

SYNTHESIS OF PAMPS-MODIFIED OLIGOCHITOSAN HYDROGELS VIA ACRYLAMIDOMETHYLATION BY NMA/NH₄Cl

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Abstract

Under an acidic condition, acrylamidomethylation took place between *N*-methylol groups of *N*-hydroxymethylacrylamide (NMA) and C-6-hydroxyl groups of oligochitosan ($M_n \approx 5,400$ g/mol), resulting in acrylamidomethyl group-containing oligochitosan (OC-NMA). The pendant double bonds were readily vulnerable to a free-radical attack. Polymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) initiated by $K_2S_2O_8$ in the presence of OC-NMA led to a full interpenetrating polymer network of PAMPS-modified oligochitosan hydrogel. Various contents of $K_2S_2O_8$ and AMPS were employed to synthesize the hydrogels with different extents of swelling ability. The swelling ability appeared directly proportional to the amount of AMPS incorporated and inversely proportional to the amount of the initiator used. The amounts of the gel and sol fractions obtained were also altered, accordingly. The chemical structure and thermal stability of resulting hydrogels were analyzed by solid state ¹³C NMR and TGA, respectively.

Introduction

Recently, oligochitosan (OC), depolymerized chitosan, has been extensively studied due to its solubility in water. Its biological properties are expected to be quite similar to those of chitosan. *N*-hydroxymethylacrylamide (NMA) is a reagent that possesses two reactive functional groups, *N*-methylol and vinyl groups. It was known that the *N*-methylol group was able to react with a hydroxyl group in polymers, e.g., chitosan, cellulose and poly(vinyl alcohol), in an acidic condition (e.g. in NH₄Cl) at elevated temperature, yielding free vinyl group containing polymers. The use of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) as a monomeric starting material for the preparation of hydrogels is well established. Its corresponding polymer (PAMPS) is water-soluble. In this study, PAMPS-modified oligochitosan hydrogels were prepared by a two-step process : (1) acrylamidomethylation between *N*-methylol groups of NMA and C-6-hydroxyl groups of OC, yielding a water-soluble product denoted as OC-NMA, and (2) polymerization of AMPS initiated by $K_2S_2O_8$ in the presence of OC-NMA. The resulting hydrogels were characterized by ¹H and ¹³C NMR and TGA. The effects of the contents of $K_2S_2O_8$ and AMPS employed on the degree of swelling (DS) of the hydrogels were investigated.

Experimental

Acrylamidomethylation

Typically, OC ($M_n \approx 5,420$ g/mol, %DD = 96, 2 g, 0.012 mol) dissolved in H₂O (8 mL) was mixed with 48% aq. NMA (18.7 mL, 0.096 mol), 4-methoxyphenol (polymerization inhibitor, 0.038 g, 0.3 mmol) and NH₄Cl (catalyst, 1.926 g, 36 mmol). The homogeneous solution was then heated at 140°C for 10 min before being coagulated in acetone. The product, OC-NMA, was purified by

repeatedly washing it with a mixed solvent of acetone and ethanol (1:1 v/v) and dried in a vacuum oven.

Polymerization of AMPS in the presence of OC-NMA

To synthesize PAMPS-modified OC hydrogels, OC-NMA (0.5 g) dissolved in H₂O (5 mL) was mixed with given amounts of AMPS and K₂S₂O₈ (oxidizer) based on the amount of OC-NMA started. The whole solution was subsequently poured into a mold and heated in an oven at 70°C for 2 hr. The cast film was washed and sequentially extracted with water and methanol to separate out the sol fractions, i.e. unmodified OC, uncrosslinked OC-NMA and PAMPS homopolymer. The gel fraction was denoted as CL-OC-NMA-PAMPS.

Results and Discussion

The reaction scheme of the synthesis of PAMPS-modified OC hydrogels is illustrated in Figure 1. The acrylamidomethylation was not quite efficient; an excess amount of NMA was employed, i.e., when the ratio of [OC] : [NMA] = 1:8 was used, only 25 mol% of NMA was found in the synthesized product. The ¹H NMR spectrum of OC-NMA is shown comparatively with that of OC in Figure 2. The acrylamidomethyl groups in OC-NMA were readily vulnerable to a free-radical attack, leading to the crosslinking of OC-NMA (the crosslinked products denoted as CL-OC-NMA). Table 1 reveals the crosslinking efficiency of OC-NMA by K₂S₂O₈ conducted at 70°C for 2 hr. It was noted that 5 wt% of K₂S₂O₈ used was the optimum value. The sol fraction analyzed by ¹H NMR spectroscopy appeared to be a mixture of unmodified OC and uncrosslinked OC-NMA (spectrum not shown here). The incorporation of PAMPS into the CL-OC-NMA hydrogel did improve the swelling ability of the modified hydrogels as demonstrated in Table 2. The ¹³C NMR spectra of the gel and sol fractions are shown in Figure 3. The carbonyl carbon (at δ ≈ 176 ppm) was vividly observed in the spectrum of the gel fraction, indicating the presence of PAMPS in the hydrogel. The thermal stability of the hydrogel investigated by TGA was found to be quite broad, as revealed in Figure 4.

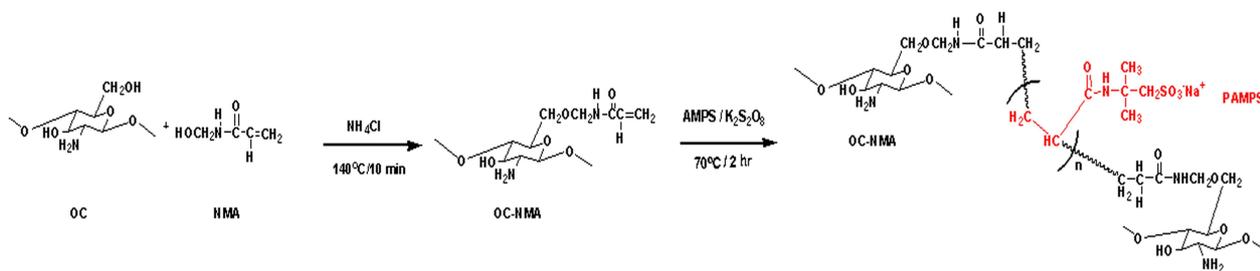


Figure 1 : The synthesis of PAMPS-modified OC hydrogels.

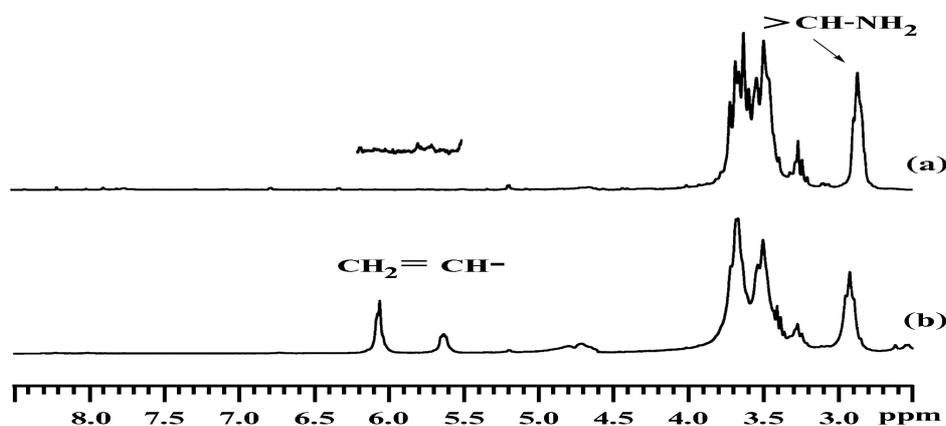


Figure 2 : The ¹H NMR spectra of (a) OC and (b) OC-NMA.

Table 1 : Effect of amount of $K_2S_2O_8$ used on crosslinking of OC-NMA.

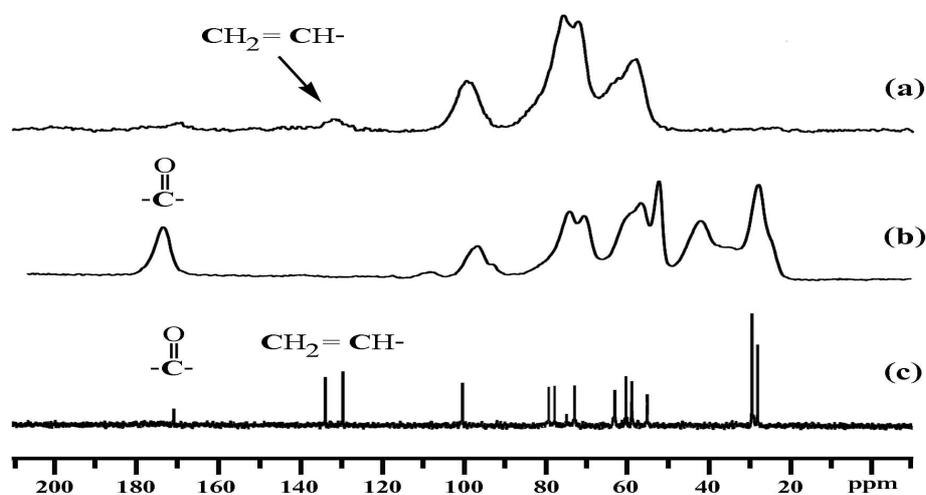
Run #	Product code	$K_2S_2O_8$ (wt% based on OC-NMA)	Sol fraction (wt%)	DS*
1	CL-OC-NMA1	2	27.40	1.42
2	CL-OC-NMA2	3	18.34	1.27
3	CL-OC-NMA3	5	18.09	1.16
4	CL-OC-NMA4	7	14.93	1.09
5	CL-OC-NMA5	10	17.73	ND

* DS = $(W_s - W_d)/W_d$ (where W_s and W_d are the weights of swollen and dry samples, respectively).

Table 2 : Effect of amount of PAMPS incorporated on degree of swelling of resulting hydrogels*.

Run #	Product code	Weight ratio		Sol fraction (wt%)	DS
		OC-NMA	AMPS		
1	CL-OC-NMA	1	0	18.09	1.16
2	CL-OC-NMA-PAMPS1	1	0.8	20.39	1.60
3	CL-OC-NMA-PAMPS2	1	1	27.54	1.83
4	CL-OC-NMA-PAMPS3	1	1.2	31.96	2.30

* 5 wt% of $K_2S_2O_8$ (based on OC-NMA) was used.

**Figure 3 :** The ^{13}C NMR spectra of (a) OC-NMA, (b) CL-OC-NMA-PAMPS2, and (c) sol fraction.

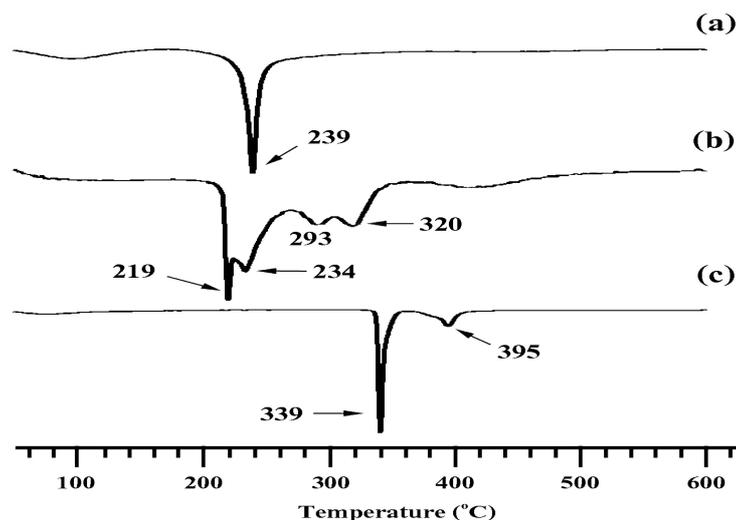


Figure 4 : The TGA thermograms of (a) OC-NMA, (b) CL-OC-NMA-PAMPS2, and (c) PAMPS.

Conclusions

The PAMPS-modified oligochitosan hydrogels were successfully synthesized. The swelling ability of the hydrogel was directly dependent on the content of PAMPS incorporated and the amount of $K_2S_2O_8$ used.

Acknowledgement

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References

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