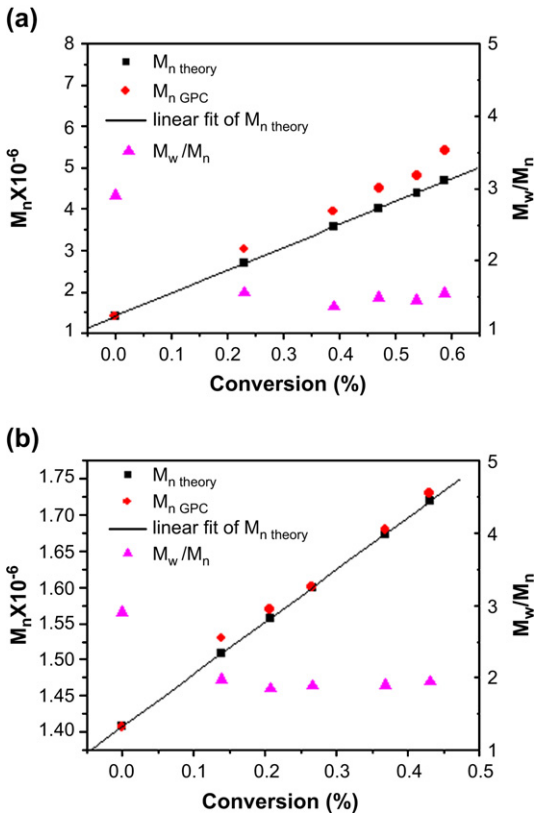


Fig. 6. The variation of M_n and M_w/M_n of EC−Br macro-initiator and EC-*g*-P*t*BA graft copolymer with the monomer conversion: (a) G1 and (b) G2.

of EC−Br macro-initiator are shown in Fig. 5. The variation of $\ln([M]_0/[M]_t)$ is linear with time, where $[M]_0$ is the initial monomer concentration and $[M]_t$ is the monomer concentration at time *t*, which indicates that the polymerization is of first-order with respect to the monomer. That is, the concentration of the growing radical species in the system is constant during the polymerization. Fig. 6 shows the variation of $M_{n\ theory}$, $M_{n\ GPC}$ and M_w/M_n versus monomer conversion during the polymerization of two examples. The molecular weight of the graft copolymer is increased with the monomer conversion and the variation of the molecular weight with the monomer conversion is closed to the theoretical forecast. It can also be observed that the polydispersity is decreased after the grafting polymerization. These results confirm again that the graft copolymerization is living and controlled.

The FTIR spectrum of the P*t*BA graft copolymer (Fig. 7) illustrates the occurrence of the grafting copolymerization and in the spectrum the peak at 1730 cm^{-1} that is assigned to the stretching absorption of the carbonyl group on the graft chains, is obvious. The ^1H NMR spectrum of the EC-*g*-P*t*BA copolymer is shown in Fig. 2b. The remarkable feature of the spectrum of the EC-*g*-P*t*BA graft copolymer is the absence of the resonance at $\delta = 1.85$ ppm for methyl protons in the ester group ($-(CH_3)_3Br$). This demonstrates that all $-C(CH_3)_2Br$ bonds are disassociated to initiate the polymerization. The cellulose protons at $\delta = 3.0-4.8$ ppm in macro-initiator are clearly observed. The resonance at $\delta = 1.45$ ppm is assigned to the methyl proton of *tert*-butyl group in *t*BA and that at $\delta = 1.27$ ppm is assigned to the methyl proton of $-C(CH_3)_2-$ in macro-initiator.

3.3. Synthesis of EC-g-PAA copolymers

EC-*g*-PAA was prepared by the hydrolysis of the *tert*-butyl group on the P*t*BA block according to the methods described

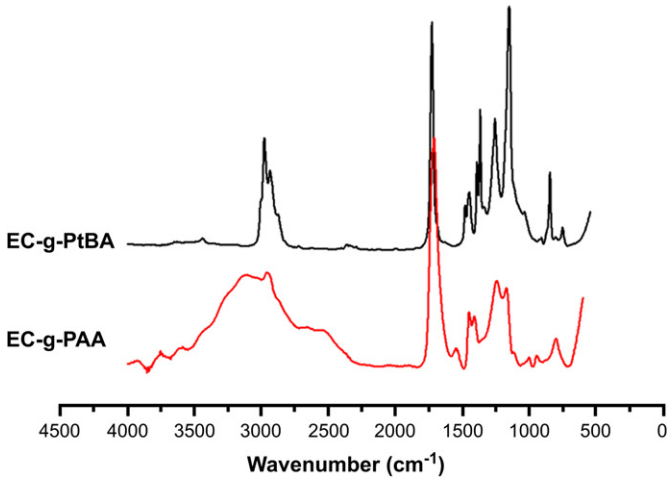


Fig. 7. FTIR spectra of EC-*g*-P*t*BA and EC-*g*-PAA.

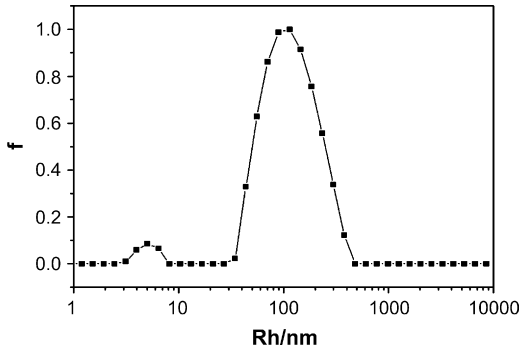


Fig. 8. Hydrodynamic radius distribution of the aggregates of $EC_{0.25}$-*g*-PAA_{13} in the solution with the concentration of 1.0 mg/ml by dynamic light scattering (DLS) at a scattering angle of 90°.

in Section 2. FTIR spectrum in Fig. 7 shows the characterization of the EC-*g*-PAA copolymers after hydrolysis. There is a strong carboxyl peak at 1714 cm^{-1} in the FTIR spectrum. A wide peak between 3200 and 2800 cm^{-1} ascribed to the associating hydroxyl of the carboxyl exists. In addition, the stretching vibration peak of the *tert*-butyl group at 1400 cm^{-1} disappears after hydrolysis, which indicates that complete hydrolysis occurs. Meanwhile, the ^1H NMR spectrum of the product gives more evidence for the hydrolysis of the EC-*g*-P*t*BA copolymers. In Fig. 2c, the resonance at $\delta = 1.45$ ppm that is assigned to the methyl proton of the *tert*-butyl group in the P*t*BA side chains disappears and that at $\delta = 12.1$ ppm that is assigned to the proton of hydroxyl group comes out. The results of the characterization of the products confirm that amphiphilic EC-*g*-PAA copolymers are obtained after the hydrolysis of the *tert*-butyl group on the P*t*BA side chains of EC-*g*-P*t*BA copolymers.

3.4. Self-assembly behavior of EC-g-PAA

$EC_{0.25}$-*g*-PAA_{13} grafting copolymers with the grafting density of 0.25 and the graft-chain lengths of 13 constitutional units were used to prepare the grafting copolymer solutions and the aggregation of copolymers in the solution was studied. The detailed process has been described in Section 2.6. The results of the dynamic light scattering (DLS) show that EC-*g*-PAA copolymers can be self-assembled to micelles or particles with the diameter of 5 nm and 100 nm in water (pH = 10) when the concentration is 1.0 mg/ml (Fig. 8), which means that the copolymers are self-assembled to aggregates with a single molecular chain and with many chains, respectively. Moreover, AFM images in Fig. 9 show the spherical morphologies of the aggregates of EC-*g*-PAA copolymers after the solution is spinning coated on freshly cleaved mica surface and the solvent is evaporated at the room temperature in vacuum. The diameter of the sphere in the AFM observation is less than that in the DLS measurement because of the shrinkage of EC-*g*-PAA copolymer chains during the evaporation of the solvent. It is suggested, therefore, that the amphiphilic EC-*g*-PAA grafting copolymers can be self-assembled in the solution and the copolymer chains are self-assembled to the particles with both single chain and multi-chains, the diameter of which is different.

4. Conclusions

Ethyl cellulose macro-initiator was prepared by the reaction of the residual hydroxyl group of ethyl cellulose with 2-bromoisobutyryl bromide. The GPC, ^1H NMR and FTIR measurements indicate that macro-initiator with degree of Br substitution of 0.04 and 0.25 can successively initiate the atom transfer radical polymerization of *tert*-butyl acrylate. The kinetic study confirms that the grafting polymerization is living and controlled. Finally, amphiphilic EC-*g*-PAA copolymers were prepared by hydrolyzing the *tert*-butyl group on the poly(*tert*-butyl acrylate) side chains of the EC-*g*-P*t*BA copolymers. The amphiphilic EC-*g*-PAA graft copolymer chains can form the particles with both single grafting copolymer chains and multi-grafting copolymer chains in water.

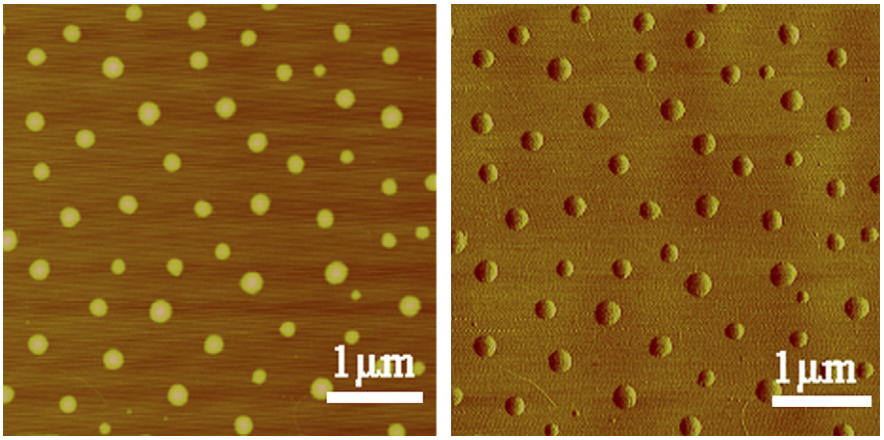


Fig. 9. AFM images of the $EC_{0.25}$-*g*-PAA_{13} copolymer aggregation on mica: height image (left) and phase image (right).

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