Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Kadokawa, Jun-Ichi , Karasu, Masa , Tagaya, Hideyuki and Chiba, Koji(1996) 'Synthesis of a Block Copolymer Consisting of Oligocellulose and Oligochitin', Journal of Macromolecular Science, Part A, 33: 11, 1735 — 1743
To link to this Article: DOI: 10.1080/10601329608010937
URL: http://dx.doi.org/10.1080/10601329608010937

J.M.S.—PURE APPL. CHEM., A33(11), pp. 1735–1743 (1996)

SYNTHESIS OF A BLOCK COPOLYMER CONSISTING OF OLIGOCELLULOSE AND OLIGOCHITIN

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ABSTRACT

Block copolymerization of a hydroxy-terminated oligotriacetylcellulose (**1**) with a hydroxy-terminated oligodihexanoylchitin (**2**) was carried out using 4,4′-methylenedi(phenyl isocyanate) as a coupling reagent. The product copolymer has a structure **4** consisting of alternating oligotriacetylcellulose and oligodihexanoylchitin units. The complete deprotection of **4** was achieved to give a cellulose–chitin block copolymer **5**.

INTRODUCTION

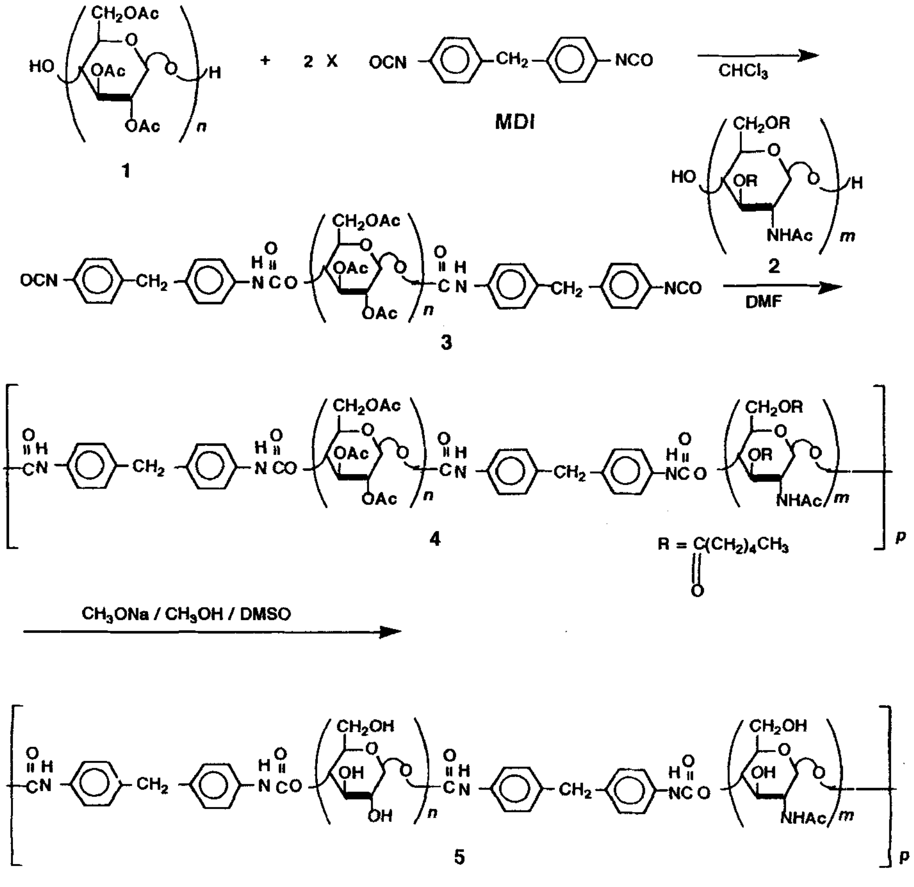
Block copolymers consisting of poly- or oligosaccharide are of considerable interest because of such unique properties as elasticity, water sorption, and biocompatibility [1–3]. With a view to incorporating the natural polysaccharide structures *into the block* copolymers, a hydroxy-terminated triacetylcellulose (**1**) or triacetylamylose oligomer has been prepared by acid hydrolysis of triacetylcellulose or triacetylamylose without deacetylation [1–6]. In connection with these synthetic approaches, we have recently found that oligodihexanoylchitin (**2**) having hydroxy groups at both ends was prepared by acid hydrolysis of a parent dihexanoylchitin in a mixed solvent of acetic acid and concentrated hydrochloric acid [7, 8]. These oligosaccharides have been employed for block copolymerization with synthetic polymers using diisocyanate compounds as a coupling reagent.

These investigations inspired us to examine block copolymerization between hydroxy-terminated oligosaccharides. This paper describes the block copolymerization of **1** with **2** using 4,4′-methylenedi(phenyl isocyanate) (MDI) as a coupling reagent, followed by deprotection of the product copolymer **4** to give a cellulose-chitin block copolymer **5** (Scheme 1).

EXPERIMENTAL

Materials

A hydroxy-terminated oligotriacetylcellulose (**1**) was prepared according to the literature (reaction time 6 hours) [3]. The molecular weight of **1** was determined as 3040 by the integrated ratio between the methyl peaks of acetyl groups and the aromatic peaks in the ^{1}H-NMR spectrum after the reaction of terminal hydroxy groups of **1** with phenyl isocyanate. A hydroxy-terminated oligodihexanoylchitin (**2**) was prepared as previously reported by us [7]. A reaction time of 13 hours was



SCHEME 1.

employed, and the molecular weight was 7200 as determined by ^{1}H-NMR analysis, as previously reported. Other reagents were commercially available as an extra grade and used without further purification. Solvents, chloroform, DMF, methanol, and dimethylsulfoxide (DMSO) were purified by distillation according to the usual manner.

Preparation of Isocyanate-Terminated Oligotriacetylcellulose (3)

Under argon, 0.030 g (0.01 mmol) of **1** was mixed with 0.005 g (0.02 mmol) of MDI in 1.0 mL of $CHCl_3$ at room temperature. Then the mixture was refluxed for 3 hours and evaporated under reduced pressure. The residue was dried at 120°C for 3 hours in vacuo to give oligotriacetylcellulose (**3**) having isocyanate groups at both ends quantitatively.

Block Copolymerization of 3 with 2

A typical example was as follows (Entry 5, Table 1). Under argon, 0.035 g (0.01 mmol) of **3** was dissolved in 1.0 mL of DMF. To the solution was added 0.072 g (0.01 mmol) of **2** and 0.010 g (0.10 mmol) of triethylamine, and the mixture was heated at 150°C for 120 hours. After cooling, the precipitated material was filtrated off and the yield of the block copolymer was directly calculated by GPC measurement of the filtrate.

Isolation Procedure of Block Copolymer 4

In order to isolate the block copolymer **4**, the reaction mixture (Entry 8, Table 1) was poured into a large amount of $CCl_4/CHCl_3$ (1:1 in volume) to precipitate the product. The product was isolated by filtration and dried in vacuo to give 0.039 g of **4** (36.0% yield).

Deprotection of 4

To a solution of **4** (0.056 g) in DMSO (3.0 mL) was added sodium methoxide (0.030 g) in methanol (1.0 mL) under argon, and the mixture was stirred for 11 hours at room temperature. The reaction mixture was neutralized by acetic acid, and water (5.0 mL) was added. The product was isolated by filtration and dried in vacuo to give 0.014 g of **5**.

Measurements

^{1}H- and ^{13}C-NMR spectra were recorded on a Jeol EX-270 spectrometer. IR spectra were recorded on a Horiba FT-200 spectrometer. GPC analyses were performed by using an Hitachi 655A-11 with a RI detector under the following conditions: TSKgel G2500H$_{XL}$ or G4000H$_8$ column with DMF eluent at a flow rate of 1.0 mL/min with polystyrene standards.

RESULTS AND DISCUSSION

Preparation of Isocyanate-Terminated Oligotriacetylcellulose (3)

In order to prepare an isocyanate-terminated oligotriacetylcellulose (**3**), **1** was reacted with 2 equivalents of MDI in $CHCl_3$ solvent under argon. The IR spectrum of the product showed a new absorption at 2296 cm^{-1} due to the isocyanate groups. The ^{1}H-NMR spectrum of the product showed broad peaks at δ 6.9–7.3 due to aromatic protons of the terminal groups in **3**. The peak due to aromatic protons of MDI was not observed in the spectrum, indicating no unreacted MDI in the product. Figure 1(B) shows the GPC profile of the product with DMF eluent in comparison with that of **1** in Fig. 1(A). These figures indicate that the elution volume of the GPC peak of the product is almost same as that of **1**. The molecular weight and the distribution of the GPC peak in Fig. 1(B) were calculated as 7070 and 1.8 with polystyrene standards, respectively, whereas those of the GPC peak in Fig. 1(A) were 5930 and 1.7 [9]. Furthermore, the elution volume of the GPC peak of **3** is almost same as that of **6** in Fig. 1(C) which was prepared by the reaction of **1** with phenyl isocyanate. These GPC data indicate that the content of the block copolymerized product between **1** and MDI is small, if it exists at all. All the above results support the isocyanate-terminated structure **3** of the product.

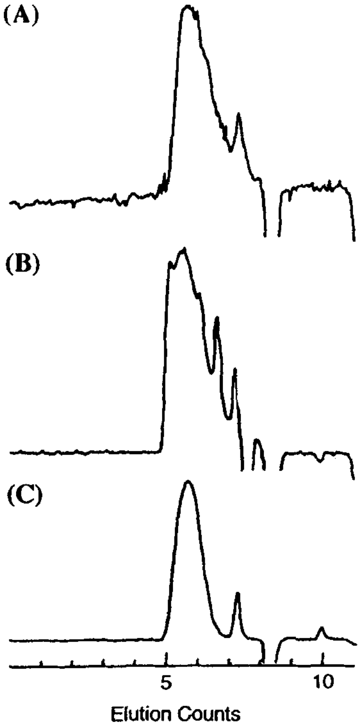
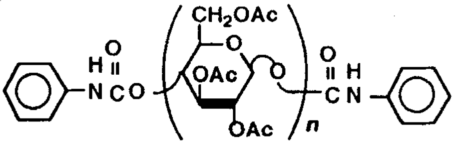


FIG. 1. GPC charts (TSKgel G2500H_{XL} column) of **1** (A), **3** (B), and **6** (C).



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Block Copolymerization of 3 with 2

The block copolymerization of **3** with **2** was carried out in DMF as solvent under various conditions (Table 1). After the desired reaction time, the precipitate, if any, was separated by filtration. Then the yield of the block copolymer was directly calculated by GPC measurement of the reaction mixture. The GPC charts of the reaction mixtures (Entries 6 and 8) in Fig. 2(A and B) show two peaks due to the block copolymer at lower elution volume and due to **2** and **3** at higher elution volume. The GPC peaks due to the block copolymer obtained under various conditions always appeared around the area corresponding to a molecular weight of 1.0×10^5 by a calibration curve with polystyrene standards [9]. From the area ratio between two peaks, the yield of the block copolymer can be calculated.

The block copolymerization did not proceed without added catalyst at a temperature below 130°C. The yield of the block copolymer was low at 150°C for 20 hours, but the longer reaction time (120 hours) at that temperature gave a large amount of the precipitate from the reaction mixture (Entries 1 and 2). When triethylamine or 4-dimethylaminopyridine (DMAP) was added as a polyaddition catalyst, the block copolymerization proceeded even at 100–130°C (Entries 3, 4, and 6).

TABLE 1. Block Copolymerization of **3** with **2** under Various Conditions[a]

	Condition			Product			
Entry	Catalyst[b]	Temperature, °C	Time, hours	Precipitate, %	Block copolymer, %	M_n[c] $\times 10^5$	M_w/M_n[c]
1	–	150	20	Trace	6.90		
2	–	150	120	42.9	5.14		
3	Et_3N	100	120	Trace	12.8		
4	Et_3N	130	120	Trace	31.6		
5	Et_3N	150	120	40.2	21.6		
6	DMAP	130	120	Trace	36.2		
7	DMAP	150	120	85.0	11.6		
8[d]	DMAP	150	120	0	84.6 (36.0)[e]	1.4	2.4

[a] Each olgiomer (0.01 mmol) in 1.0 mL of DMF.
[b] Catalyst (0.01 g) was added.
[c] Determined by GPC with DMF.
[d] Each oligomer (0.01 mmol) in 4.0 mL of DMF.
[e] Isolated yield as CCl_4-$CHCl_3$ (1:1 in volume) insoluble part.

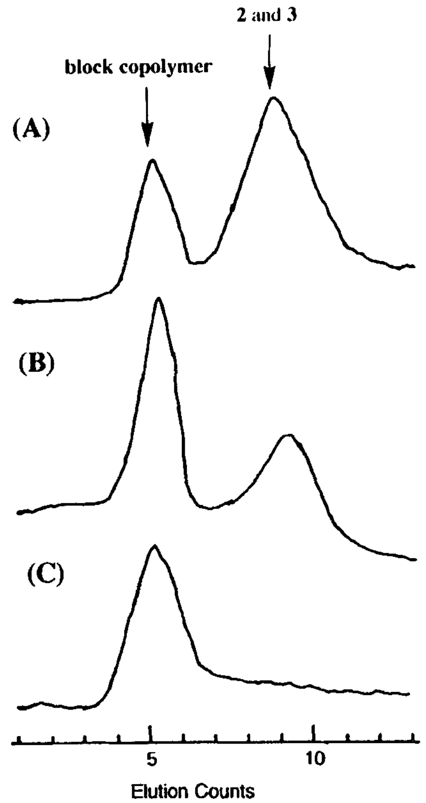

FIG. 2. GPC charts (TSKgel G4000H$_8$ column) of reaction mixtures [Entry 6 (A) and Entry 8 (B)] and isolated block copolymer 4 [Entry 8 (C)].

At 150°C, however, a large amount of the precipitate was yielded (Entries 5 and 7). Under the dilute condition in the presence of DMAP, no precipitation occurred during the reaction and the yield of the block copolymer was highest (84.6%, Entry 8). Then the reaction mixture obtained under this condition was poured into a large amount of a mixture of $CHCl_3$ and CCl_4 (1:1 in volume) to precipitate the block copolymer (isolated yield, 36.0%). The GPC profile of the isolated material in Fig. 2(C) shows only one peak due to the block copolymer at a lower elution volume; there was no peak due to **2** and **3** at a higher elution volume. The molecular weight was estimated as 1.4×10^5 by using a calibration curve with polystyrene standards [9].

The structure of the isolated block copolymer was determined by ^{1}H-NMR and IR spectroscopies. Figure 3 shows the ^{1}H-NMR spectrum of the block copolymer (DMSO-d_6). Peaks i, h, g, and d at δ 0.84, 1.22, 1.45, and 2.29, respectively, are due to methyl and methylene protons of hexanolyl groups. Peaks f and e at δ 1.67 and 2.07 are ascribable to methyl protons of acetamide and acetate groups, respectively. Broad multiplet at δ 2.7–5.0 are assignable to sugar protons. Broad peaks at δ 6.7–7.1 are due to aromatic protons. Two broad peaks at δ 7.85 and 8.22 are ascribable to NH protons. Peak c due to methylene protons between aromatics overlaps with

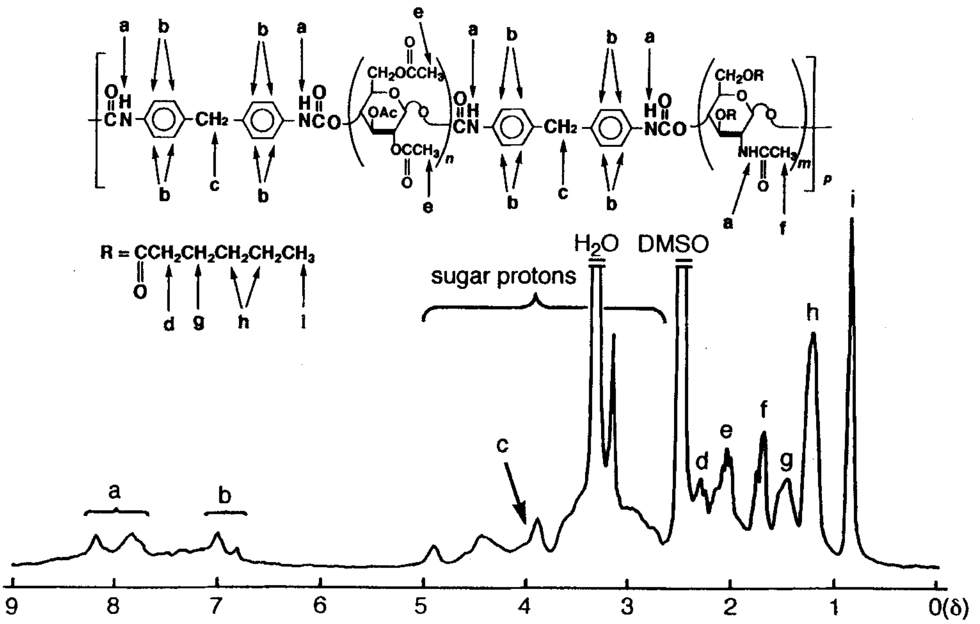

FIG. 3. ^{1}H-NMR spectrum of block copolymer **4** (Entry 8) in DMSO-d_6.

sugar protons, which is generally observed at around δ 4.0. The IR spectrum of the block copolymer in Fig. 4(A) exhibits two characteristic absorptions at 1736 and 1655 cm^{-1} due to C=O of ester and amide, respectively. These spectroscopic data support structure **4** of the block copolymer.

The structure of the precipitate from the reaction mixture is not yet clear and is now under further investigation.

Deprotection of 4

Deprotection of **4** was carried out in a mixed solvent of DMSO and methanol containing sodium methoxide to give block copolymer **5** which consists of alternating oligocellulose and oligochitin units. The product was insoluble in common solvents. The IR spectrum of the product in Fig. 4(B) shows absorptions at 1696 and 1637 cm^{-1} due to C=O of urethane and amide groups, respectively. The absorption due to ester carbonyl groups of **4**, shown in Fig. 4(A), is not observed, indicating the occurrence of complete deprotection to give block copolymer **5**.

CONCLUSION

The block copolymerization of a hydroxy-terminated oligotriacetylcellulose (**1**) with a hydroxy-terminated oligodihexanoylchitin (**2**) using MDI as a coupling reagent was carried out. The yields were determined by GPC analysis under various reaction conditions. Structure **4** of the isolated block copolymer was confirmed by ^{1}H-NMR and IR analyses. In addition, the deprotection of **4** took place completely

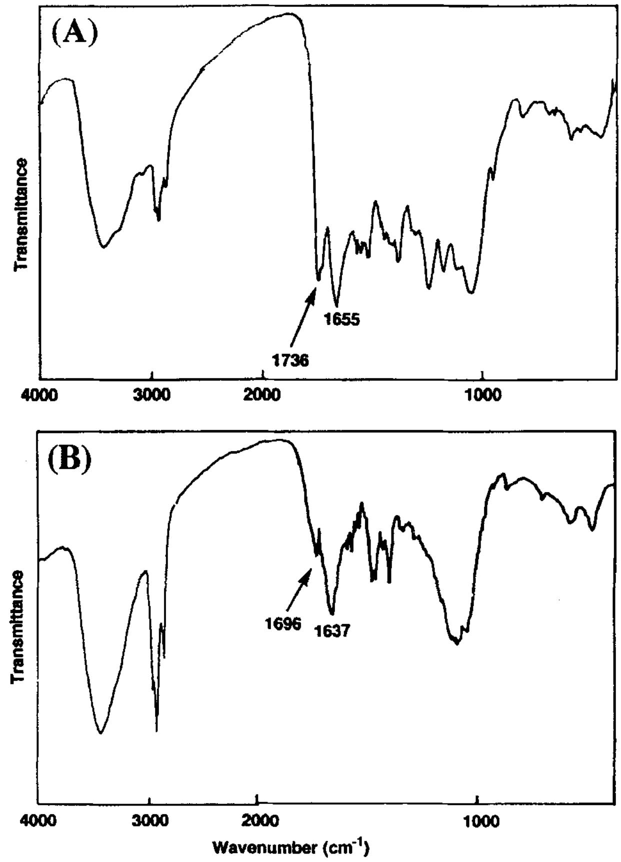

FIG. 4. IR spectra of block copolymer **4** [Entry 8 (A)] and deprotected block copolymer **5** (B).

to give block copolymer **5** which consists of alternating oligocellulose and oligochitin units.

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Received October 25, 1995
Revision received March 11, 1996