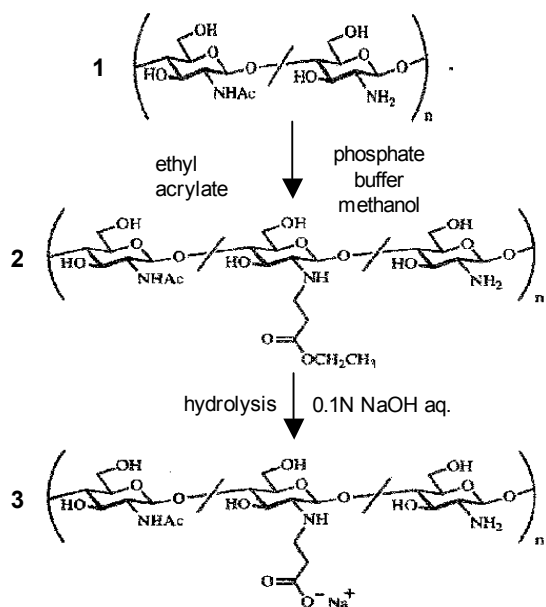


Novel N-selective ester functionalized chitin derivatives estimated by Py-GC

[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 ¹H NMR and Py-GC equipped with a Frontier Lab PY-2010D vertical microfurnace pyrolyzer (pyrolyzer temp., 450°C, He carrier gas). The extent of ester group introduction was estimated by ¹H NMR and Py-GC.

[Results] The polymer reaction of **1** with ethyl acrylate to the D-glucosamine residue was carried out at 40°C (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 ¹H 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 -NHCH₂- 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.

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

Table 1. Synthesis of N-(2-ethoxycarbonyl)ethylchitin (**2**) of partially deacetylated chitin (**1**) to ethyl acrylate

Run No.	1		Yield in mg (%)	Product polymer		
	in mg	-NH ₂ of 1 in mmol		Degrees of substitution		
				¹ H NMR Based on -CO ₂ CH ₂ CH 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

Keyword : Chitin, Glucosamine, Degree of substitution (DS), Py-GC, ¹H NMR, Michael addition reaction

Applications : General polymer analysis

Related technical notes :

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