Synthesis and lower critical solution temperature behavior of chitosan and N-isopropylacrylamide graft copolymers

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Introduction

Chitosan (CS) is nontoxic, biocompatible and biodegradable, pH-sensitive polymer with antimicrobial activity. Because of these properties, it is an interesting biopolymer which can be further modified *via* grafting reactions. One of the most attractive compounds which can be used for grafting of chitosan is N-isopropylacrylamide (NIPAAm). Poly(N-isopropylacrylamide) (PNIPAAm) is highly thermo-sensitive polymer and shows sharp solubility changes in water around a specific temperature which is known as lower critical solution temperature (LCST) [1]. Beyond 32 °C PNIPAAm turns into precipitate which can be composed of nanosized particles. Therefore, the graft copolymers with CS in the backbone and NIPAAm in the side chains could have dual stimuli responsive behavior and may be interesting in terms of drug delivery system.

Experimental results

In this study, chitosan-graft-N-isopropylacrylamide (CS-g-NIPAAm) copolymers were synthesized by free-radical polymerization in aqueous solution using potassium persulfate (PPS) as an initiator.

By changing the molar ratio of CS:NIPAAm from 1:0.25 to 1:10 the copolymers with different grafting ratio were prepared (see Table 1).

Table 1. Feed composition and reaction conditions

Copolymer sample	Molar ratio of reagents			Molar ratio CS / NIPAAm	Reaction temp., ◦C	Reaction time, h
	CS	NIPAAm	PPS			
CS-g-NIPAAm-1	1	0.25	0.16	1 : 0.25		
CS-g-NIPAAm-2	1	0.5	0.16	1 : 0.5		
CS-g-NIPAAm-3	1	0.8	0.16	1 : 0.8		
CS-g-NIPAAm-4	1	1	0.16	1 : 1	60	6
CS-g-NIPAAm-5	1	3	0.16	1 : 3		
CS-g-NIPAAm-6	1	5	0.16	1 : 5		
CS-g-NIPAAm-7	1	10	0.16	1 : 10		

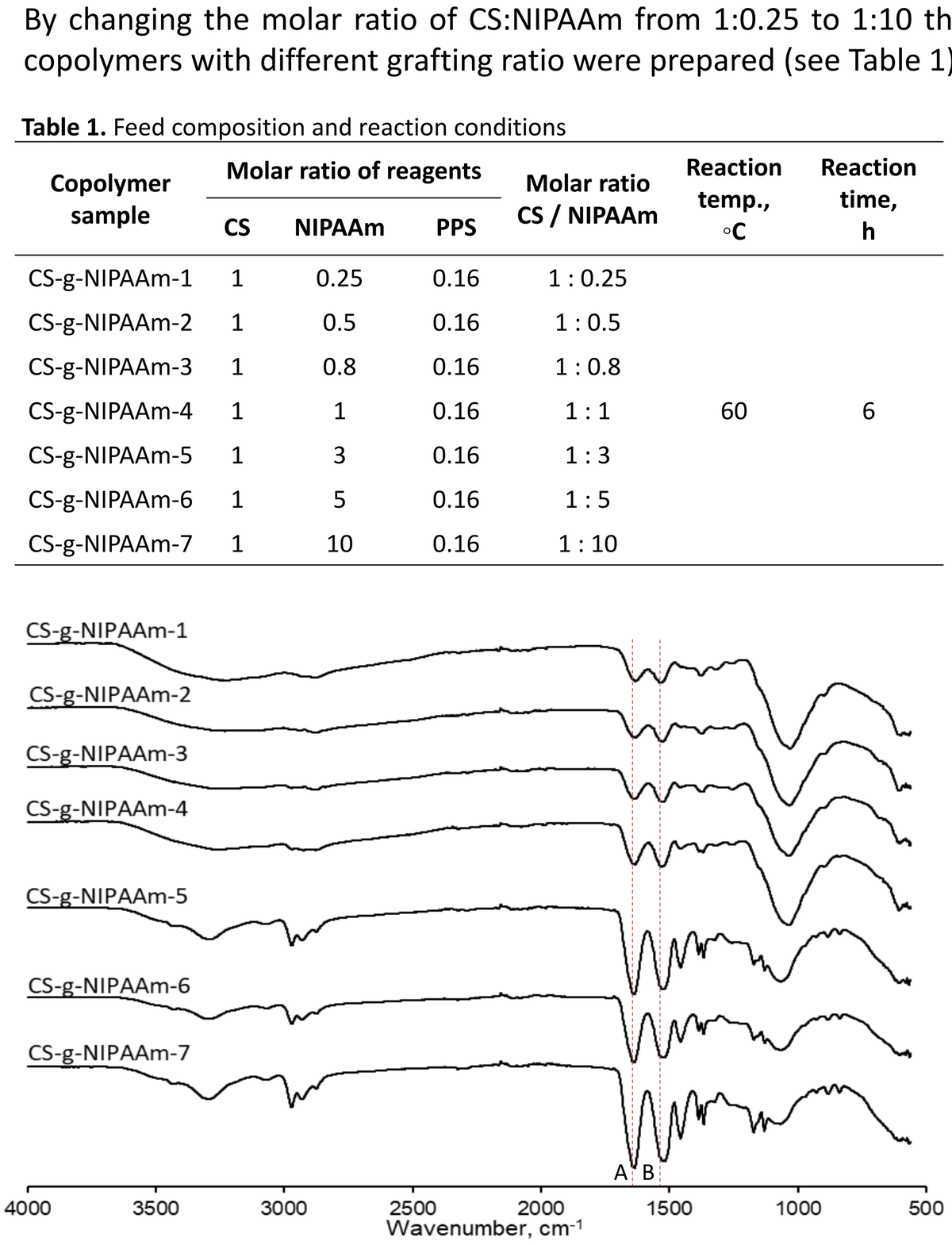

Fig.1 FTIR spectra of copolymers

The formation of graft copolymers was confirmed by FTIR and H-NMR spectra. As it is shown in Fig. 1, by increasing the content of NIPAAm in the copolymers, the intensity of characteristic peaks at 1638 cm^{-1} (peak A) and 1516 cm^{-1} (peak B) corresponding to C=O and N-H vibrations, are increasing.

The thermoresponsive behavior (LCST) of PNIPAAm and CS-g-NIPAAm copolymers in aqueous media was determined by cloud point and particle size measurements. It was revealed that aqueous solutions of almost all synthesized copolymers exhibit LCST behavior i.e. sharp solubility changes in water around 32 °C. The amplitude of those changes was also NIPAAm content and copolymer concentration dependent. Furthermore, above this temperature CS-g-NIPAAm copolymer aqueous solutions are present in the form of nanoparticle dispersions (see Table 2).

Table 2. Particle size measurements data of CS-g-NIPAAm in water above LCST (at ~45 °C)

Copolymer sample	Molar ratio of reagents		Concentration of solution g/L	Average particle diameter, nm	Polydispersity index
	CS	NIPAAm			
CS-g-NIPAAm-3	1	0.8	0.5	46.6±5.3	0.19±0.03
CS-g-NIPAAm-4	1	1	0.5	51.2±4.8	0.15±0.03
CS-g-NIPAAm-5	1	3	0.1	113.3±14.5	0.11±0.02
CS-g-NIPAAm-6	1	5	0.1	115.1±14.7	0.13±0.06
CS-g-NIPAAm-7	1	10	0.1	142.3±17.1	0.17±0.01
PNIPAAm	-	-	0.1	138.9±19.6	0.10±0.01

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References:

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