



Synthesis and thermal properties of paramylon mixed esters and optical, mechanical, and crystal properties of their hot-pressed films



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ABSTRACT

Acylation of paramylon, a storage polysaccharide of *Euglena gracilis*, using multiple acid anhydrides yielded thermoplastic paramylon mixed esters without significant depolymerization. DSC examination showed that the shorter the acyl chain, the higher both the melting and glass transition temperature of the ester. TG analyses revealed their higher thermostability with the 5% weight loss temperature of ~ 330 °C. Melt volume flow rate examination revealed that the longer the acyl chain, the higher the thermoplasticity of the ester and that the esters exhibited higher thermoplasticity than structurally analogous esters made from cellulose and curdlan. A notable feature of the thermoplastic paramylon mixed esters is the availability of hot-pressing as a means of molding them into a film. Light transmittance and XRD measurements revealed that these films were transparent and in the amorphous state. Tensile tests indicated that the films had adequate mechanical strength comparable to those of the cellulose and curdlan analogues.

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1. Introduction

Development of naturally occurring polysaccharide-based materials have recently attracted special attention in terms of reducing dependence on fossil fuels. Specifically, intensive efforts aimed at efficient production of microalgae-derived biofuels have been undertaken by many research groups (Banerjee, Sharma, Chisti, & Banerjee, 2002; Kaya et al., 2011; Mata, Martins, & Caetano, 2010; Tucci, Vacula, Krajcovic, Proksch, & Martin, 2010; Yamane et al., 2013). Our objective in this research area is the creation of high-value-added materials from *Euglena*-derived chemicals (Shibakami, Sohma, & Hayashi, 2012; Shibakami, Tsubouchi, & Hayashi, 2014; Shibakami, Tsubouchi, Nakamura, & Hayashi, 2013; Shibakami, Tsubouchi, Sohma, & Hayashi, 2015a; Shibakami, Tsubouchi, Sohma, & Hayashi, 2015b). A promising *Euglena*-derived substance meeting this purpose is a storage polysaccharide (i.e., β -1,3-glucan), which is commonly referred to as paramylon. We think that it is promising for three reasons. First, a substantial amount of paramylon is stored inside the euglenoid cell (Barsanti, Vismara, Passarelli, & Gualtieri, 2001; Santeck, Friehs, Lotz, & Flaschel, 2012).

Second, since a paramylon particle is exclusively composed of β -1,3-glucan, further purification is not needed for material creation. Third, paramylon forms helices that β -1,4-glucans such as cellulose, chitin, and chitosan cannot form (Barras & Stone, 1968).

Our group recently reported the synthesis of thermoplastic paramylon derivatives (Shibakami et al., 2014). The structural requirements for thermoplastic derivatives include site-specific introduction of a long-chain acyl group into the primary hydroxyl group and modification of the remaining hydroxyl groups by introducing acetyl ones. Although this synthesis was successful in terms of thermoplasticity, purification of the intermediate is time-consuming. Moreover, the mechanical fragility of the thermoplastic products due to the presence of long-chain acyl groups is a potential disadvantage.

We have thus been looking for an alternative molecular design that features both higher thermoplasticity and easier fabrication. As a result, we have developed a synthesis process that features simultaneous acylation of a medium-chain acyl group and an acetyl one using multiple acid anhydrides. Here we describe the preparation, structure, and thermal properties of the paramylon derivatives in comparison with structurally analogous derivatives made from cellulose and curdlan. We also discuss the mechanical, optical, and crystalline properties of hot-pressed films made from the paramylon derivatives. Examination of these properties suggested that the

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higher thermoformability of the paramylon mixed esters and their films of practical use essentially stem from the chain length (~ 3.0 and $\sim 2.0 \times 10^5$ for M_w and M_n , respectively) and a glucose linkage mode (β -1,3-mode) of paramylon.

2. Experimental

2.1. General methods

^1H nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker AVANCE 500 spectrometer (500 MHz). Fourier transform infrared (FT-IR) spectra were recorded using a JASCO FT/IR-480ST spectrophotometer equipped with an attenuated total reflectance accessory (ATR Pro 400-S, ZnSe prism, JASCO) with a resolution of 4 cm^{-1} . The degree of substitution (DS) values, which are the average number of functional groups attached to a glucose unit, were determined by comparing the integral values of the methyl/methylene protons of the medium-chain acyl groups and acetyl ones with those of the glucosic protons in the ^1H NMR spectrum; DS_{mc} and DS_{ace} in the text represent the DS of the medium-chain acyl (i.e., propyl, butyl, pentyl, and hexyl) group and acetyl one, respectively.

All chemicals and reagents are commercially available and were used without further purification. Paramylon was extracted from *Euglena gracilis* NIES-48 (NIES Culture Collection). Dissolving pulp (α -cellulose of $>92\%$, NDPS) was obtained from Nippon Paper Industries Co., Ltd. Curdlan was purchased from Wako Pure Chemical Industries, Ltd.

2.2. Synthesis of paramylon mixed esters

2.2.1. Paramylon acetate propionate from acetic acid and propionic anhydride (1)

A mixture of paramylon (3.001 g, 18.39 mmol), lithium chloride (LiCl) (2.367 g, 55.84 mmol), and *N,N*-dimethylacetamide (DMAc) (150 mL) was heated at 90°C for 1.5 h under a nitrogen atmosphere. To the resultant homogeneous solution was added 4-dimethylaminopyridine (DMAP) (428 mg, 3.50 mmol) in one portion and then dropwise a solution prepared by heating a mixture of acetic acid (3.302 g, 54.99 mmol) and propionic anhydride (14.462 g, 111.12 mmol) prepared at 90°C for 1.5 h under a nitrogen atmosphere. After stirring at $\sim 108^\circ\text{C}$ for 4 h, methanol (150 mL) was added to the reaction mixture, followed by dropwise adding of the mixture to water (300 mL) to yield a white precipitate. The precipitate was separated by suction filtration and then washed with water (100 mL) on the filter. The white solid was mechanically stirred with methanol (350 mL), followed by separation by suction filtration. This purification process was repeated three times. The resultant solid was then dissolved in chloroform (150 mL) and the homogeneous solution was added dropwise to methanol (500 mL) to give a thin fibrous precipitate. The precipitate was mechanically stirred with methanol (150 mL). Suction filtration, air-drying overnight and subsequent vacuum-drying at 70°C for 7 h yielded the desired product (1) as a white solid (4.483 g, 13.97 mmol, yield 75.9%). Successful preparation was confirmed by ^1H NMR and FT-IR measurements: ^1H NMR (CDCl_3) δ 4.87 (brs), 4.30 (brs), 4.02 (brs), 3.72 (brs), 3.60 (brs), 2.40–1.99 (m), 1.61 (s), 1.18–1.09 (s); DS_{ace} 0.78; DS_{mc} 2.18; FT-IR (cm^{-1}) 2945, 1737, 1386, 1389, 1365, 1155, 1051, 871, 806.

2.2.2. Paramylon acetate butyrate from acetic acid and butyric anhydride (2)

By using a process similar to that described for the preparation of product (1) except for using butyric anhydride instead of propionic anhydride, a 18.1% yield of product (2) (1.204 g, 3.34 mmol) was obtained from paramylon (3.014 g, 18.47 mmol),

acetic acid (3.323 g, 55.34 mmol), and butyric anhydride (17.608 g, 111.30 mmol). Successful preparation was confirmed by ^1H NMR and FT-IR measurements: ^1H NMR (CDCl_3) δ 4.80 (brs) 4.35 (brs), 4.24 (brs), 4.05 (brs), 3.72–3.59 (m), 2.47–2.10 (m), 1.62–1.52 (m), 0.94–0.80 (m); DS_{ace} 0.98; DS_{mc} 2.16; FT-IR (cm^{-1}) 2963, 2874, 1739, 1457, 1391, 1369, 1219, 1154, 1041, 893, 793, 750.

2.2.3. Paramylon acetate pentanoate from acetic acid and pentanoic anhydride (3)

By using a process similar to that described for the preparation of product (1) except for using pentanoic anhydride instead of propionic anhydride, a 35.4% yield of product (3) (2.145 g, 5.49 mmol) was obtained from paramylon (2.534 g, 15.53 mmol), acetic acid (2.813 g, 46.84 mmol), and valeric anhydride (17.447 g, 93.68 mmol). Successful preparation was confirmed by ^1H NMR and FT-IR measurements: ^1H NMR (CDCl_3) δ 4.81 (brs) 4.38 (brs), 4.23 (brs), 3.73 (brs), 3.57 (brs), 2.31–1.99 (m), 1.61–1.34 (m), 0.96–0.92 (m); DS_{ace} 1.12; DS_{mc} 1.88; FT-IR (cm^{-1}) 2957, 2871, 1741, 1456, 1389, 1370, 1173, 1151, 1046, 892, 754, 734, 594.

2.2.4. Paramylon acetate hexanoate from acetic acid and hexanoic anhydride (4)

By using a process similar to that described for the preparation of product (1) except for using hexanoic anhydride instead of propionic anhydride, a 80.2% yield of product (4) (6.185 g, 14.78 mmol) was obtained from paramylon (3.005 g, 18.42 mmol), acetic acid (3.336 g, 55.55 mmol), and hexanoic anhydride (23.501 g, 109.65 mmol). Successful preparation was confirmed by ^1H NMR and FT-IR measurements: ^1H NMR (CDCl_3) δ 4.86 (brs), 4.79 (brs), 4.33 (brs), 4.25 (brs), 3.76 (brs), 3.60 (brs), 3.55 (brs), 2.35–1.99 (m), 1.60 (s), 1.38 (s), 1.31 (s), 0.94–0.90 (m); DS_{ace} 1.05; DS_{mc} 1.95; FT-IR (cm^{-1}) 2955, 2930, 2862, 1743, 1457, 1390, 1371, 1217, 1149, 1045, 889, 732, 597.

2.2.5. Paramylon acetate propionate from acetic anhydride and propionic acid (5)

A mixture of paramylon (0.994 g, 6.09 mmol), LiCl (0.783 g, 18.47 mmol), and DMAc (50 mL) was heating at 90°C for 1 h under a nitrogen atmosphere. To the resultant homogeneous solution was added DMAP (146 mg, 1.20 mmol) in one portion and then dropwise a solution prepared by heating a mixture of acetic anhydride (3.780 g, 37.03 mmol) and propionic acid (1.369 g, 18.48 mmol) prepared by heating at 100°C for 1.25 h under a nitrogen atmosphere. After stirring at $\sim 102^\circ\text{C}$ for 3.5 h, the reaction mixture was added dropwise to water (500 mL) to yield a transparent precipitate. The precipitate was separated by suction filtration and then mechanically stirred with water (400 mL) for 1 h. After dissolving the precipitate in chloroform (500 mL), the opaque solution was poured into methanol (500 mL). Gradual removal of solvent yielded a heterogeneous solution. The desired product (5) was obtained as a white solid by suction filtration (1.428 g). Yield is unknown because DS values of the product could not be determined due to its insolubility in deuterated chloroform. Successful preparation was confirmed by FT-IR measurement: FT-IR (cm^{-1}) 2954, 1734, 1635, 1371, 1211, 1029, 893, 703, 599.

2.2.6. Paramylon acetate butyrate from acetic anhydride and butyric acid (6)

By using a process similar to that described for the preparation of product (5) except for using butyric acid instead of propionic acid, a 78.8% yield of product (6) (4.450 g, 14.72 mmol) was obtained from paramylon (3.009 g, 18.44 mmol), acetic anhydride (11.298 g, 105.09 mmol), and butyric acid (4.986 g, 55.57 mmol). Successful preparation was confirmed by ^1H NMR and FT-IR measurements: ^1H NMR (CDCl_3) δ 4.89 (brs), 4.83 (brs), 4.36 (brs), 4.32 (brs), 4.04 (brs), 3.74 (brs), 3.65 (brs), 2.12–2.00 (m), 1.64 (s), 1.02–0.93 (m);

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