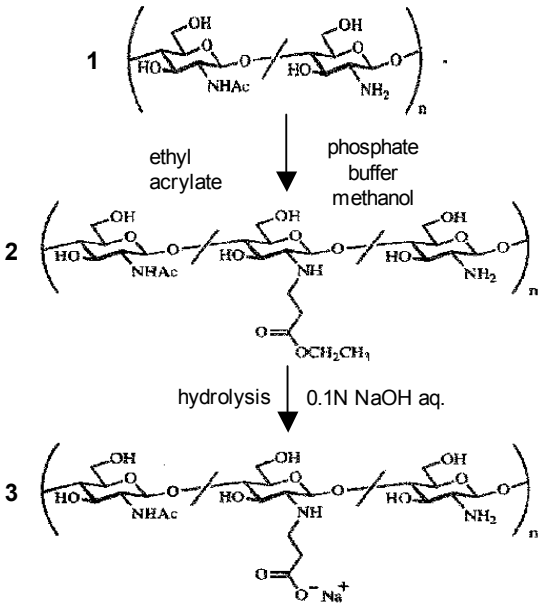
Novel N-selective ester functionalized chitin derivatives estimated by Py-GC

[Background] Chitin, which mainly consists of N-acetyl-D-glucosamine, is a representative and important amino polysaccharide. Despite its abundance in nature, chitin remains an almost unused natural resource due to its intractability and low solubility. Here, Michael-type nucleophilic addition of partially deacetylated chitin to ethyl acrylate as an alkylating agent is evaluated by Py-GC.

[Experimental] Partially deacetylated chitin was commercially obtained. The average degree of N-acetylation (DA) of the chitin was determined by ^{1}H NMR and Py-GC equipped with a Frontier Lab PY-2010D vertical microfurnace pyrolyzer (pyrolyzer temp., 450ºC, He carrier gas). The extent of ester group introduction was estimated by ^{1}H NMR and Py-GC.

[Results] The polymer reaction of **1** with ethyl acrylate to the D-glucosamine residue was carried out at 40ºC (Scheme 1). The results are summarized in Table 1. Hydrolysis of pendant ester groups of the product was observed in phosphate buffer solution, while **2** (Scheme 1) was successfully obtained in the solvent containing methanol (run No's. 2 and 3 in Table 1). It was found that the Michael addition proceeded exclusively at the amino groups of **1**. Degrees of substitution (DS) to the amino group of the D-glucosamine residue of **2** were determined by ^{1}H NMR spectroscopy using the methyl protons of the N-acetyl-D-glucosamine residue of **2** and the newly formed methylene protons adjacent to the 2-amino group of the D-glucosamine residue. DS values determined based on -NHCH$_2$- were further supported by quantitative analysis of Py-GC technique. The Py-GC is a powerful and convenient methodology to determine chemical structures without considering physical structures and physical properties of polymers (Table 1).



Scheme 1. Synthesis of N-selective ester functionalized chitin derivative and water-soluble carboxyethylchitin.

Table 1. Synthesis of N-(2-ethoxycarbonylethyl)chitin (**2**) from partially deacetylated chitin (**1**) and ethyl acrylate

Run No.	**1**		Product polymer			
	in mg	-NH2 of **1** in mmol	Yield in mg (%)	Degrees of substitution		
				^{1}H NMR Based on -$CO_2CH_2CH_2$-	^{1}H NMR Based on -$NHCH_2$-	Py-GC
1	250	0.68	189 (-)	-	0.63	0.69
2	250	0.68	160 (52)	3.2	1.07	0.92
3	250	0.68	178 (59)	1.7	0.87	0.85
4	100	0.24	71 (-)	-	0.68	-

* Reaction condition: Temperature, 40°C; time. 240hr

*Contents excerpted from K. Aoki, M. Okada, H. Sato, S. Mizutani, H. Ohtani, S. Tsuge, Y. Shiogai, *Macromol. Chem. Phys.* 2000, 201, 1701-1708

Key word : Chitin, Glucosamine, Degree of substitution (DS), Py-GC, ^{1}H NHR, Michael addition reaction

Applications : General polymer analysis

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