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ARTICLE TYPE

Synthesis of Chitin-*graft*-Polystyrene *via* Atom Transfer Radical Polymerization Initiated from Chitin Macroinitiator

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In this study, we synthesized chitin-*graft*-polystyrene by graft polymerization of styrene from a chitin macroinitiator by atom transfer radical polymerization (ATRP). First, the chitin macroinitiators for ATRP were synthesized by acylation of chitin with 2-bromopropionyl bromide in 1-allyl-3-methylimidazolium bromide (AMIMBr) of an ionic liquid. Because the products, which were obtained by the reaction using 20 and 30 equiv. of 2-bromopropionyl bromide for a repeating unit of chitin, were soluble in DMSO, the degrees of substitution (DS) values were calculated by ^{1}H NMR measurement in DMSO-d_6 to be 1.66 and 1.86, respectively. Then, graft polymerization of styrene from the obtained chitin macroinitiator with DS=1.86 was performed by ATRP using *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine and CuBr as the catalytic system. The yields of the products increased with increasing the feed ratios of styrene to an initiating site of the chitin macroinitiator. To estimate the M_n values of the grafted polystyrenes (PSs), furthermore, separation of the PS chains from chitin main-chain was conducted by alkaline hydrolysis. Their GPC traces were monomodal and the M_n values calculated using polystyrene standards increased with increasing the feed ratios of styrene to an initiating site.

1. Introduction

Natural polysaccharides are widely distributed in nature and have been regarded as structural materials and as suppliers of water and energy.[1] They have increasingly been important because of possessing unique structures and properties being recently better understood, which are much different from those of typical synthetic polymers. Compared with synthetic polymeric materials, therefore, natural polysaccharide-based materials have many promising properties, for example, good biocompatibility, biodegradability, non-toxicity, non-immunogenic, and so on.[2] Of the many kinds of natural polysaccharides, cellulose and chitin are the most important biomass resources; [3,4] cellulose is the most abundant organic substance on the earth and chitin is the second most common one. Modification of cellulose by graft polymerization provides a significant route to combine both the advantageous properties of natural and synthetic polymers for a wide range of potential applications.[5] For example, self-assembled nanoparticles of cellulose-based graft polymers are drawing increasing attention due to their potential as the nanocarriers for drug/gene delivery and sensing.[6] As the new graft polymerization method using cellulose, recently, grafting of synthetic polymers on cellulose via atom transfer radical polymerization (ATRP) has been studied.[7-12] ATRP is a robust and versatile technique to accurately control chain length and polydispersity of the resulting polymers, and thus has been used to synthesize a wide range of copolymers with the controlled structure, unit length, and block sequence.[13,14] In the studies on such graft polymerization from cellulose and its derivatives, the initiating moieties for ATRP were first immobilized on cellulose by proper reactions such as acylation to give cellulose macroinitiators. Then, ATRP of various monomers initiated from the macroinitiators was performed under appropriate conditions to give the desired cellulosic graft copolymers. To the best of own knowledge, on the other hand, such graft copolymers based on chitin main-chain via ATRP have hardly been prepared, probably due to less solubility of chitin in the most common solvents even compared with cellulose, as also the well-known polysaccharide with less solubility.

Chitin is structurally similar to cellulose, but it is an aminopolysaccharide having acetamido groups at the C-2 positions in place of hydroxy groups of cellulose.[4] Despite its huge annual production and easy accessibility, chitin still remains as an unutilized biomass resource primary because of its intractable bulk structure and only limited application has been paid to chitin, principally from its biological properties.[4] Moreover, modification of chitin is generally difficult owing to a lack of solubility as aforementioned, and thus the reactions often take place under heterogeneous conditions, leading to low degree of substitution (DS).

Ionic liquids, low-melting point salts that form liquids at temperatures below the boiling point of water, have recently been found to be used as good solvents for polysaccharides such as cellulose.[15-18] Since it was reported that 1-butyl-3-methylimidazolium chloride of an ionic liquid dissolved cellulose

in relatively high concentrations,[19] various types of the chemical modifications of cellulose such as acylation, carbanilation, and carboxymethylation in ionic liquids have been studied.[11,12,15,16, 20-23] However, little has been reported regarding the dissolution of chitin with the ionic liquids.[24-26] Recently, we found that an ionic liquid, 1-allyl-3-methylimidazolium bromide (AMIMBr), formed a clear liquid with chitin using a simple procedure without the strict purification of AMIMBr and evaluated its weak gel nature by rheological analysis.[27,28] We also reported the acetylation of chitin using acetic anhydride in AMIMBr, which gave the acetylated chitin with a high DS under selected conditions.[29]

On the basis of our previous investigations, in this study, we synthesized chitin-*graft*-polystyrene (chitin-*graft*-PS) by grafting technique via ATRP using a chitin macroinitiator. The chitin macroinitiator for ATRP was first prepared by immobilization of the initiating moieties attached through ester linkage on chitin in AMIMBr. Then, the graft polymerization of styrene from the macroinitiator via ATRP was performed under the appropriate conditions to produce chitin-*graft*-PS. Because the present grafting technique using the chitin macroinitiator has a potential to employ various monomers, we are convinced that it will contribute to the development of chitin-based functional nanomaterials such as the self-assembled nanoparticles in the future.

2. Experimental

Materials

Chitin powder from crab shells was purchased from Nakalai Tesque, Inc., Kyoto, Japan. The values of weight-average molecular weight (M_w) and degree of deacetylation of the chitin sample were estimated by the viscometric and IR analyses[30,31] to be 5 x 10^5 and less than 5%, respectively. An ionic liquid, AMIMBr, was prepared by reaction of 1-methylimidazolium with 3-bromo-1-propene according to the method modified from the literature procedure.[32] 2-Bromopropionyl bromide was purchased from Tokyo Chemical Industry, Tokyo, Japan. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylene triamine (PMDETA) and copper(I) bromide (CuBr) were purchased from Wako Pure Chemicals. Styrene was purchased from Nakalai Tesque, Inc., Kyoto, Japan. All other reagents and solvents were used as received from commercial sources.

Synthesis of Chitin Macroinitiator in AMIMBr

A typical procedure for the synthesis of the chitin macroinitiator was as follows (Table 1, entry 3). A mixture of chitin (60.0 mg, 0.30 mmol/unit) in AMIMBr (3.0 g, 15 mmol) was heated at 100 ℃ for 24 h with stirring under argon to dissolve chitin. After the solution was cooled to room temperature, 2-bromopropionyl bromide (2.06 g, 9.0 mmol; 30 equiv. for a unit of chitin) was added and the mixture was stirred at room temperature for overnight. Then, the reaction mixture was poured into a large amount of water to precipitate the product. The precipitate was isolated by filtration, washed with water, and dried under reduced pressure to give the chitin macroinitiator (85.6 mg, DS=1.86) in 63.3 % yield.

Graft Polymerization of Styrene from Chitin Macroinitiator by ATRP

A typical experimental procedure for the graft polymerization was as follows (Table 2, entry 3). First, chitin macroinitiator (61.2 mg, 0.14 mmol) was dissolved with DMSO (8.0 mL), and then, styrene (1.35 g, 13.0 mmol), PMDETA (66.9 mg, 0.39 mmol) and CuBr (56.2 mg, 0.39 mmol) were added to the solution. Thereafter, the mixture was stirring at 60 ℃ for 10 h. The reaction mixture was poured into a large amount of water to precipitate the product. After it was washed successively with water, methanol, and acetone, the product was dried under reduced pressure to give chitin-*graft*-PS (752.5 mg).

Alkaline Hydrolysis of Chitin-*graft*-polystyrene

First, the chitin-*graft*-PS (60.0 mg) was dispersed in *N*,*N*-dimethylacetamide (DMAc) (3.0 mL). After 5 mol/L NaOH aq.(3.0 mL) was added to the dispersion, the mixture was stirred at room temperature for 12 h. The product was extracted with chloroform and the insoluble material present in the chloroform layer was removed by filtration. Then, the filtrate was poured into a large amount of water to precipitate the product. The precipitate was isolated by filtration, washed with water, and dried under reduced pressure. The M_n and molecular weight distribution (M_w / M_n) of the obtained PS were estimated by the GPC measurement with chloroform as the eluent.

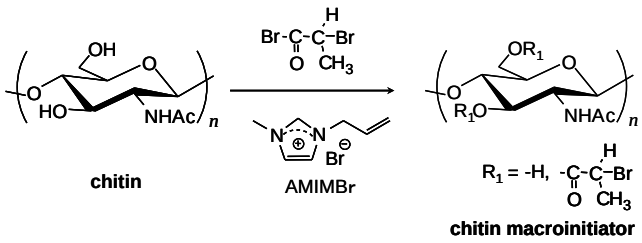
Measurements

IR spectra were recorded with samples in KBr using a SHIMADZU FFTIR-8400 spectrometer. ^{1}H NMR spectra were 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.

3. Results and Discussion

3.1. Synthesis of Chitin Macroinitiator

The chitin macroinitiator having the initiating moieties (2-bromopropionyl group) was synthesized by acylation of chitin with 2-bromopropionyl bromide in AMIMBr as shown in Scheme 1. First, chitin powder was dissolved with AMIMBr (2% w/w) by heating the mixture at 100 ℃ for 24 h with stirring. Then, the desired amounts of 2-bromopropionyl bromide were added to the solution and the mixtures were stirred at room temperature for overnight. The products were isolated as a fraction insoluble in water and the presence of the initiating moieties was evaluated by the IR and ^{1}H NMR analyses. Fig. 1 shows the IR spectra of the products obtained using 10, 20, and 30 equiv. of 2-bromopropionyl bromide for a repeating unit of chitin. All the IR spectra exhibited the carbonyl absorptions not only due to amido I of acetoamido (ca. 1665 cm^{-1}) but also due to ester of 2-bromopropionate (ca. 1745 cm^{-1}), suggesting the occurrence of acylation of chitin with 2-bromopropionyl bromide in AMIMBr. Furthermore, the intensity ratios of the ester absorptions to the



Scheme 1 Synthesis of chitin macroinitiator in AMIMBr.

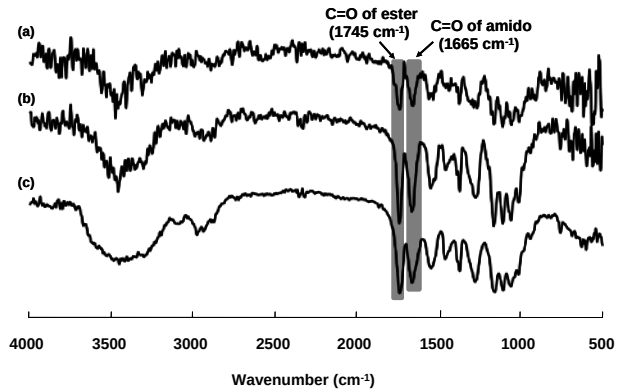


Fig. 1 IR spectra of chitin macroinitiators obtained under conditions of entries 1 (a), 2 (b), and 3 (c) in Table 1.

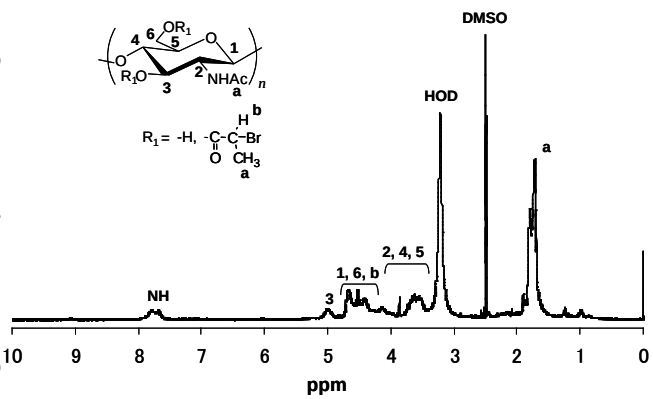


Fig. 2 ^{1}H NMR spectrum of chitin macroinitiator in DMSO-d_6 (entry 3, Table 1).

amido absorptions, which were estimated by similar method as those for the acelyation of chitin,[33] increased with increasing the feed amounts of 2-bromopropionyl bromide (from 10 to 30 equiv.). Because the products, which were obtained by the reaction using 20 and 30 equiv. of 2-bromopropionyl bromide for a repeating unit of chitin, were soluble in DMSO, the structures of these products were further confirmed by the ^{1}H NMR analysis measured in DMSO-d_6. Fig. 2 shows the ^{1}H NMR spectrum of the product obtained using 30 equiv. of 2-bromopropionyl bromide for a repeating unit of chitin (Table1, entry 3). The signals in the ^{1}H NMR spectrum were assignable to the structure of the chitin macroinitiator as follows; δ1.72-1.95 (br, CH_3), 3.22-3.77 (br, H2, H4, H5), 4.14-4.67 (br, H1, H6, CHBr), 5.01 (br, H3), 7.69 (br, NH). On the basis of the integrated ratio of the signals due to the methyl protons of 2-bromopropionyl and acetyl groups to the signals due to the H1, H3, and H6 protons of chitin, the DS value was calculated to be 1.86. Similarly, the DS value of the product yielded using 20 equiv. of 2-bromopropionyl bromide was calculated to be 1.66. However, the product by the reaction using 10 equiv. of 2-bromopropionyl bromide (Table 1, entry 1) was insoluble in DMSO, and thus, the DS value was not calculated by the ^{1}H NMR analysis. Furthermore, we prepared a chitin sample from the chitin macroinitiator by alkaline cleavage of the introduced 2-bromopropionyl groups and measured its M_w by viscometric analysis.[30] Consequently, the M_w value was of the same digit as that of the original chitin, indicating the degradation of the chitin main-chain did not frequently happened during the synthetic procedure of the chitin macroinitiator.

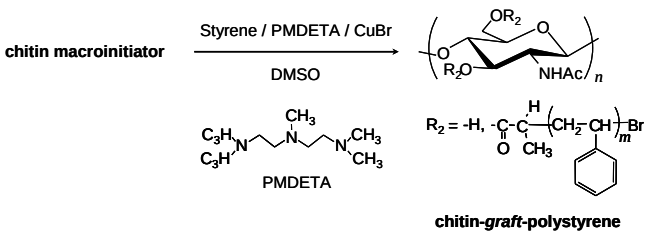
Table 1 Synthesis of chitin macroinitiators by reaction of chitin with 2-bromopropionyl bromide in AMIMBr

Entry	Equiv.[a]	DS[b]	Yield, %[c]	Solubility in DMSO
1	10	-	-	Insoluble
2	20	1.66	68.8	Soluble
3	30	1.86	63.3	Soluble

[a] [2-bromopropionyl bromide]$_0$ / [a unit of chitin]$_0$.
[b] DS = degrees of substitution, which were determined by ^{1}H NMR spectra.
[c] Yields were fractions insoluble in water and calculated by taking DS values into consideration.

3.2. Graft Polymerization of Styrene from Chitin Macroinitiator by ATRP

The graft polymerization of styrene from the chitin macroinitiator (Table 1, entry 3) was performed by ATRP in various feed ratios of styrene to an initiating site with PMDETA/CuBr (1.5 equiv. for an initiating site each) as the catalytic system (Scheme 2), and DMSO was used as the solvent because the chitin macroinitiator was dissolved well with it. The reaction was carried out at 60 ℃ for 10 h and the product was isolated as a fraction insoluble in water. The monomer conversions were calculated on the basis of the isolated yields of the products in weight. Fig. 3 shows the ^{1}H NMR spectrum of the product obtained using 5 equiv. of styrene for an initiating site of the macroinitiator in DMSO-d_6 (Table 2, entry 1), which supported the structure of chitin-*graft*-PS as follows. The signals at δ0.81-2.32 are assignable to -CH_2-CH- of PS, CH_3-CH-C=O of the initiating site, and CH_3-C=O of chitin, the signals at δ3.74-5.01 are assignable to sugar protons, and signals at δ7.13-7.76 assignable to aromatics of PS. Because the products obtained by the higher feed ratios were not soluble in any solvents, the ^{1}H NMR analysis was not conducted.



Scheme 2 Graft polymerization of styrene from chitin macroinitiator by ATRP.

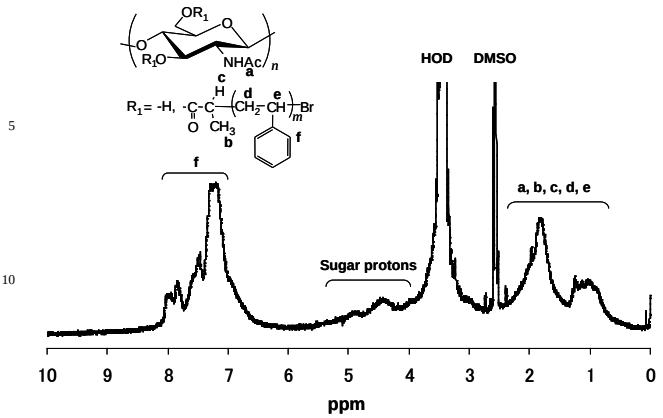
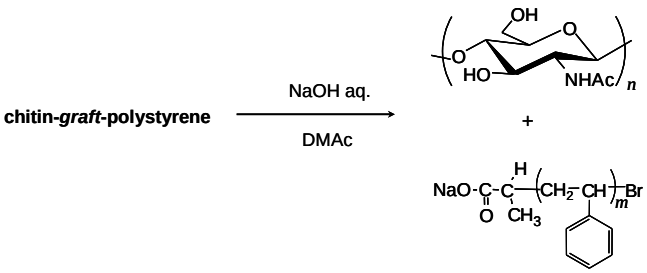


Fig. 3 ^{1}H NMR spectrum of chitin-*graft*-polystyrene in DMSO-d_6 (entry 1, Table 2).



Scheme 3 Alkaline hydrolysis of chitin-*graft*-polystyrene.

Table 2 shows the results of the graft polymerization under various feed ratios of styrene for an initiating site of chitin macroinitiator (5, 10, 50 and 100 equiv.). The yields/conversions of the products increased with increasing the feed ratios. However, their products were mostly insoluble in any common eluents, and thus, their molecular weights were not calculated by the GPC measurement. To confirm the M_n values of the graft PS chains, therefore, their separation from the chitin main-chain was conducted by alkaline hydrolysis of the products in a mixed solution of DMAc and 5 mol/L NaOH aq. The water-insoluble fractions in the alkaline hydrolysis experiment were characterized by the ^{1}H NMR analysis in DMSO-d_6 to be the structure of PS (data not shown). Fig. 4 a-d shows the GPC traces of the separated PS chains by the alkaline hydrolysis of the chitin-*graft*-PSs of entries 1-4, respectively.

Table 2 Graft polymerization by ATRP under various feed ratios of styrene to an initiating site of macroinitiator[a]

Entry[a]	Styrene/ initiating site	Yield, %	Conversion of styrene, %	Solubility in DMSO	M_n[b]	M_w/M_n[b]	Theoretical value
1	5.1	145.7	62.3	Soluble	970	1.73	320
2	10.9	196.1	53.6	Insoluble	1490	1.46	550
3	50.5	725.5	51.0	Insoluble	13600	1.68	2660
4	100.6	1432.2	50.0	Insoluble	17800	1.73	5200

[a] A feed amount of chitin macroinitiator was 60.0 mg (0.14 mmol).
[b] The number-average molecular weight(M_n) and molecular weight distribution (M_w/M_n) of grafted polystyrene was estimated by GPC measurement with chloroform as eluent using polystyrene standards.

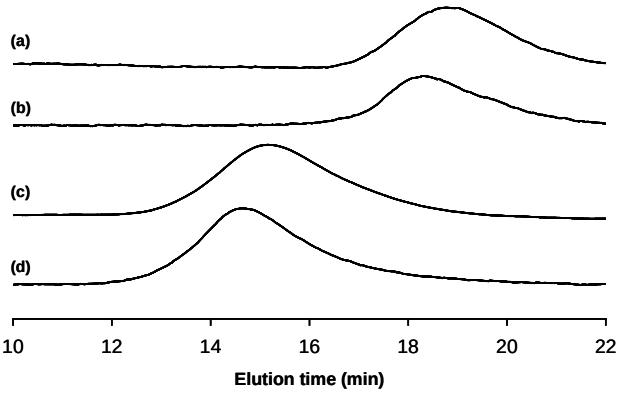


Fig. 4 GPC traces of polystyrenes obtained by alkaline hydrolysis of (chitin-*graft*-polystyrene)s of entries 1 (a), 2 (b), 3 (c), and 4 (d) in Table 2.

When the feed ratios of styrene to an initiating site of the chitin macroinitiator increased, the GPC peaks shifted to higher molecular weight region with keeping monomodal fashion and relatively narrows distribution (1.46-1.73). However, the M_n values estimated using polystyrene standards were higher than the theoretical M_n ones calculated on the basis of the monomer conversions. Because such poor agreements between experimental and theoretical M_ns are not common in the controlled radical polymerization such as ATRP, the detailed polymerization process was confirmed by the time-course experiment of the monomer conversion. Fig. 5 shows the kinetics of monomer concentration for the graft-polymerization of styrene in the feed ratio of 50 at 60 ℃ in DMSO. The first order kinetics plots showed significant downward curvature, indicating that the termination reaction gradually occurred with the progress of polymerization. Fig. 6 shows the M_n and M_w/M_n values of the graft PS chains obtained by each reaction time, which are estimated by the GPC measurement after the alkaline hydrolysis. At the lower conversions (< 30 %), the M_w/M_n values were relatively low (1.29-1.81) and the M_ns agreed with the theoretical ones. At the higher conversions, however, the differences between them as well as the M_w/M_n values became larger. A similar result was observed in the polymerization of various methacrylate monomers in DMSO using ligand/CuBr catalyst system by Monge S. et al.[34] When ATRP is performed from a multifunctional initiator, radical-radical coupling in the propagating chains likely occur because of the high local concentration of radicals. For example, in the case of ATRP using a cellulose macroinitiator with the DS of initiating site=0.43;[7] namely there was almost an initiating site in every two glucose residues, termination by the radical-radical coupling was prone to occur more than in the general ATRP because of the densely presence of graft chains.[35,36] In the present research, the use of the chitin macroinitiator with the high DS (1.86) might also cause the radica-radical coupling reaction in the macroradicals. With the prolonged polymerization times, therefore, the M_n values were larger than theoretical ones and the insolubility of the products in DMSO as reaction solvent happened, leading to unquantification of the monomer conversions.

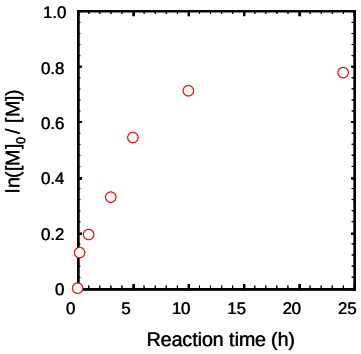


Fig. 5 Plots of ln([M]$_0$/[M]) vs. reaction time for the polymerization of styrene at 60 ℃ in DMSO ([Styrene]$_0$: [an initiating site of chitin macroinitiator, DS=1.86]$_0$:[PMDETA]$_0$:[CuBr]$_0$ = 50 : 1.0 : 1.5 : 1.5).

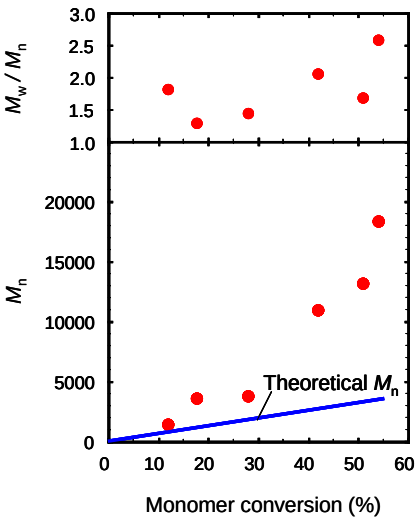


Fig. 6 Evolution of M_n and M_w/M_n values of the separated PS chains as a function of monomer conversion for the polymerization of styrene at 60 ℃ in DMSO ([Styrene]$_0$: [an initiating site of chitin macroinitiator, DS=1.86]$_0$:[PMDETA]$_0$:[CuBr]$_0$ = 50 : 1.0 : 1.5 : 1.5).

4. Conclusions

In this study, first, the chitin macroinitiator for ATRP was synthesized by acylation of chitin with 2-bromopropionyl bromide in AMIMBr. The IR spectra of the products indicated introduction of the initiating sites to chitin. The products with the higher DS (>1.6) were soluble in DMSO and their structures were confirmed further by the ^{1}H NMR spectra in DMSO-d_6. Then, the graft polymerization of styrene from the chitin macroinitiator was carried out by ATRP using PMDETA/CuBr as the catalytic system in DMSO to produce the chitin-*graft*-PS. The grafted PS chains were separated by the alkaline hydrolysis of the products, and whose M_n values were estimated by the GPC measurement. The M_n values increased with increasing the feed ratios of styrene to an initiating site. The present approach will be applied to the other monomers, which form useful polymers, such as hydrophilic, amphiphilic, and stimuli-responsive, to create new chitin-based functional materials in future.

Notes and references

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1 C. Schuerch, Polysaccharides, in *Encyclopedia of Polymer Science and Engineering*, eds. H. F. Mark, N. Bilkales and C. G. Overberger, 2nd edn, John Wiley & Sons, New York, 1986, p. 87.
2 L. N. Hassani, F. Hendra and K. Bouchemal, *Drug Discovery Today*, 2012, **17**, 608.
3 D. Klemm, B.Heublein, H. P. Fink and A. Bohn, *Angew. Chem., Int. Ed.*, 2005, **44**, 3358.
4 R. A. A. Muzzarelli, Chitin nanostructures in living organisms, in *Chitin Formation and Diagenesis*, ed. S. N. Gupta, Springer, New York, 2011, chap.1.
5 Y. Nishio, *Adv. Polym. Sci,*. 2006, **205**, 97.
6 H. J. Dou, M. Jiang, H. S. Peng, D. Y. Chen and Y. Hong, *Angew. Chem., Int. Ed.*, 2003, **42**, 1516.
7 D. Shen and Y. Huang, *Polymer*, 2004, **45**, 7091.
8 P. Vlcek, M. Janata, P. Latalova, J. Kriz, E. Cadova and L. Toman, *Polymer*, 2006, **47**, 2587.
9 D. Shen, H. Yu and Y.Huang, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 4099.
10 S. Ifuku and J. F. Kadla, *Biomacromolecules*, 2008, **9**, 3308.
11 X. Sui, J. Yuan, M. Zhou, J. Zhang, H. Yang, W. Yuan, Y. Wei and C. Pan, *Biomacromolecules*, 2008, **9**, 2615.
12 T. Meng, X. Gao, J. Zhang, J. Yuan, Y. Zhang and J. He, *Polymer*, 2009, **50**, 447.
13 M. Kamigaito, T. Ando and M. Sawamoto, *Chem. Rev.*, 2001, **101**, 3689.
14 K. Matyjaszewski, *Macromolecules*, 2012, **45**, 4015.
15 T. Liebert and T. Heinze, *BioResources*, 2008, **3**, 576.
16 L. Feng and Z. I. Chen, *J. Mol. Liq.*, 2008, **142**, 1.
17 A. Pinkert, K. N. Marsh, S. Pang and M. P. Staiger, *Chem. Rev.*, 2009, **109**, 6712.
18 M. E. Zakrzewska, E. B. Lukasik and R. B. Lukasik, *Energy Fuels*, 2010, **24**, 737.
19 R. P. Swatloski, K. S. K. Spear, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, 2002, **124**, 4974.
20 J. Wu, J. Zhang, H. Zhang, J. He,; Q. Ren and M. Guo, *Biomacromolecules*, 2004, **5**, 266.
21 T. Heinze, K. Schwikal and S. Barthel, *Macromol. Biosci.*, 2005, **5**, 520.
22 S. Barthel and T. Heinze, *Green Chem.*, 2006, **8**, 301.
23 K. Schlufter, H. P. Schmauder, S. Dorn and T. Heinze, *Macromol. Rapid Commun.*, 2006, **27**, 1670.
24 Y. Wu, T. Sasaki, S. Irie and K. Sakurai, *Polymer*, 2008, **49**, 2321.
25 Y. Qin, X. Lu, N. Sun and R. D. Rogers, *Green Chem.*, 2010, **12**, 968.
26 W. T. Wang, J. Zhu, X. L. Wang, Y. Huang and Y. Z. Wang, *J. Macromol. Sci. Part B: Phys.*, 2010, **49**, 528.
27 S.Yamazaki, A. Takegawa, Y. Kaneko, J. Kadokawa, M. Yamagata and M. Ishikawa, *Electrochem. Commun.*, 2009, **11**, 68.
28 K. Prasad, M. Murakami, Y. Kaneko, A. Takada, Y. Nakamura and J. Kadokawa, *Int. J. Biol. Macromol.*, 2009, **45**, 221.
29 S. Mine, H. Izawa, Y. Kaneko and J. Kadokawa, *Carbohydr. Res.*, 2009, **344**, 2263.
30 M. Poirier and G. Charlet, *Carbohydr. Polym.*, 2002, **50**, 363.
31 Y. Shigemasa, H. Matsuura, H. Sashiwa and H. Saimoto, *Int. J. Biol. Macromol.*, 1996, **18**, 237.
32 D. Zhao, Z. Fei, T. J. Geldbach, R. Scopelliti, G. Laurenczy and P. J. Dyson, *Helv. Chim. Acta.*, 2005, **88**, 665.
33 A. Yoshifuji, Y. Noishiki, M. Wada, L. Heux and S. Kuga, *Biomacromolecules*, 2006, **7**, 2878.
34 S. Monge, V. Darcos and D. A. Haddleton, *J. Polym. Sci. A. Polym. Chem.*, 2004, **42**, 6299.

35 K.Beers, S. G. Gaynor and K. Matyjaszewski, *Macromolecules*, 1998, **31**, 9413.
36 H. G. Borner, K. Beers and K. Matyjaszewski, *Macromolecules*, 2001, **34**, 4375.

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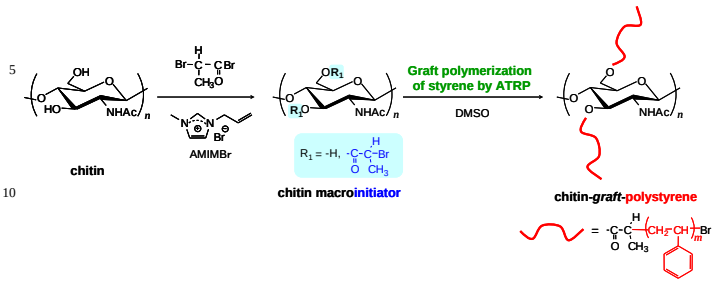

We prepared chitin macroinitiator in an ionic liquid of AMIMBr, which was used for the synthesis of chitin-*graft*-polystyrene by graft polymerization of styrene via ATRP.