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Surface-initiated atom transfer radical polymerization from chitin nanofiber macroinitiator film

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ABSTRACT

This paper reports the preparation of chitin nanofiber-*graft*-poly(2-hydroxyethyl acrylate) (CNF-*g*-polyHEA) films by surface-initiated atom transfer radical polymerization (ATRP) of HEA monomer from a CNF macroinitiator film. First, a CNF film was prepared by regeneration from a chitin ion gel with an ionic liquid. Then, acylation of the CNF surface with α-bromoisobutyryl bromide was carried out to obtain the CNF macroinitiator film having the initiating moieties (α-bromoisobutyrate group). The surface-initiated graft polymerization of HEA from the CNF macroinitiator film by ATRP was performed to produce the CNF-*g*-polyHEA film. The IR, XRD, and SEM measurements of the resulting film indicated the progress of the graft polymerization of HEA on surface of CNFs. The molecular weights of the grafted polyHEAs increased with prolonged polymerization times, which affected the mechanical properties of the films under tensile mode.

1. Introduction

Polysaccharides are widely distributed in nature and have been regarded as structural materials and as suppliers of energy (Schuerch, 1986). Because of better recent understanding of their possessing unique structures and properties, much attention has been paid to them as material sources. Of the many kinds of polysaccharides, chitin, which is an aminopolysaccharide composed of *N*-acetyl-D-glucosamine residues linked through β-(1→4)-glycosidic bonds, is one of the most abundant polysaccharides in nature and occurs mainly in exoskeletons of crustaceans, shellfish, and insects (Kurita, 2006; Muzzarelli, 2011; Pillai, Paul, & Sharma, 2009; Rinaudo, 2006). However, it still remains mostly as an unutilized biomass resource primary because of its intractable bulk structure and insolubility in water and common organic solvents. Therefore, research concerning conversion of chitin into various useful bio-based materials after proper dissolution of it in suitable solvents has attracted much attention even in recent years.

To efficiently provide new chitin-based materials, we have focused on ionic liquids, which are low-melting point salts that form liquids at temperatures below the boiling point of water. Since it was reported that 1-butyl-3-methylimidazolium chloride of an ionic liquid dissolved cellulose in relatively high concentrations (Swatloski, Spear, Holbrey, & Rogers, 2002), various ionic liquids have been used as good solvents for the derivatization and material processing of cellulose (Feng & Chen, 2008; Liebert & Heinze, 2008; Pinkert, Marsh, Pang, & Staiger, 2009; Zakrzewska, Lukasik, & Lukasik, 2010). However, only the limited investigations have been reported regarding the dissolution of chitin with ionic liquids (Bochek et al., 2012; Jaworska, Kozlecki, & Gorak, 2012; Muzzarelli, 2012; Qin, Lu, Sun, & Rogers, 2010; Wang, Zhu, Wang, Huang, & Wang, 2010; Wu, Sasaki, Irie, & Sakurai, 2008). We also found that an ionic liquid, 1-allyl-3-methylimidazolium bromide (AMIMBr), dissolved or swelled chitin to form weak gel-like materials (ion gels) (Prasad et al., 2009; Yamazaki et al., 2009). By using AMIMBr as a solvent, acetylation of chitin using acetic anhydride produced an acetylated chitin with a high degree of substitution (DS) under selected conditions (Mine, Izawa, Kaneko, & Kadokawa, 2009). Furthermore, this reaction manner, *i.e.*, the esterification of hydroxy groups in chitin in the AMIMBr solvent was employed to introduce initiating moieties for atom transfer radical polymerization (ATRP) attached through ester linkages on chitin. Then, grafting of styrene from the resulting macroinitiator *via* ATRP was performed to produce a chitin-*graft*-polystyrene (Yamamoto, Yoshida, Mine, & Kadokawa, 2013). ATRP is a robust and versatile technique to accurately control chain length and polydispersity of the resulting

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polymers, and thus has been used to synthesize a wide range of copolymers with the controlled structure, unit length, and block sequence (Kamigaito, Ando, & Sawamoto, 2001; Matyjaszewski, 2012).

On the other hand, graft copolymers based on a chitin nanofiber (CNF) film have been prepared by us. In the previous study, we reported that CNF film was facilely obtained by regeneration from the aforementioned chitin ion gel with AMIMBr in methanol, followed by filtration (Fig. 1a) (Kadokawa, Takegawa, Mine, & Prasad, 2011; Tajiri, Setoguchi, Wakizono, Yamamoto, & Kadokawa, 2013). Approaches to the production of nanofibers from chitin have often been performed upon top-down procedures that break down the starting bulk materials from native chitin resources (Fan, Saito, & Isogai, 2008; Ifuku & Saimoto, 2012; Zeng, He, Li, & Wang, 2012). Our method applies a completely different approach from the above to produce CNFs, that accords to a self-assembling generative (bottom-up) route. We have continuously studied surface-initiated graft polymerization approach from the CNF film to prepare new chitin-based materials. For example, we performed the surface-initiated ring-opening graft copolymerization of L-lactide (LA)/ε-caprolactone (CL) from the CNF film to produce a environmentally benign composite material because the ring-opening copolymerization is initiated from a hydroxy group and has been known to efficiently produce a biodegradable and biocompatible poly(LA/CL) (Setoguchi, Yamamoto, & Kadokawa, 2012). Recently, the surface-initiated grafting technique from the CNF film was extended to use a synthetic polypeptide as another biocompatible polymer. Because it has been well-known that synthetic polypeptides with well-defined structures are synthesized by ring-opening polymerization of α-amino acid *N*-carboxyanhydride (NCA) accompanied with decarboxylation initiated from amino groups, we reported the surface-initiated graft polymerization of NCA from amino initiating groups on surface of a partially deacetylated CNF film to give a CNF-*graft*-polypeptide film (Kadokawa, Setoguchi, & Yamamoto, 2013). By free radical polymerization approach, grafting of acrylic acid on CNFs, which were prepared by the aforementioned top-down procedure, was also carried out with potassium persulfate as a initiator, where radicals are formed along the chitin back-bone, followed by the progress of free radical propagation (Ifuku, Iwasaki, Morimoto, & Saimoto, 2012).

In this paper, on the basis of the above previous investigations, we report the preparation of CNF-*graft*-poly(2-hydroxyethyl acrylate) (CNF-*g*-polyHEA) films by the surface-initiated grafting technique *via* ATRP using a CNF macroinitiator film. The CNF macroinitiator film for ATRP was first prepared by introduction of the initiating moieties attached through ester linkages on CNF surfaces. Then, the surface-initiated graft polymerization of HEA from the CNF macroinitiator film by ATRP was performed under the appropriate conditions to produce the CNF-*g*-polyHEA films. To the best of our knowledge, this is the first example of the surface-initiated ATRP from CNF materials. Because the present surface-initiated ATRP technique using the CNF macroinitiator film has a potential to employ various monomers, we are convinced that the present approach will contribute to the development of practical chitin-based composite materials in the future.

2. Experimental

2.1. Materials and methods

Chitin powder from crab shells was purchased from Wako Pure Chemical Industries, Ltd., Japan. The weight-average molecular weight value of the chitin sample was estimated by viscometric analysis to be 7×10^5 (Poirier & Charlet, 2002). An ionic liquid, AMIMBr, was prepared by reaction of 1-methylimidazole with 3-bromo-1-propene according to the method adapted from the literature procedure (Zhao et al., 2005). All other reagents and solvents were used as received from commercial sources. IR spectra were recorded with samples in KBr using a SHIMADZU FTIR-8400 spectrometer. The powder X-ray diffraction (XRD) measurements were conducted using a PANalytical X'Pert Pro MPD with Ni-filtered CuKα radiation (λ = 0.15418 nm). The SEM images were obtained using Hitachi S-4100H electron microscope. The energy-dispersive X-ray spectroscopy was performed using a Philips XL30 CP scanning electron microscope (SEM-EDX). ^{1}H NMR spectrum was recorded on a JEOL ECX 400 spectrometer. GPC measurement was performed with two Shodex GPC KF-804L and KF-803L columns and equipped with HITACHI pump L-2130 connected to HITACHI RI detector L-2490. Chloroform was used as the eluent at a flow rate of 1.0 mL min^{-1}. The calibration was established with polystyrene standards. The stress–strain curves were measured using a tensile tester (Little Senster LSC-1/30, Tokyo Testing Machine).

Table 1
Surface-initiated ATRP of HEA from CNF macroinitiator films with different DSs under conditions of different reaction times.[a]

Entry	DS	Time/h	Yield/mg	Conversion of HEA/%[b]
1	0.61	3	52	6
2	0.61	6	65	13
3	0.61	12	161	51
4	0.61	24	216	71
5	0.20	24	68	68
6	0.30	24	143	71

[a] A feed amount of chitin macroinitiator film was 34 mg (0.17 mmol, DS; 0.20, 0.30, and 0.61). Reaction conditions; [Initiating site]/[HEA]/[Bpy]/[CuBr] = 1/20/4/2, Temp.; 60 °C.
[b] Estimated by the weight increases of the products from the CNF macroinitiator film.

2.2. Preparation of chitin macroinitiator film

First, the preparation of CNF film was conducted according to the method reported in our previous publication (Kadokawa et al., 2011). Chitin powder (0.125 g, 0.61 mmol) was immersed in AMIMBr (1.0 g, 4.9 mmol) at room temperature for 24 h, followed by heating the mixture at 100 °C for 24 h to give a chitin/AMIMBr ion gel. After methanol (40 mL) was added to the gel and the system was left standing at room temperature for 24 h, the mixture was sonicated for 5 min to give a chitin dispersion. Then, the dispersion was subjected to filtration and a residue was dried under reduced pressure to give a film. The film was subjected to Soxhlet extraction with methanol (70 mL) for 5 h, followed by drying under reduced pressure to give a CNF film. A typical procedure for the synthesis of the CNF macroinitiator film was as follows (entries 1–4, Table 1; DS = 0.61). For the pre-treatment of the resulting CNF film (49 mg, 0.24 mmol/unit), it was immersed in 3.2 wt% LiCl/*N*,*N*′-dimethylacetamide (DMAc) solution (5 g) and the mixture was heated at 80 °C for 14 h. Then, the solution was removed and the film was washed with DMAc. After the pre-treated CNF film was immersed in DMAc (1.0 mL) and α-bromoisobutyryl bromide (1.73 g, 7.6 mmol; 30 equiv. for a unit of chitin) and pyridine (96 mg, 1.2 mmol; 5 equiv. for a unit of chitin) were added to the mixture, it was heated at 60 °C for 24 h. The film was taken out, subjected to Soxhlet extraction with methanol for 6 h, and dried under reduced pressure at 60 °C for 24 h to produce a CNF macroinitiator film (44 mg, DS = 0.61 by SEM-EDX analysis). By the same acylation procedure using 10 and 20 equiv. of α-bromoisobutyryl bromide, CNF macroinitiator films with DSs = 0.20 and 0.30 were prepared.

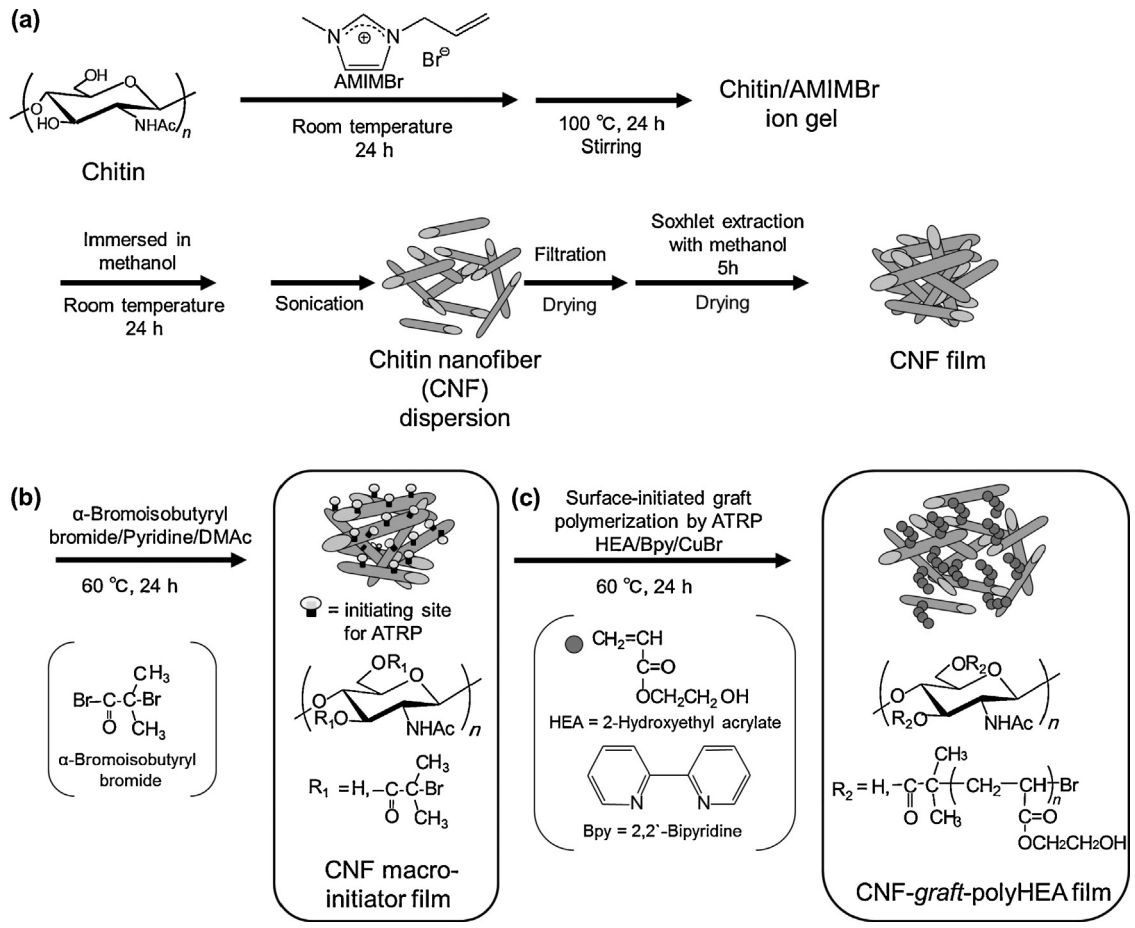


Fig. 1. Procedures for preparations of (a) CNF film through chitin ion gel with AMIMBr, (b) chitin macroinitiator film, and (c) CNF-*graft*-polyHEA film *via* surface-initiated ATRP.

2.3. Surface-initiated ATRP of HEA from CNF macroinitiator film

A typical experimental procedure for the surface-initiated ATRP was as follows (entry 4, Table 1). For the pre-treatment of the CNF macroinitiator film (34 mg, 0.17 mmol, DS = 0.61), it was immersed in 3.0 wt% LiCl/DMAc solution (5 g) and the mixture was heated at 80 °C for 48 h. Then, the film was taken out and subjected to Soxhlet extraction with methanol for 15 h. Then, HEA (254 mg, 2.20 mmol; 20 equiv. for an initiate site), 2,2′-bipyridine (Bpy) (70 mg, 0.45 mmol; 4 equiv. for an initiate site) and copper(I) bromide (CuBr) (33 mg, 0.23 mmol; 2 equiv. for an initiate site) were added to the pre-treated mixture, it was heated at 60 °C for 24 h under argon. After water was added to the reaction mixture and the solution was filtered off, the film was washed successively with methanol and acetone, and dried under reduced pressure to produce a CNF-*g*-polyHEA film (216 mg) in 71% yield.

2.4. Separation and methyl esterification of grafted polyHEAs on CNF Films

A mixture of the CNF-*g*-polyHEA film (46 mg, entry 4, Table 1) with 5.0 mol/L NaOH aqueous solution (5.0 mL) was heated at 60 °C for 18 h. After the insoluble residue was filtered off, the filtrate was diluted with water and treated with cation-exchange resin (Dowex™ 50 W H^+ form) at room temperature. The resin was removed by filtration and the filtrate was concentrated and dried under reduced pressured at 60 °C for 8 h. The obtained product (24 mg) was dispersed in a mixed solvent of THF/methanol (1/3 v/v). After trimethylsilyldiazomethane (0.5 mL, 0.3 mmol) was added to the dispersion, the mixture was stirred at room temperature for 15 h under nitrogen. The reaction mixture was diluted with water and extracted with chloroform. After the insoluble material present in the chloroform layer was removed by filtration, the filtrate was dried over anhydrous Na_2SO_4 and concentrated. Then, the concentrated solution was poured into a large amount of hexane to precipitate the product. The precipitate was isolated by filtration, and dried under reduced pressure at 60 °C for 8 h to give poly(methyl acrylate) (6 mg); ^{1}H NMR ($CDCl_3$) δ 1.31–2.46 (br, —CH_2—CH—, 3 H), δ 3.60 (br, —CH_3, 3H). The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the product were estimated by the GPC measurement with chloroform as the eluent.

3. Results and discussion

As previously reported by us, the CNF film was obtained through the gelation of chitin with AMIMBr, followed by regeneration in methanol and filtration according to Fig. 1a. The CNF macroinitiator film having the initiating moieties (α-bromoisobutyrate group) was prepared by acylation on the CNF surface with α-bromoisobutyryl bromide as shown in Fig. 1b. To promote the solid–liquid reaction, the CNF film was first pre-treated in 3.2 wt% LiCl/DMAc solution. Then, the pre-treated CNF film was reacted with 10, 20, and 30 equiv. of α-bromoisobutyryl bromide for a repeating unit of chitin in the presence of pyridine in DMAc. Then, the structure and the presence of the initiating moieties of the obtained film were evaluated by the IR, XRD, SEM, and SEM-EDX analyses. Fig. 2b shows the IR spectrum of the product obtained

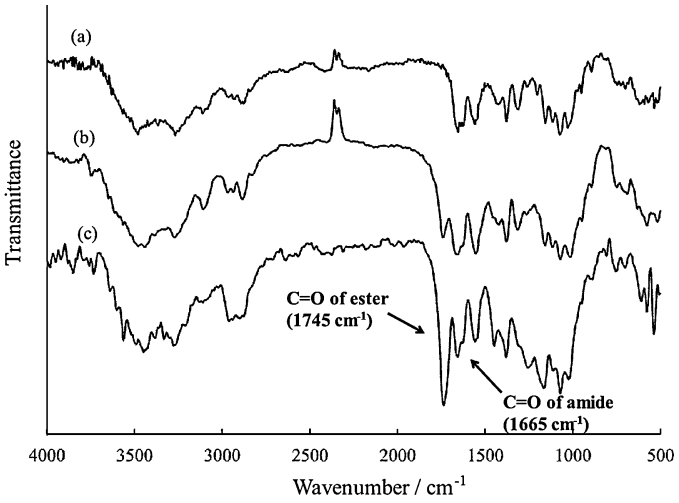


Fig. 2. IR spectra of (a) CNF film, (b) CNF macroinitiator film (30 equiv. of α-bromoisobutyryl bromide), and (c) CNF-*g*-polyHEA film (entry 4, Table 1).

using 30 equiv. of α-bromoisobutyryl bromide for a repeating unit of chitin in comparison with that of the CNF film (Fig. 2a). In addition to the carbonyl absorption at 1665 cm^{-1} due to acetamide, the detection of that at 1745 cm^{-1} due to ester suggested the presence of the initiating moieties in the product. The XRD profile of the product (Fig. 3b) showed typical four diffraction peaks at around 9.5°, 19.5°, 20.5°, and 23.4° assignable to 0 2 0, 1 1 0, 1 2 0, and 1 3 0 planes, respectively, of the antiparallel α-chitin arrangement and the pattern was same as that of the original CNF film (Fig. 3a). These results indicated the crystalline structure of α-chitin in CNFs was still maintained even after the acylation, indicating the introduction of the initiating moieties on surface of CNFs with remaining the nanofiber morphology. The SEM images of the produced films further revealed remaining the nanofiber morphology as seen in Fig. 5a (30 equiv. of α-bromoisobutyryl bromide). The SEM-EDX spectra of the products also suggested the presence of the initiating moieties (α-bromoisobutyrate group) on the film surface, because signals assignable to C, O, and Br elements were observed. By comparison of the signal intensities of the O and Br elements, the DS values on the film surfaces of the products obtained using 10, 20, and 30 equiv. of α-bromoisobutyryl bromide were calculated to be 0.20, 0.30, and 0.61, respectively.

Then, the surface-initiated graft polymerization of HEA from the CNF macroinitiator film *via* ATRP was performed to produce the

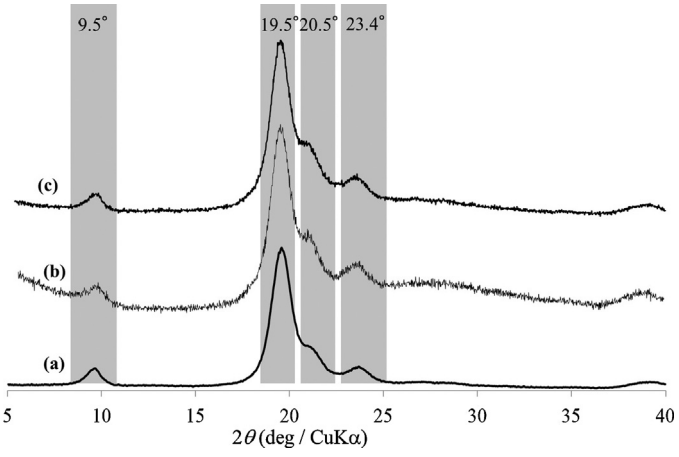


Fig. 3. XRD patterns of (a) CNF film, (b) CNF macroinitiator film and, (c) CNF-*g*-polyHEA film (entry 4, Table 1).

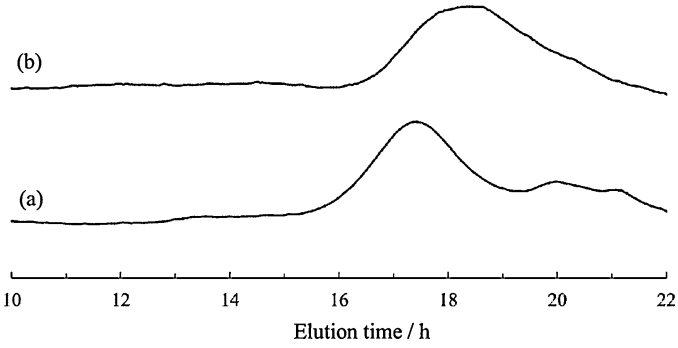
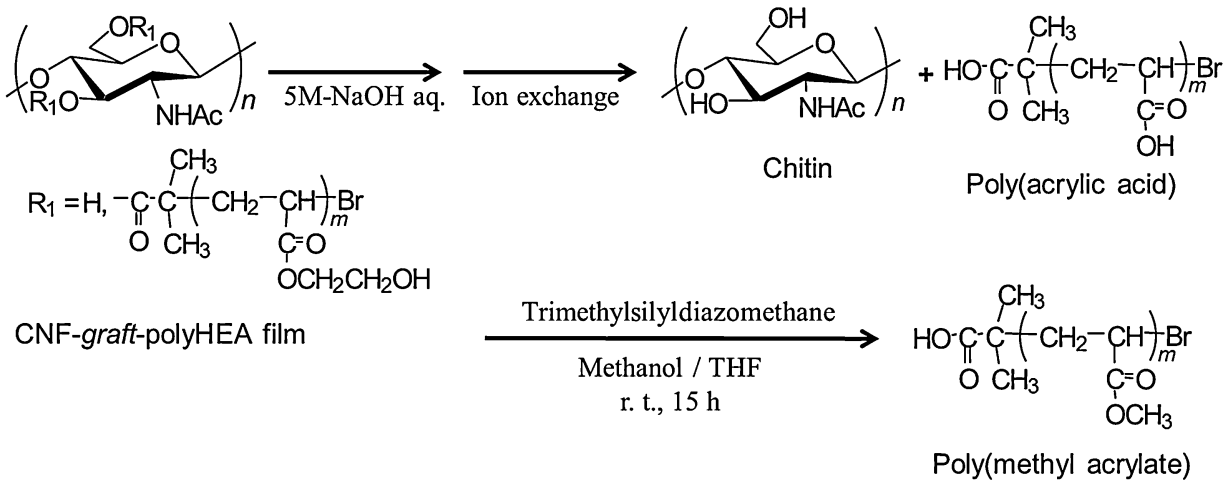


Fig. 4. GPC traces of poly(methyl acrylate)s from CNF-*g*-polyHEA films of (a) entry 3 and (b) entry 4 in Table 1.

CNF-*g*-polyHEA film as shown in Fig. 1b. The CNF macroinitiator films with the different DSs (0.20, 0.30, and 0.61) were pre-treated in 3.0 wt% LiCl/DMAc solution. Then, the surface-initiated ATRP of HEA (20 equiv. for an initiate site) from the pre-treated films was performed in the presence of Bpy (4 equiv. for an initiate site) and CuBr (2 equiv. for an initiate site) at 60 °C for desired times under argon. After water was added to the mixtures, the films were taken out, washed successively with methanol and acetone, and dried under reduced pressure. Table 1 shows the results of the surface-initiated graft polymerization of HEA from the CNF macroinitiator films under conditions of different reaction times (3, 6, 12, and 24 h). The conversions of HEA were estimated by the weight increases of the products from the CNF macroinitiator film. The yields/conversions of the products obtained using the CNF macroinitiator films with DS = 0.61 increased with increasing polymerization times (entries 1–4, Table 1). When the surface-initiated graft polymerization of HEA from the CNF macroinitiator films with the lower DSs (0.20 and 0.30) was carried out for 24 h, similarly, the polymerization proceeded (entries 5 and 6, Table 1, conversion 68 and 71%). Fig. 2c shows the IR spectrum of product (entry 4, Table 1, conversion 71%). The intensity ratio of the ester absorption (1745 cm^{-1}) to the amide I absorption (1665 cm^{-1}) of acetamide group increased in comparison with the CNF macroinitiator film (Fig. 2b), suggesting the progress of the graft polymerization of HEA. The XRD pattern (Fig. 3c) of the product was almost the same as that of the original CNF and CNF macroinitiator film (Fig. 3a and b), indicating the crystalline structure of the chitin chains was not disrupted owing to the occurrence of the graft polymerization only on surface of CNFs.

To estimate the M_n values of the grafted polyHEA chains, their separation from the CNFs was conducted by alkaline hydrolysis of the products in 5 mol/L NaOH aq. (Scheme 1). For the GPC measurement, the hydrolysate, *i.e.*, poly(acrylic acid) produced by alkaline hydrolysis of polyHEA, was modified by methylation of the carboxylic acid groups using trimethylsilyldiazomethane. The water-insoluble fraction in the methylation experiment was characterized by the ^1H NMR analysis in $CDCl_3$ to be the structure of poly(methyl acrylate). Fig. 4 shows the GPC traces of poly(methyl acrylate)s obtained from the CNF-*g*-polyHEA films of entries 3 and 4 in Table 1, respectively. When the polymerization time increases, the GPC peaks shifted to higher molecular weight region (M_n; 1490 and 4000, estimated using polystyrene standards) and their M_w/M_n values were relatively low (1.64 and 1.22). The GPC analysis supported that the longer polyHEA chains were grafted on the CNF films by the further progress of ATRP with prolonged reaction time. The surface morphologies of the CNF-*g*-polyHEA films were investigated by SEM measurement. At lower conversion of HEA in the graft polymerization (entry 1, Table 1), the SEM image (Fig. 5b) indicated that the morphology of the nanofibers on the films still remained, but the fiber widths (*ca.* 40 nm) increased compared with those of



Scheme 1. Alkaline hydrolysis of grafted polyHEA on CNF film and methylation of carboxylic acid groups.

the CNF macroinitiator film (*ca.* 30 nm, Fig. 5a). On the other hand, the nanofiber morphologies were not seen in the SEM images of the films produced at higher conversions of HEA (Fig. 5c–e), indicating that the nanofibers were covered by the grafted longer polyHEA chains. When the CNF macroinitiator films with the lower DSs (0.20 and 0.30, entries 4 and 5, Table 1) were used for the graft polymerization of HEA, the SEM images showed the morphology of the nanofibers on the films (*ca.* 40 nm, Fig. 5f and *ca.* 51 nm, Fig. 5g). Because the conversions of HEA in the graft polymerization from the three CNF macroinitiator films were comparable, which in turn suggested the similar molecular weights of the grafted polyHEAs (entries 4–6, Table 1), the functionality of the grafted chains on CNF surfaces was also shown to affect the nanofiber morphologies. The above SEM results supported the presence of the grafted polyHEA chains on surface of the CNF films and suggested that the nanofiber morphologies of the films were affected by both the molecular weight and functionality of the grafted polyHEAs.

The mechanical properties of the CNF-*g*-polyHEA films were evaluated by tensile testing (Fig. 6). The stress–strain curves of the films obviously showed the larger fracture strain values (3.9–12.6%)

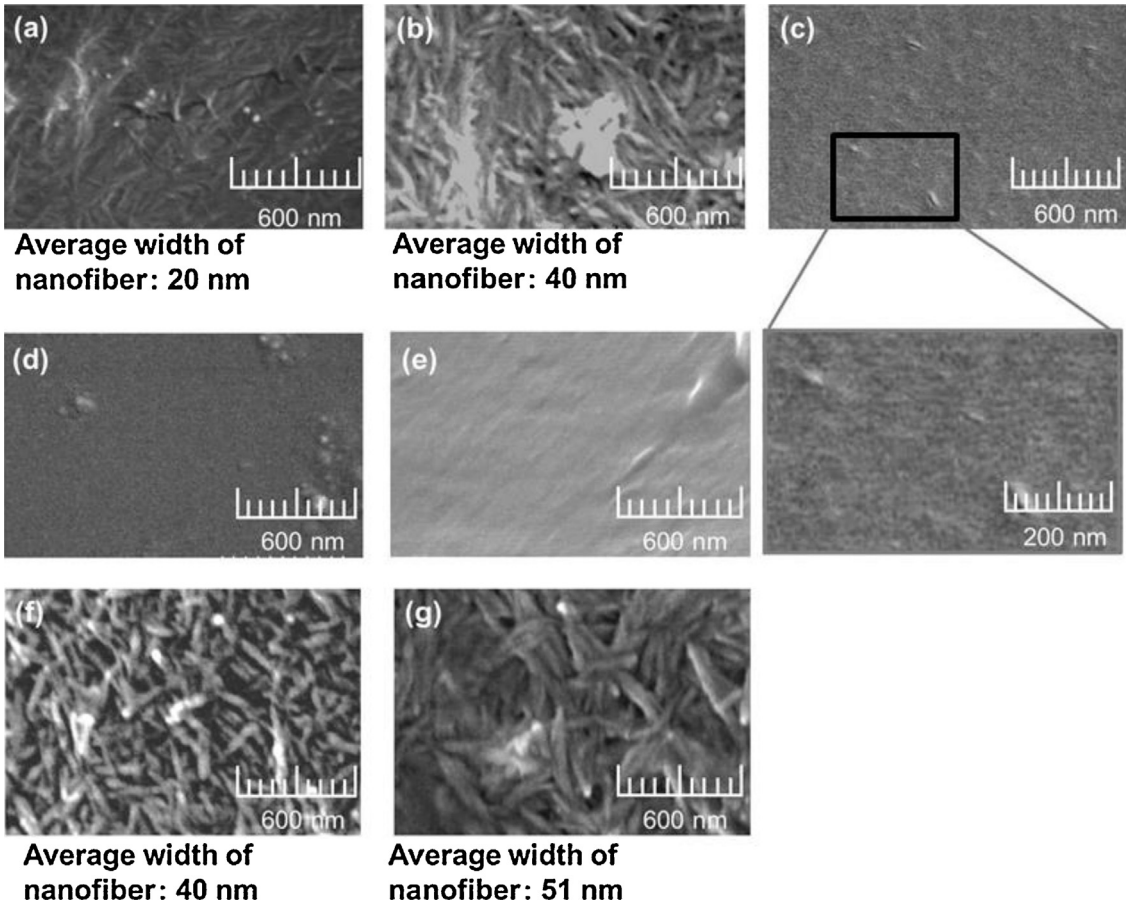


Fig. 5. SEM images of (a) chitin macroinitiator film (30 equiv. of α-bromoisobutyryl bromide) and (b)–(g) CNF-*g*-polyHEA films of entries 1–6 in Table 1, respectively.

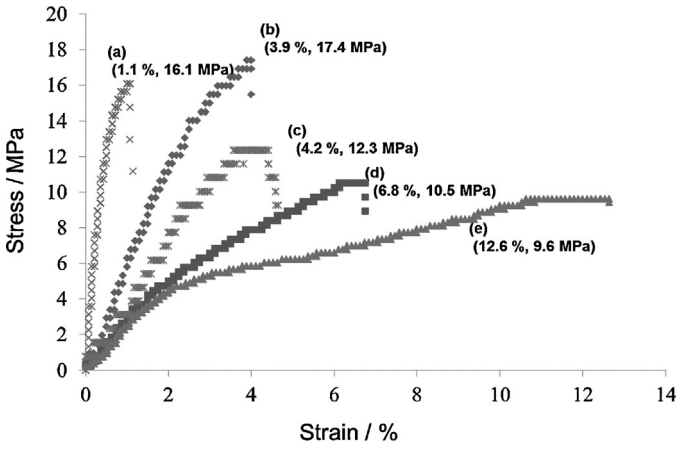


Fig. 6. Stress–strain curves of (a) chitin macroinitiator film (30 equiv. of α-bromoisobutyryl bromide) and (b)–(e) CNF-*g*-polyHEA films for of entries 1–4 in Table 1, respectively; the fracture strain and stress values are shown in parentheses.

compared with those of the original films (1.1%). Furthermore, the fracture strain values increased with increasing the conversions of HEA, whereas the fracture stress values decreased in this order and the film with the longer polyHEA graft chains showed the much larger fracture strain value than that of CNF-*graft*-poly(LA/CL) and CNF-*graft*-polypeptide films, which were provided in our previous studies (Kadokawa et al., 2013; Setoguchi et al., 2012). These results suggested the effect on enhancement of the flexibility by grafting the longer polyHEA chains on the CNFs films.

4. Conclusions

In this study, we prepared the CNF macroinitiator film for ATRP by introduction of the initiating moieties on surface of the CNF films. The surface-initiated graft polymerization of HEA from the CNF macroinitiator film by ATRP was performed to produce the CNF-*g*-polyHEA films. The IR, XRD, and SEM measurements of the resulting films as well as the GPC analysis after separation of the graft chains indicated the progress of the graft polymerization of HEA on surface of CNFs. Furthermore, the CNF-*g*-polyHEA films showed more flexible nature than the original CNF film. Because the present films are efficiently obtained by the surface-initiated ATRP, this approach has a potential to produce the CNF composite materials with various synthetic polymers, which will be used as practical bio-based materials in the future.

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