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Graft polymerization of acrylic acid onto chitin nanofiber to improve dispersibility in basic water

Shinsuke Ifuku[a,*], Masayoshi Iwasaki[a], Minoru Morimoto[b], Hiroyuki Saimoto[a]

[a] *Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, 4-101 Koyama-cho Minami, Tottori 680-8552, Japan*
[b] *Research Center for Bioscience and Technology, Tottori University, 4-101 Koyama-cho Minami, Tottori 680-8550, Japan*

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ABSTRACT

Graft copolymerization of acrylic acid (AA) on chitin nanofibers was carried out with potassium persulfate as a free radical initiator in an aqueous medium. The molar ratio of grafted AA increased with the AA concentration. The grafted chitin nanofibers were characterized by FT-IR, FE-SEM, UV–vis, XRD, and TGA. After polymerization, the characteristic morphology of chitin nanofibers was maintained. Chitin nanofibers grafted with AA were efficiently dissociated and dispersed homogeneously in basic water because of the electrostatic repulsion effect between nanofibers. AA was grafted on the surface and amorphous part of chitin nanofibers, and the original crystalline structure of α-chitin was maintained. At 330 °C, the weight residue of the graft copolymer increased with the grafted AA content.

1. Introduction

Chitin is known to be a cellulose analog with a (1,4)-α-*N*-acetyl glycosaminoglycan repeating structure. After cellulose, chitin is the most widely occurring natural carbohydrate polymer. It is biosynthesized in quantities of approximately 10^{10}–10^{11} tons each year (Nair & Dufresne, 2003). It is the main component of the exoskeletons of crabs, prawns, and insects as well as of the cell walls of mushrooms. Recently, we succeeded in preparing α-chitin nanofibers from crabs, prawns, and mushrooms by a simple mechanical treatment after the removal of proteins and minerals (Ifuku et al., 2009; Ifuku, Nogi, et al., 2011; Ifuku, Nomura, Morimoto, & Saimoto, 2011). The obtained nanofibers had fine nanofiber networks and uniform widths of approximately 10–20 nm.

The characteristic morphology of chitin nanofibers with a nano-sized structure, high surface-to-volume ratio, and a high aspect ratio has the potential to be converted into novel green materials. Surface modification through a chemical process is a useful way to enhance the application of chitin nanofibers. Recently, we studied the surface acetylation of chitin nanofibers to protect hydrophilic hydroxyl groups with hydrophobic functional groups (Ifuku, Morooka, Morimoto, & Saimoto, 2010). The surface modification improved hygroscopicity, dimensional stability, and affinity to nonpolar solvents or hydrophobic products.

In the surface modification of chitin nanofibers, the grafting of vinyl polymer is an interesting and promising approach to increase the possibility of developing chitin based materials. Grafting high-density polymers onto nanofibers can change their surface properties effectively (Carlmark & Malmström, 2003).

Chitin nanofibers can disperse homogeneously in acidic water (Fan, Saito, & Isogai, 2008b). Slight C2 amino groups on the chitin fiber surface were cationized under acidic conditions, enabling the stable dispersion of nanofibers by electrostatic repulsion between them. On the other hand, chitin nanofibers precipitate in basic water. This behavior is a disadvantage in the development of nanofiber applications, especially chemical reactions under basic conditions or compounding with basic materials. If anionic functional groups, such as carboxylate or sulfate groups, are introduced onto the surface of chitin nanofibers, the surface will have a negative charge under basic conditions, resulting in stable dispersion (Fan, Saito, & Isogai, 2008a).

Accordingly, we studied the grafting of an acrylic monomer on chitin nanofibers. The dispersibility of chitin nanofiber in basic water will change if acrylic acid polymer was grafted onto chitin nanofiber with high density. The grafting reaction was carried out with potassium persulfate (KPS) as an initiator, which allows facile radical polymerization in aqueous media (Loría-Bastarrachea, Carrillo-Escalante & Aguilar-Vega, 2002; Mahdavinia, Pourjavadi, Hosseinzadeh, & Zohuriaan, 2004; Wang & Xu, 2006). The process is based on a grafting-from process, where radicals are formed along the chitin polymer backbone followed by a free radical polymerization of acrylic acid monomer.

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* Corresponding author. Tel.: +81 857 31 5592; fax: +81 857 31 5813.
E-mail address: sifuku@chem.tottori-u.ac.jp (S. Ifuku).

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2. Experimental

2.1. Materials

Chitin powder was purchased from Nakalai Tesque. Potassium persulfate (KPS) and polyacrylic acid were purchased from Sigma–Aldrich and used as received. Acrylic acid monomer (AA, Wako Pure Chemical Industries) was purified by vacuum distillation prior to use.

2.2. Graft co-polymerization of acrylic acid onto chitin nanofibers

Chitin nanofibers were prepared from commercially available chitin powder according to a previously described procedure (Ifuku, Nogi, et al., 2010). The chitin nanofibers were dispersed well in water, which contained acetic acid to adjust the pH to 3.

The chitin nanofiber dispersion at a fiber content of 1 wt.% (100 mL) was purged with argon gas for 2 h. A KPS initiator (0.21 mol/GlcNAc unit) was added to the dispersion. After stirring for 2 h at 60 °C, variable amounts of AA (1–10 g) were added to the dispersion and stirred for 4 h at 60 °C under an argon atmosphere. After graft copolymerization, the reaction mixture was cooled to room temperature and washed by a centrifuge using deionized water (three times), acetone (three times), and then distilled water (one time) to remove nongrafted polyacrylic acid and other chemicals. The precipitates were collected and suspended in distilled water at 1 wt.%, and then the pH was adjusted to 10 by the addition of aqueous NaOH. The suspension was redispersed in basic water by an ultrasonic generator (Sonifier 250, Branson) for 10 min.

2.3. Characterization

The graft ratio of AA onto chitin nanofibers was calculated from the C and N contents in the elemental analysis data obtained using an elemental analyzer (Vario EL III, Elementar) and estimated according to

$$C/12.01 : N/14.01 = (8 + 3n) : 1$$

where C and N are the weight percentages of carbon and nitrogen atoms of grafted nanofiber samples and n is the molar ratio of grafted AA against an *N*-acetyl glucosamine (GlcNAc) unit of chitin nanofiber. The monomer consumption rate was calculated from the ratio of the consumed weight of the AA monomer for the graft polymerization to the initial weight of AA. Infrared spectra of the samples were recorded with an FT-IR spectrophotometer (Spectrum 65, Perkin-Elmer Japan Co. Ltd.) equipped with an ATR attachment. X-ray diffraction profiles of the nanofibers were obtained with Ni-filtered CuKα from an X-ray generator (Ultima IV, Rigaku) operating at 40 kV and 30 mA. The diffraction profile was detected using an X-ray goniometer scanning from 5° to 35°. The crystalline index (CI) was determined by the following equation: $CI = (I_{110} - I_{am}) \times 100/I_{110}$, where I_{110} is the maximum intensity of the 110 plane and I_{am} is the intensity of the amorphous diffraction at 15° (Zhang, Xue, Xue, Gao, & Zhang, 2005). Light transmittances of graft polymerized chitin nanofiber dispersions from 400 to 800 nm were measured using a UV-vis spectrometer (JASCO-V550). For FE-SEM observation, the prepared nanofiber slurry was diluted with EtOH and dried in an oven to prepare a chitin nanofiber film. The film was coated with about a 2 nm layer of Pt by an ion sputter coater and observed with a field emission scanning electron microscope (FE-SEM, JSM-6700F; JEOL, Ltd.) operating at 1.5 kV. The average diameter of isolated nanofibers was estimated by measuring 30 nanofibers manually. Thermogravimetric analysis (TGA) was carried out on a TG8120 (Rigaku) under nitrogen. The sample mass was approximately 5 mg, and a heating rate of 10 °C min^{-1} was used.

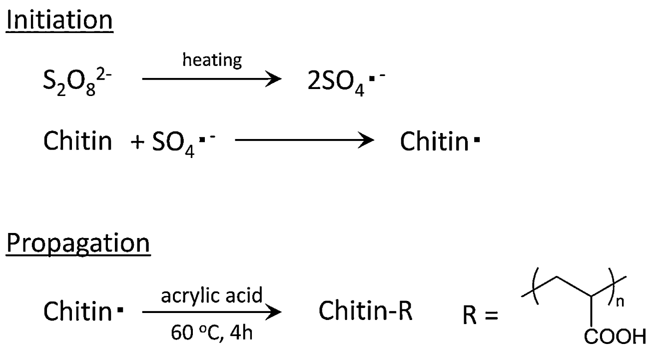

Fig. 1. Graft copolymerization of AA on chitin nanofibers.

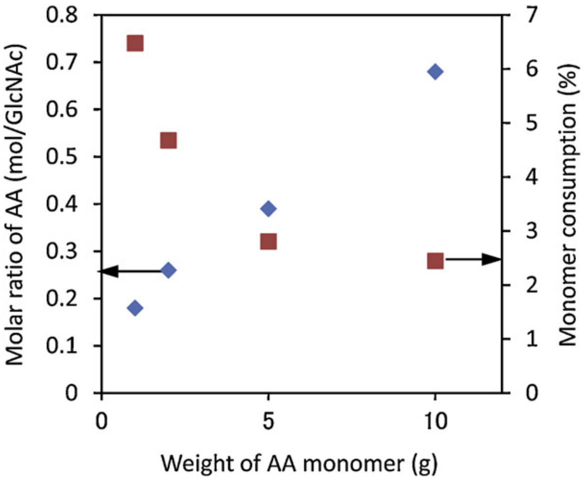

Fig. 2. Effect of additive amount of AA on molar ratio of grafted AA and monomer consumption.

3. Results and discussion

Chitin nanofibers with a width of 10–20 nm and a high aspect ratio were easily prepared from commercially available dry chitin powder, assisted by an electrostatic repulsion force (Ifuku, Nogi, et al., 2010). AA was grafted on the nanofibers in water using KPS as a radical initiator (Fig. 1). When the KPS initiator is heated, it

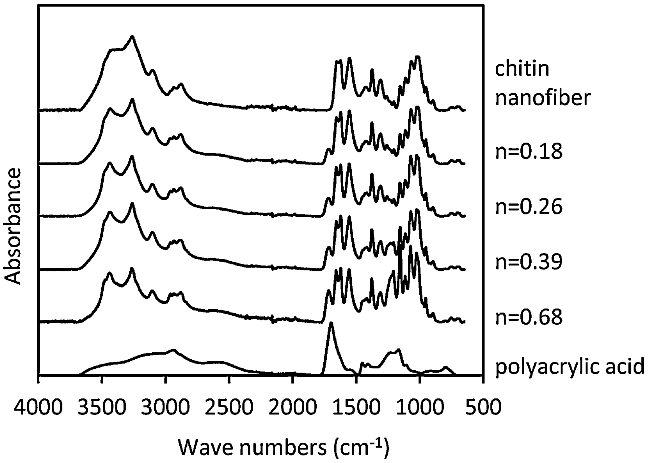

Fig. 3. FT-IR spectra of AA grafted chitin nanofibers.

generates sulfate radical anions. The sulfate radicals react with chitin nanofibers to form chitin radicals on surface and in amorphous part of nanofibers. The radical initiates graft polymerization of AA onto chitin nanofibers.

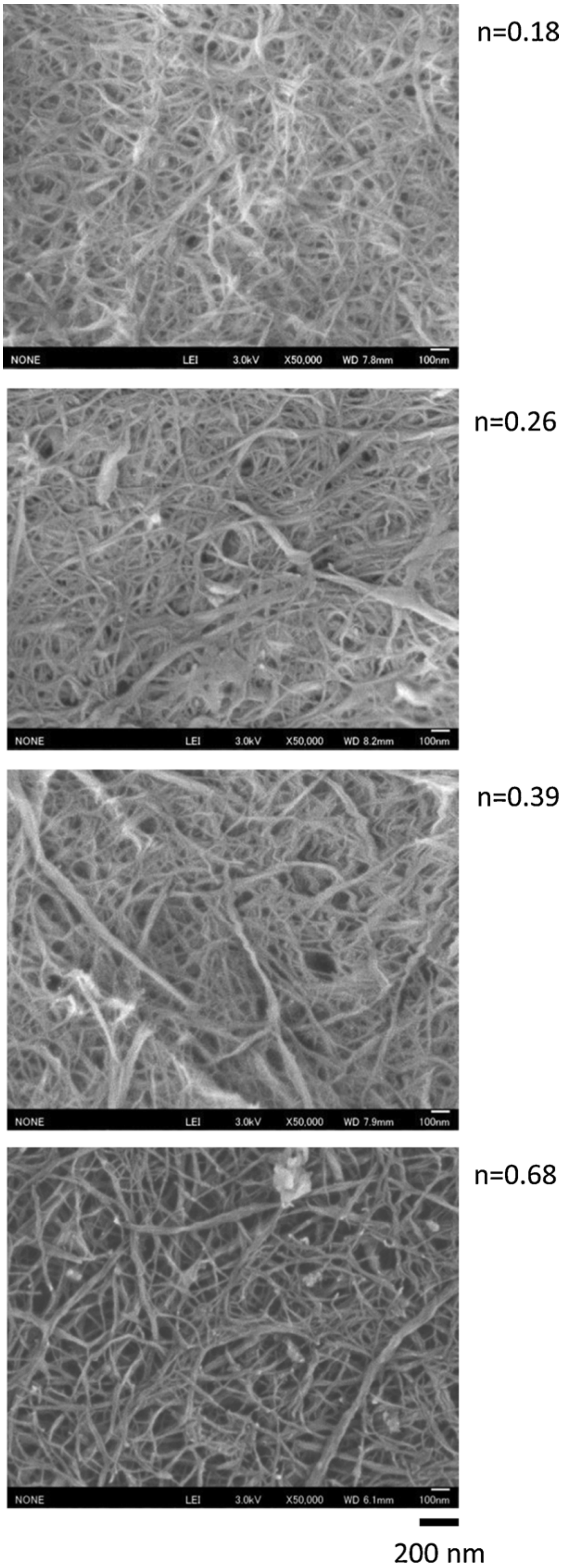

Fig. 4. FE-SEM micrographs of AA grafted chitin nanofibers.

The effect of the amount of AA monomer on the grafting parameters was studied at a fixed chitin nanofiber and KPS concentration under an argon atmosphere at 60 °C for 4 h. The molar ratio of grafted AA against the GlcNAc unit of chitin and the monomer consumption ratio of AA against the initial dose of AA monomer are shown in Fig. 2 and Table 1. They were calculated based on the C and N contents in the elemental analysis data. The molar ratio of grafted AA increased linearly from 0.18 to 0.68 with an increase in the amount of AA monomer in the range of 1–10 g. The increase in the amount of grafted AA as the AA concentration increases can be attributed either to more trapped radicals initiating a polymerization or the fact that the higher AA concentration will increase the polymerization rate which enables that higher molecular weight grafts are forming. The monomer consumption ratio decreased consistently from 6.48% to 2.45% with the increase in the amount of AA monomer added. This is because that the graft polymerization is competing with homopolymerization catalyzed by persulfate radicals in the solution phase. Therefore, as the concentration of acrylic acid is increased, the rate of homopolymerization increased and the monomer consumption rate grafted to the backbone decreased.

Fig. 3 shows the FT-IR spectra of the grafted AA onto chitin nanofiber with a molar ratio of grafted AA from 0.18 to 0.68 mol/GlcNAc unit. The O—H stretching band at 3482 cm^{-1}, the N—H stretching band at 3270 cm^{-1}, the amide I bands at 1661 and 1622 cm^{-1} of the chitin nanofibers were observed, as was the amide II band at 1559 cm^{-1}. These strong absorption peaks in the carbonyl region are characteristic of chitin (Nair & Dufresne, 2003). As the graft amount of AA increased, two characteristic bands, at 1154 and 1717 cm^{-1} increased, corresponding respectively to the C—O and C═O stretching vibration modes of the carboxylic acid. The presence of new absorption bands is evidence for the grafting of AA onto the chitin nanofibers.

After polymerization, the graft copolymer was treated with an ultrasonic generator in aqueous NaOH for dispersion again. SEM images of the chitin nanofibers with a series of molar ratios of grafted AA from 0.18 to 0.68 are shown in Fig. 4. These fibers looked like the original nanofibers and had the characteristic morphologies of chitin nanofibers: a nano-sized network structure, and a high aspect ratio were maintained without coagulation. This structure indicates that the nanofiber bundles dissociate well in basic water. Under basic conditions, anionically charged carboxylate groups with high density on the chitin nanofiber surfaces contributed to efficient dissociation. The average thicknesses of chitin nanofibers are listed in Table 1. Thickness increased gradually as the molar ratio of grafted AA increased. The changes in size were due to the bulky AA polymers introduced on the chitin nanofiber surfaces.

Fig. 5a and b shows the appearance and UV–vis transmittances of the AA grafted chitin nanofibers dispersed in basic water (pH 10) with 1 wt.%. The original chitin nanofibers precipitated immediately in basic water. On the other hand, the AA grafted chitin nanofibers dispersed well in water and did not precipitate for one month. The dispersion was stable also obviously because of the electrostatic repulsion effect between nanofibers. Carboxylic acid groups of AA grafted chitin nanofiber surfaces were anionized under basic conditions, which enabled stable dispersion in water as mentioned above. The amount of carboxylate on the surface affected dispersibility in water. As the molar ratio of grafted AA increased from 0.18 to 0.68, the nanofibers dispersed more homogeneously and the transmittance decreased due to high levels of anionic charges.

Fig. 6 shows the X-ray diffraction patterns of chitin nanofibers with a series of molar ratios of grafted AA. In the original chitin

Table 1
Graft copolymerization of chitin nanofibers.

Reaction condition			Results			
Chitin (g)	Acrylic acid (g)	KPS (mol/GlcNAc)	Molar ratio of grafted AA (mol/GlcNAc unit)	Monomer consumption (%)	Fiber thickness (nm)	Crystalline index (%)
1	1	0.21	0.18	6.48	20	65.2
	2		0.26	4.68	22	51.4
	5		0.39	2.81	22	48.2
	10		0.68	2.45	24	35.2

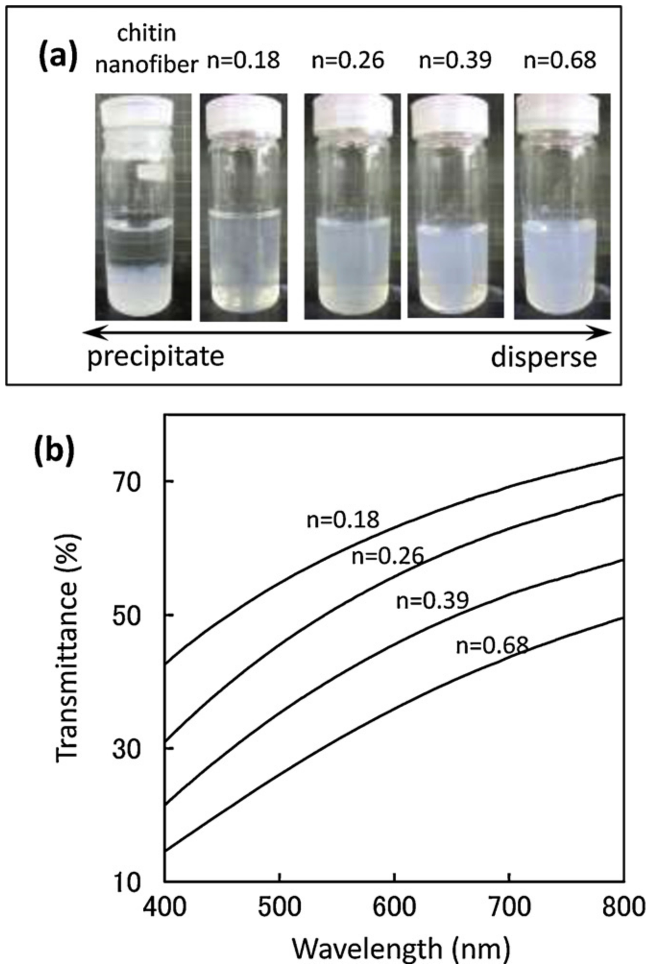

Fig. 5. (a) Photographs of AA grafted chitin nanofibers dispersed in basic water, and (b) their UV–vis transmittance spectra.

nanofiber, the characteristic four diffraction peaks of chitin were observed at 9.2°, 19.2°, 20.7°, and 22.8°; this was a typical antiparallel crystal pattern of alpha chitin, corresponding to 020, 110, 120, and 130 planes, respectively (Minke & Blackwell, 1978). After graft polymerization, all diffraction patterns coincided with those of original chitin nanofibers. Thus, the original crystalline structure of α-chitin was maintained after AA grafting. This indicates that AA was grafted on the surface and amorphous region of chitin nanofibers. Relative crystalline indices of AA grafted chitin nanofibers were determined from the X-ray diffraction profiles and listed in Table 1. The indices decreased from 65.2 to 35.2% as the molar ratio of grafted AA increased. This indicates amorphous regions of the nanofibers relatively increased after polymerization. Intense peaks at approximately 17.8° increased as the molar ratio of grafted AA increased. These peaks were derived from AA grafted on the fiber surface.

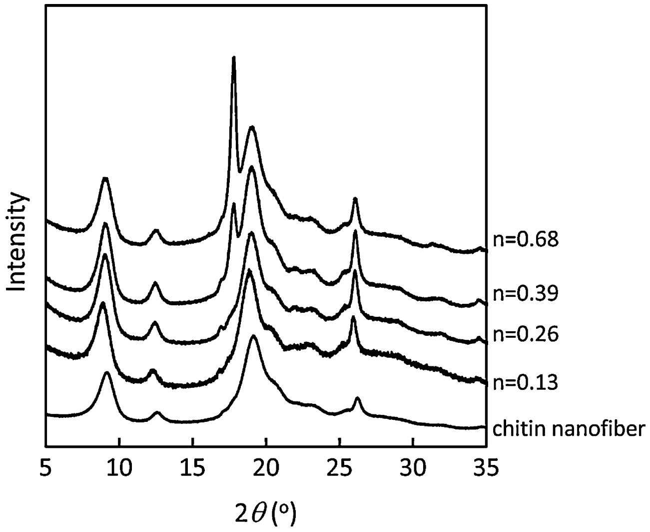

Fig. 6. X-ray diffraction profiles of AA grafted chitin nanofibers.

Fig. 7 shows the TGA curves of chitin nanofibers with a series of molar ratios of grafted AA from 0.18 to 0.68 mol/GlcNAc. All copolymers showed the same degradation step, which started from approximately 265 °C with a major degradation at 320 °C, determined by the derivative TGA curves. The thermal degradation derived from chitin crystals (Ifuku, Nogi, et al., 2011). This also indicates that AA was grafted on the chitin nanofiber surface and that the chitin crystalline structure was maintained. The first degradation steps ended at approximately 330 °C. After the first degradation step, the weight residue was increased from approximately −58.5 to −48.8% as the molar ratio of grafted AA increased from 0.18 to 0.68, respectively. This is attributed

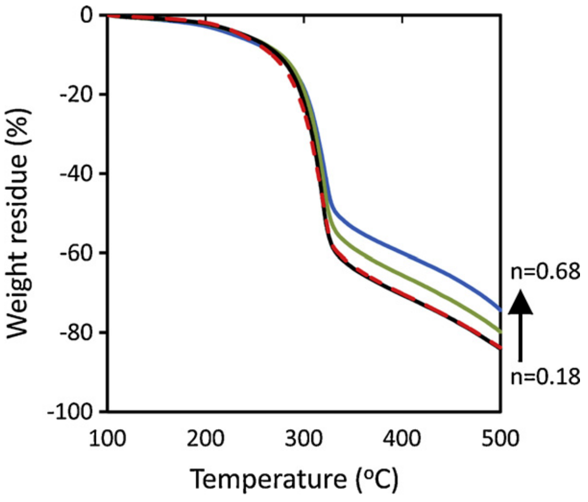

Fig. 7. TGA analysis of AA grafted chitin.

to the presence of grafted AA on the chitin nanofiber surface. Since the AA polymer has a high thermal degradation temperature with a major degradation at 414 °C, the weight residue increased as the grafted AA content of chitin nanofiber copolymer increased.

4. Conclusions

Chitin nanofibers were modified by grafting with AA by free radical polymerization initiated using KPS. The amount of the grafted AA depended on the monomer concentration. The grafted nanofibers were observed by FE-SEM, which showed that a fine nanofiber network structure was maintained. The grafted chitin nanofiber dispersed homogeneously in basic water. The stable dispersion was due to the electrostatic repulsion effect between nanofibers. XRD revealed that AA polymers were grafted on the surface and amorphous part of the nanofibers, and the core of the crystalline structure did not change after polymerization. Thus, AA polymers grafted on the chitin nanofiber surface at high density enable the stable dispersion of nanofibers without losing the characteristic nanomorphology and crystalline structure. This allows for the chemical reaction under basic conditions or compounding with basic materials. Moreover, the surface graft polymerization could be applicable to other vinyl monomers, depending on the application. We expect that this study will expand the application of chitin nanofibers to the development of environmentally friendly bionanomaterials.

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