Carbohydrate Polymers 80 (2010) 711–719

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

α,α-Trehalose-based polyacetals and macrocyclic acetals

Sylwia Kukowka, Jolanta Maślińska-Solich *

Department of Physical Chemistry and Technology of Polymers, Faculty of Chemistry, Silesian University of Technology, ul. M. Strzody 9, 44-100 Gliwice, Poland

ARTICLE INFO

Article history:
Received 15 October 2007
Received in revised form 12 November 2009
Accepted 4 December 2009
Available online 11 December 2009

Keywords:
Polyacetals
Macrocycles
α,α-Trehalose
Mass spectrometry

ABSTRACT

The polycondensation of 1,*x*-bis(2-formylphenoxy)alkanes with α,α-trehalose using acidic catalyst leads to the formation of linear polymers and macrocyclic compounds. The structure of the polymer was determined by ^{1}H and ^{13}C NMR spectroscopy, electrospray ionization mass spectrometric (ESI-MS) and matrix-assisted laser desorption/ionization-time of flight mass spectrometric (MALDI-TOF) analysis. These ^{1}H NMR, ESI-MS and MALDI-TOF spectra revealed that the polyacetal is composed of the molecules terminated by glucopyranosyloxy group or only aldehyde groups. The mass spectra also showed evidence of polyacetal chains with the small content of glucose-dialdehyde units.

1. Introduction

Environment-friendly polymers derived from renewable resources have attracted much attention in recent years. Sugars, which have a number of hydroxy groups, are particularly interesting as they may constitute the hydrophilic part, if associated with a hydrophobic polymer chain (Varma, Kennedy, & Galgali, 2004).

The disaccharide α,α-trehalose is widely distributed in nature. It can be found in a large range of organisms, such as bacteria, fungi, nematodes and crustaceans. In addition to its function as a storage carbohydrate and transport sugar, α,α-trehalose plays an important role in stress protection, especially during heat stress and dehydration (Crowe, Carpenter, & Crowe, 1998; Wiemken, 1990). α,α-Trehalose has high thermostability (anhydrous trehalose melts at 203 °C) and a wide pH-stability range (Higashiyama, 2002; Richards & et al., 2002). As a non-reducing sugar, this saccharide does not undergo Maillard reaction with amino compounds such as amino acids or proteins.

Its particular physical features make it an extremely attractive substance (Besson, Fayet, & Gelas, 1997; Carbonnel, Fayet, & Gelas, 1999), for industrial applications. It is not only used in the food industry, but possesses many biological and medicinal potentials (Madonna et al., 1989) applicable to sugar-based therapeutic reagents preventing starch retrogradation, protein denaturation and lipid degradation (Sampedro & Uribe, 2004).

The acetal function is well-known protecting group having its own unique reactivity and it has been used more recently to functionalize mono- and oligosaccharides (Fanton, Fayet, & Gelas, 1997).

Our group is currently working on the synthesis of polymers containing carbohydrate units in the main chain by the condensation of dialdehydes with mono- and disaccharides (Maślińska-Solich, 2001). The advantage of this procedure is that it is a single step process without the necessity to use hydroxyl group chemistry of a sugar molecule. Another interesting aspect of the study would be to obtain structure property relationships in the reaction of dialdehydes with specific hydroxyl groups of the sugar. It has been demonstrated in several recent publications that macrocycles and linear macromolecules exist in chain-ring equilibrium (Maślińska-Solich & Kukowka, 2004a, 2004b; Maślińska-Solich, Kuźnik, Kubicki, & Kukowka, 2002).

This paper will highlight an approach for the preparation of macromolecules of controlled structure in the polycondensation process of 1,*x*-bis(2-formylphenoxy)alkanes (where $x = 4–12$) with the α,α-trehalose.

2. Experimental part

2.1. Materials

α,α-D-Trehalose dihydrate **1**, D-glucose **2**, methyl α-D-glucopyranoside **3**, and *p*-toluenesulfonic acid (*p*-TsOH) were purchased from Fluka A.G. and used directly without any purification. Salicylaldehyde (Fluka) was distilled prior to use. 1,*x*-Bis(2-formylphenoxy)alkanes (**4**, **5**, **6**, **7**, **8**) were accomplished by etherification of salicylaldehyde with 1,*x*-dibromoalkanes (Fluka) (Choi, Ahn, Lee, & Jin, 2000). Solvents: *N*,*N*-dimethylformamide (DMF) was used after distillation from P_2O_5 and benzene was used after distillation

* Corresponding author. Tel.: +48 32 237 17 77.
E-mail address: jolanta.maslinska@polsl.sl (J. Maślińska-Solich).

0144-8617/$ - see front matter © 2010 Published by Elsevier Ltd.
doi:10.1016/j.carbpol.2009.12.008

from sodium. Pyridine (POCh, Poland) purified by distillation from KOH pellets, acetic anhydride (POCh Poland) was distilled.

2.2. Measurements

NMR spectra were recorded using a UNITY/*INOVA* 300 MHz (Varian Associates, Inc.) multinuclear NMR spectrometer.^{1}H and ^{13}C NMR spectra were run in deuterated chloroform ($CDCl_3$) using tetramethylsilane (TMS) as an internal standard.

IR spectra were recordedon a BioRad FTIR 175S spectrometer.

ESI-MS experiments were performed using a Finnigan MAT TSQ 700 triple stage quadrupole mass spectrometer equipped with an electrospray ionization (ESI) source (Finnigan, San Jose, CA, US). The sample was dissolved in methanol at a concentration of 0.5 mg ml^{-1} and introduced into the ESI source by continuous infusion at a rate 3 μl min^{-1} by means of the instrument syringe pump. The ESI source was operated at 4.5 kV, with the capillary heater held at 200 °C, under gas pressure (N_2) of 40 psi. Mass spectrum was acquired over the range of *m*/*z* 50–2000 in the positive ion mode.

Mass spectrometry (MALDI-ToF) was performed on Reflex IV MALDI-ToF instrument (Bruker-Saxonia, Germany) with delayed ion extraction, working in the reflectron mode (3 m flight path) with detection of positive ions. The analyzed compounds were dissolved in chloroform. Samples were prepared by mixing equal volumes of analyzed compounds samples and matrix solutions and depositing 0.7 μl of the mixture on a stainless-steel target plate. The following matrice was used 2,5-dihydroxybenzoic acid with 5 mg ml^{-1} aq. sodium iodide solution (1.4:1, v/v).

2.3. Methods

2.3.1. Condensation of ***3*** with 1,4-bis(2-formylophenoxy)butane (***4***) (Scheme 1)

A mixture of **3** (2.6 g; 10.3 mmol), **4** (2.0 g, 6.7 mmol), benzene (30 ml) and DMF (15 ml), containing *p*-TsOH (0.3 g, 1.7 mmol) was subjected to azeotropic distillation (Dean–Stark apparatus) (15 h). After the reaction, the catalyst was deactivated with $CaCO_3$ and the solvent was removed under reduced pressure. The product (**9**) was precipitated with distilled water, then dried, finally was washed with *n*-hexane and dried under a reduced pressure. Yield: 70%

^{1}H NMR ($CDCl_3$): δ = 1.90–2.15 (4H, m, –CH_2–), 3.38 (2H, s, –OCH_3), 3.20–4.40 (20 H, m, –CH_2O–, –CH–O–), 4.70 (2H, d, J = 3.9 Hz, H_{anom}), 5.00–5.40 (4H, m, –OH^2, –OH^3), 5.85 (2H, s, H^2 dioxan-2-yl), 6.88 (2H, t, J_1 = 8.1 Hz, H_D), 6.97 (2H, t, J_1 = 7.8 Hz, H_C), 7.31 (2H, td, J_1 = 6.8 Hz, J_2 = 2.1 Hz, H_B), 7.59 (2H, dd, J_1 = 7.8 Hz, J_2 = 2.1 Hz, H_A).

IR (KBr): 1010–1050, 1150–1180, 1350–1430 and 1550–1630 (–OCHO–); 2800–3020 (–CH_{Ar}–); 3100–3650 (–OH).

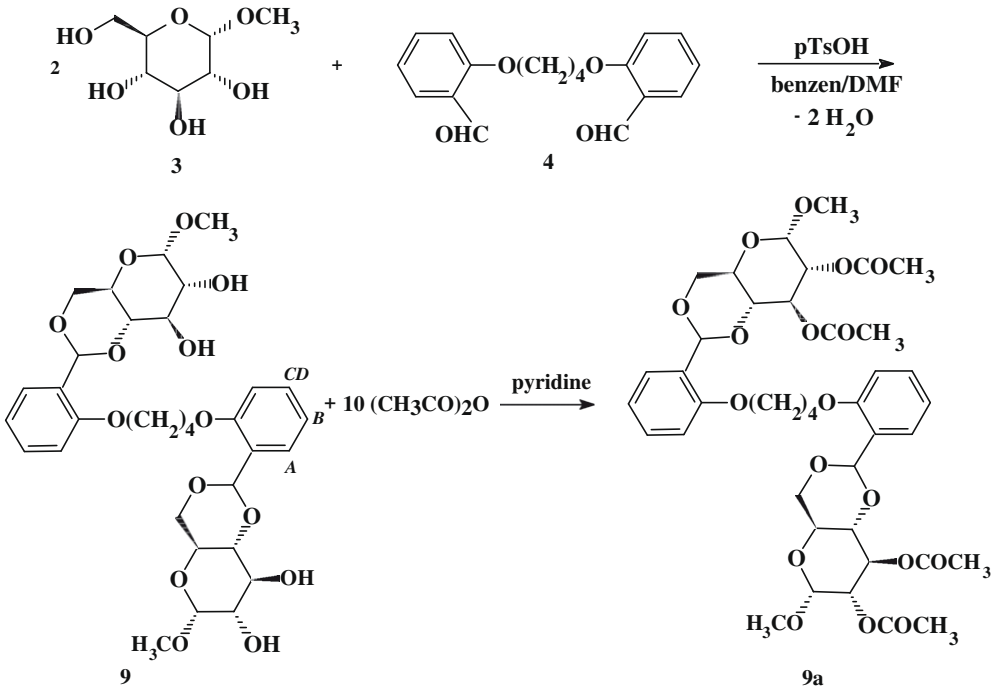
Acetylation of ***9***. The product of **9** (1 g, 1.5 mmol) and acetic anhydride (1.4 ml, 1.53 g, 15.0 mmol) in 10 ml dry pyridine were stirred in room temperature for 2 days. The reaction mixture was purred into large volume of saturated sodium hydrogen carbonate solution, filtered, washed with water and dried under a reduced pressure. Yield of **9a**: 95%.

^{1}H NMR ($CDCl_3$): δ = 1.92–2.13 (4H, m, –CH_2–), 2.01 (6H, s, –OC $OCH_3{}^2$), 2.04 (6H, s, -$OCOCH_3{}^3$), 3.42 (2H, s, –OCH_3), 3.60–4.65 (20 H, m, –CH_2O–, –CH–O–), 4.80 (2H, d, J = 3.9 Hz, H_{anom}), 5.88 (2H, s, H^2 dioxan-2-yl), 6.85–7.60 (8H, m, H_{Ar}).

2.3.2. Polycondensation of ***1*** or ***2*** with different kind of 1,x-bis(2-formylophenoxy)alkanes (***4–8***)

A mixture of **1** and **4–8** or **2** and **6** in benzene/DMF (V/V = 1:1) containing *p*-TsOH was subjected to azeotropic distillation (Dean–Stark). The selected conditions and results of experiments are shown in Table 1 and 2. After 10–24 h the catalyst was deactivated with $CaCO_3$, filtered off and the solvent was removed under reduced pressure. The residue was washed with aq. 5% $NaHCO_3$, water and dried. Polymers were purified by dissolution/reprecipitation from a tetrahydrofuran (THF)/methanol and dried under reduced pressure.

For the product of polycondensation of **10** where *x* = **4** the data are:



Scheme 1. Condensation of **3** with **4** and acetylation of product **9**.

Table 1
Selected conditions and results the polyacetalation of trehalose **1** with 1,*x*-bis(2-formylophenoxy)alkanes.[a]

No. exp.	Substrate		*p*-TsOH 10^3 (mol)	Solvent (cm^3)	Time (h)	Total conv. (%)
	Sugar 10^3 (mol)	1,*x*-*o*-dial 10^3 (mol)				
1	**1** 1.5	**4** 1.5	0.7	Benzene [10]–DMF [5]	10	59.1
2	**1** 2.9	**4** 2.9	0.6	Benzene [7.5] -DMF [7.5]	24	96.0
3	**1** 1.5	**5** 1.5	0.7	Benzene [10] -DMF [5]	10	75.7
4	**1** 1.5	**6** 1.5	0.7	Benzene [10]–DMF [5]	10	71.6
5	**1** 1.5	**7** 1.5	0.7	Benzene [10]–DMF [5]	10	67.6
6	**1** 1.5	**8** 1.5	0.7	Benzene [10]–DMF[5]	10	60.8

[a] Where $x = 4$ (**4**), $x = 5$ (**5**), $x = 6$ (**6**), $x = 8$ (**7**), $x = 12$ (**8**).

Table 2
Selected conditions and results the acetalation of D-glucose **2** with 1,6-bis(2-formylophenoxy)hexane (**6**).

No. Exp.	Substrate		*p*-TsOH 10^3 (mol)	Solvent (cm^3)	Time (h)	Total conv. (%)
	2 10^3 (mol)	**6** 10^3 (mol)				
1	2.8	2.8	1.5	Benzene [18]–DMF[9]	10	96.0
2	2.8	2.8	1.5	Benzene [18]–DMF[9]	24	83.4

After 10 h. ^{1}H NMR ($CDCl_3$): δ = 1.70–2.60 (–CH_2–), 3.00–4.60 (–OH^2, –OH^3, –CH–O–, –CH_2O–), 4.80–5.30 (H_{anom}), 5.60–6.00 (–OCHO–, H^2 dioxan-2-yl), 6.68–7.90 (H_{Ar}), 10.40–10.60 (–CHO).

^{13}C NMR ($CDCl_3$): δ = 24.4–26.8 (–CH_2–), 61.3–82.6 (–CH–O–, –CH_2O–), 91.4–94.6 (C_{anom}), 95.0–98.2 (–OCHO–, C^2 dioxan-2-yl), 110.2–137.0 (C_{Ar}), 155.2–157.6 (C_{Ar}–O–), 160.4–162.7 (–COOH), 188.3–191.5 (–CHO).

After 24 h (Fig. 1). ^{1}H NMR ($CDCl_3$): δ = 1.80–2.29 (–CH_2–), 3.00–4.56 (–OH^2, –OH^3, –CH–O–, –CH_2O–), 4.89–5.31 (H_{anom}), 5.57–6.00 (–OCHO–, H^2 dioxan-2-yl), 6.68–7.90 (H_{Ar}), 10.41–10.59 (–CHO).

^{13}C NMR ($CDCl_3$): δ = 24.7–28.5 (–CH_2–), 61.7–82.4 (–CH–O–, –CH_2O–), 91.9–94.4 (C_{anom}), 95.9–98.3 (–OCHO–, C^2 dioxan-2-yl), 110.6–136.4 (C_{Ar}), 154.8–157.0 (C_{Ar}–O–), 160.9–162.1 (–COOH), 189.1–190.4 (–CHO).

For the product of polycondensation of **2** with **6** the data are:

After 10 h. ^{1}H NMR ($CDCl_3$): δ = 1.40–2.00 (–CH_2–); 3.80–4.40 (–OCH–, –OCH_2–); 4.69 (d, H_{anom}); 6.17 (d, –OCHO–, H^2 dioxan-2-yl); 6.22 (–OCHO–, H^2 dioxolan-2-yl, exo); 6.46 (–OCHO–, H^2 dioxolan-2-yl, endo); 6.80÷7.87 (H_{Ar}), 10.45 ÷ 10.57 (–CHO).

After 24 h. ^{1}H NMR ($CDCl_3$): δ = 1.40–2.00 (–CH_2–); 3.88–4.16 (–OCH–, –OCH_2–); 6.80÷7.90 (H_{Ar}), 10.44÷10.55 (–CHO).

^{13}C NMR ($CDCl_3$): δ = 25.7–29.0 (–C–H_2–), 68.0–77.2 (–CH–O–, –CH_2O–), 111.6–135.8 (C_{Ar}), 157.4 (C_{Ar}–O–), 161.4 (–COO–), 189.7 (–CHO).

3. Results and discussion

3.1. Condensation of *3* with *4* (as a model compound)

Methyl α-D-glucopyranoside is readily reacted with aromatic aldehydes in the presence of acidic catalysts yielding of products consisting of 4,6-arylidene-monoacetals. According to the modified Hann-Hudson rules for acetal and ketal substitutions, outlined by

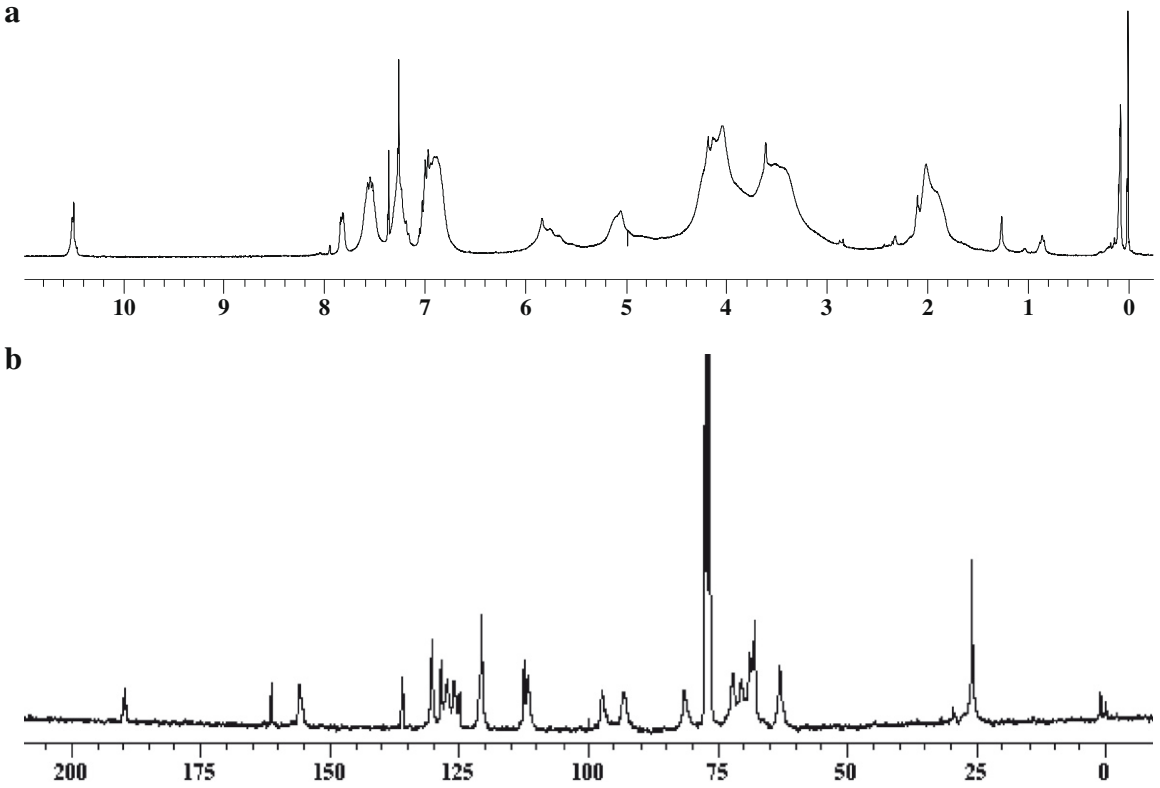
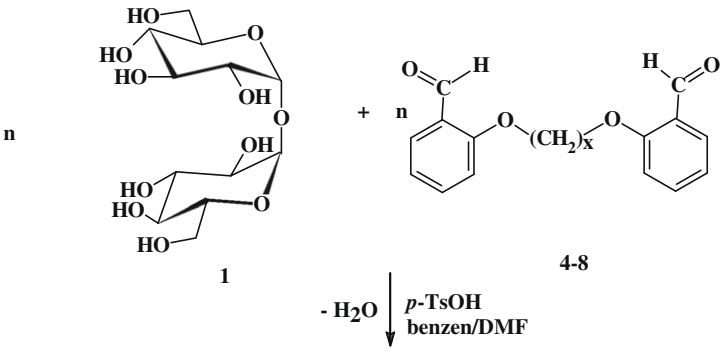
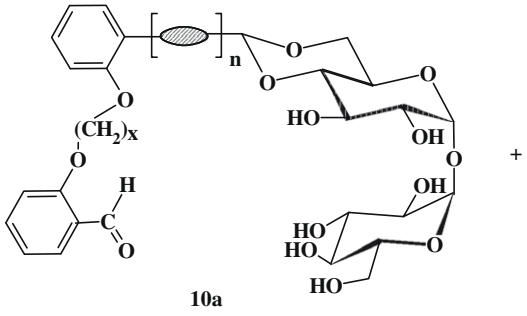
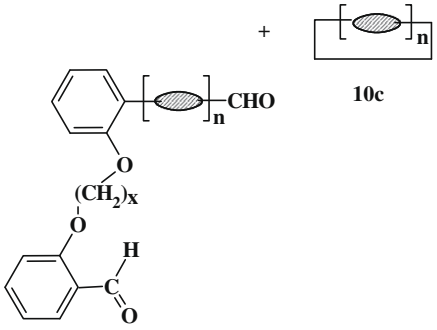


Fig. 1. (a) ^{1}H NMR (300 MHz, $CDCl_3$) spectra of polycondensation products of **1** with **4** after 24 h; (b) ^{13}C NMR (75 MHz, $CDCl_3$) spectra of polycondensation products of **1** with **4** after 24 h.

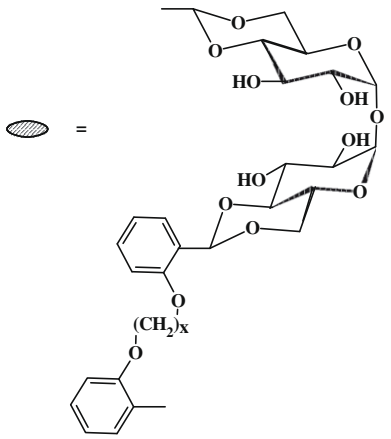
Barker and Bourne (1952) benzaldehyde derivatives also **4** with **3** might be expected to take the 1,3- (at carbon 4,6-) ring configuration rather than the 1,2- (at carbon 2,3) configuration. Examination of the structure of product **9** synthesized in the acidic medium







Where:



Scheme 2. Polycondensation of **1** with 1,*x*-bis(2-formylphenoxy)alkanes (*x* = 4–12), where *x* = 4 (**4**), *x* = 5 (**5**), *x* = 6 (**6**), *x* = 8 (**7**), *x* = 12 (**8**).

shows that the only possible of phenylidene substituent involves 4,6:4′,6′-cyclic diacetal rings. IR spectrum and ^{1}H NMR analysis of the product **9** affords one isomer. The acylation of free OH groups at C-2 and C-3 (IR analysis) of **9** with acetic anhydride in pyridine gives the tetra-*O*-ester of diacetal **9a** in 95% yield (Scheme 1).

3.2. Polycondensation of α,α-trehalose with different kind of 1,x-o-dials

Polycondensation of **1** with **4–8** were performed in mixture of solution benzene–DMF in the presence of an acidic catalyst – *p*-TsOH and the azeotropic removal of water (Scheme 2, Table 1).

The activity of hydroxyl groups of **1** can be compared to that of **3**. The *trans*-disposition of HO^2, HO$^{2'}$ and HO^3, HO$^{3'}$ is unfavorable for cyclic acetal of aromatic aldehydes formation under acidic condition. Consequently, unprotected **1** could regioselectively react with dialdehydes to give polymer compounds. Thus, the polycondensation of **1** with dialdehyde is generally accompanied by the interaction of dialdehyde substituents at C^4, C^6 and C$^{4'}$, C$^{6'}$ of **1** moiety. There is only one paper concerning the polyacetal of 1 U in backbone. The polycondensation reaction of **1** with terephthaldehyde bis(dimethylacetal) in DMF under reduced pressure was described (Teramoto, Arai, Shibasaki, & Shibata, 2003).

Our investigations in this paper concern the synthesis, structure of polyacetals **10** formed in the polyacetalization of **1** with 1, *x*-bis(2-formylphenoxy)alkanes, where *x* = 4, 5, 6, 8 (**4–7**).

The polyacetalization of **1** with **4** was performed at a molar ratio of 1:1 in a mixture of solvents (benzene/DMF) with *p*-TsOH, as a catalyst with the azeotropic removal of water. Table 1 summarizes the synthetic conditions and the results of the polycondensation reactions. The structure of the oligomeric products obtained after 10 and 24 h was determined by the NMR analysis (Fig. 1). The signals due to the alkyl –CH_2– (1.70–2.29 ppm), acetal [4.80–5.31 ppm (anomeric OCHO, H_{anom}), 5.60–6.00 ppm (–OCHO–, H^2 dioxan-2-yl)] and aromatic (6.68–7.90 ppm) protons confirm that the polymer consist of cyclic acetal rings bridged by –$O(CH_2)_4O$– units. The phenoxy groups place an equatorial orientation in 1,3-dioxane rings. ^{13}C NMR spectra of the polymer show broad peaks at 91.4–94.6 (C_{anom}) and 95.0–98.3 (C^2 dioxan-2-yl) and aldehyde end groups at 188.3–191.5 ppm (–CHO). Moreover, one can observe the signal at 160.4–162.7 ppm which is characteristic of the carboxyl carbons. All polymeric products of **10** where *x* = 5, 6, 8 displayed spectroscopic data consistent with their structure assignments.

Although NMR analysis is an important tool in studies of the structure of polymer chains, the ESI-MS measurements were helpful to determine subtle differences in chemical structures of repeating unit and end groups. The samples prepared were found to be complex mixtures of oligomeric compounds. Significant differences among the samples were observed depending on the structure of dialdehydes. The ESI positive ion mass spectrum of polycondensation products of **1** with **4** is presented in Fig. 2 and products of 1 with 6 in Table 3. Analysis of this mass spectrum has revealed the presence of sodium ion adducts of the macromolecules with *m*/*z* values corresponding to two kinds of macromolecular chains containing different end groups, i.e., –CHO plus a carbohydrate unit 10a, only –CHO groups 10b and also macrocyclic 10c compounds. The most abundant ion was located at *m*/*z* = 925.7 for 4, *m*/*z* = 982.0 for **6** and was assigned to the trimer [D-T-D+Na]$^+$ (where D – 1,*x*-bis(2-formylphenoxy)alkanes, T – α,α-trehalose). The ESI-MS^2 fragmentation pattern (Fig. 3) of the mass-selected molecular these ions, e.g., *m*/*z* = 925.7 was formed due to the loss of 297.9 (dialdehyde) followed by elimination of dehydrated D-glucose (minus two water molecules) *m*/*z* = 145.1 in the next step and one molecule of water.

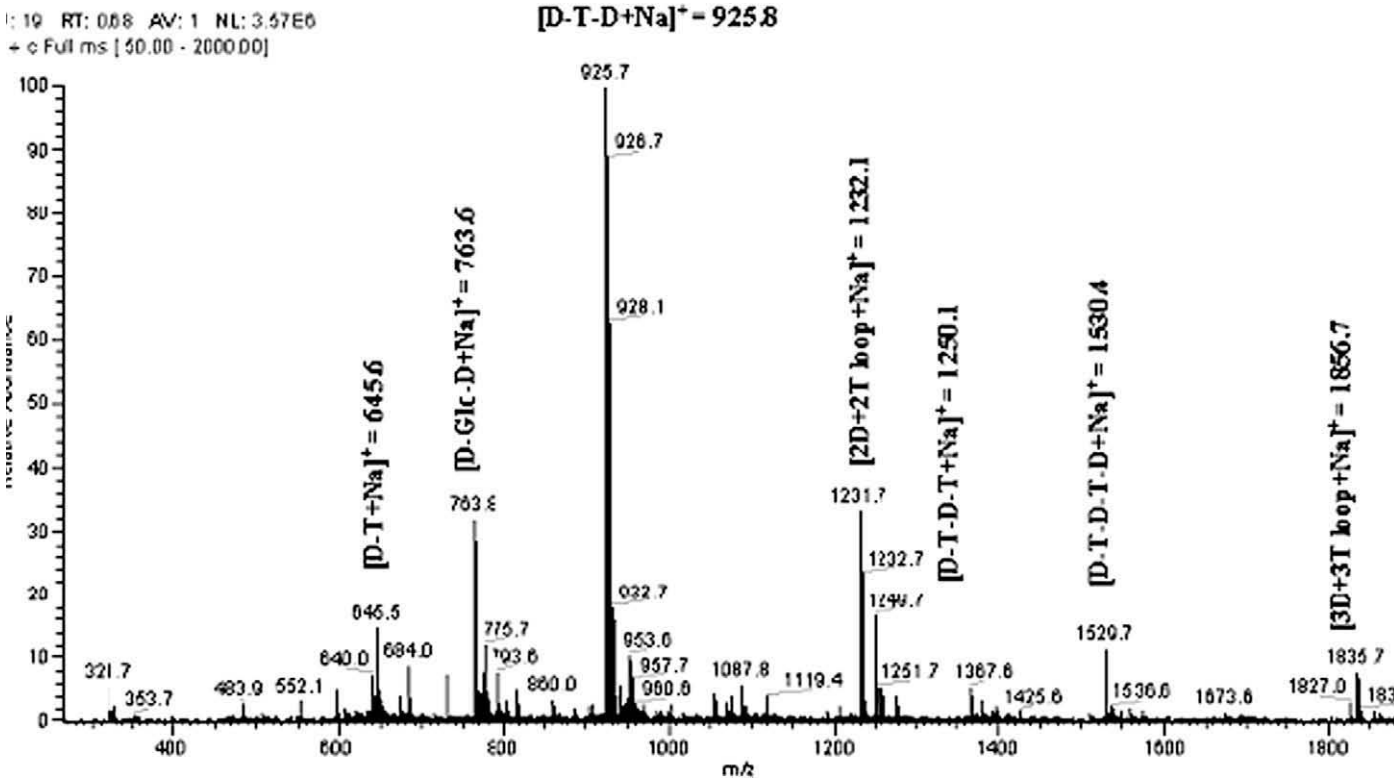


Fig. 2. ESI-MS mass spectrum of the products polycondensation of **1** with **4** in positive ion mode; D, the molecular weight of 1,4-*o*-dial ($C_{18}H_{18}O_4$ = 298.3); T, the molecular weight of α,α-trehalose ($C_{12}H_{22}O_{11}$ = 342.3); Glc, the molecular weight of glucose ($C_6H_{12}O_6$ = 180.1).

Table 3
ESI-MS data of the products polycondensation of **1** with **6**.

Signal (m/z)	Assignment[a]	Calculated (m/z)	Deviation[b]
673.7	$[T+D+Na]^+$	673.7	−0.2
819.7	$[D\text{-}Glc\text{-}D+Na]^+$	819.8	−0.1
981.7	$[D\text{-}T\text{-}D+Na]^+$	982.0	−0.3
1143.6	$[D\text{-}Glc\text{-}D\text{-}T+Na]^+$	1144.1	−0.5
1287.7	$[2+2loop+Na]^+$	1288.3	−0.6
1305.7	$[D\text{-}T\text{-}D\text{-}T+Na]^+$	1306.3	−0.6
1451.7	$[D\text{-}Glc\text{-}D\text{-}T\text{-}D+Na]^+$	1452.4	−0.7
1613.7	$[D\text{-}T\text{-}D\text{-}T\text{-}D+Na]^+$	1614.7	−1.0

[a] D, the molecular weight of **6** ($C_{20}H_{22}O_4$ = 326.4); T, represents the molecular weight of trehalose ($C_{12}H_{22}O_{11}$ = 342.3); Glc, represents the molecular weight of glucose ($C_6H_{12}O_6$ = 180.1).
[b] Deviation = (experimental value) − (calculated value).

The spectrum of the product polycondensation of **1** with **4** also displays the presence of sodium ion adducts of macrocyclic compounds with m/z values corresponding to [2 + 2loop] (m/z = 1231.7) and [3 + 3loop] (m/z = 1835.7). Whereas, polycondensation of product polycondensation of **1** with **6** display the presence only one sodium ion adduct of macrocyclic compound with m/z values corresponding to [2 + 2loop] (m/z = 1287.7). The ESI-MS^2 fragmentation is the proof of macrocyclic compounds formation in this polycondensation process (see Fig. 4). Moreover, in ESI-MS (Fig. 2) the signals of sodium adduct of the oligomer containing the glucose unit $[D\text{-}Glc\text{-}D+Na]^+$ (where Glc – glucose) are observed. Analysis of ESI mass spectrum of condensation products of **1** with **6** revealed the presence of macromolecules with glucose units $[D\text{-}Glc\text{-}D+Na]^+$ with m/z = 819.7 and [D-Glc-D-

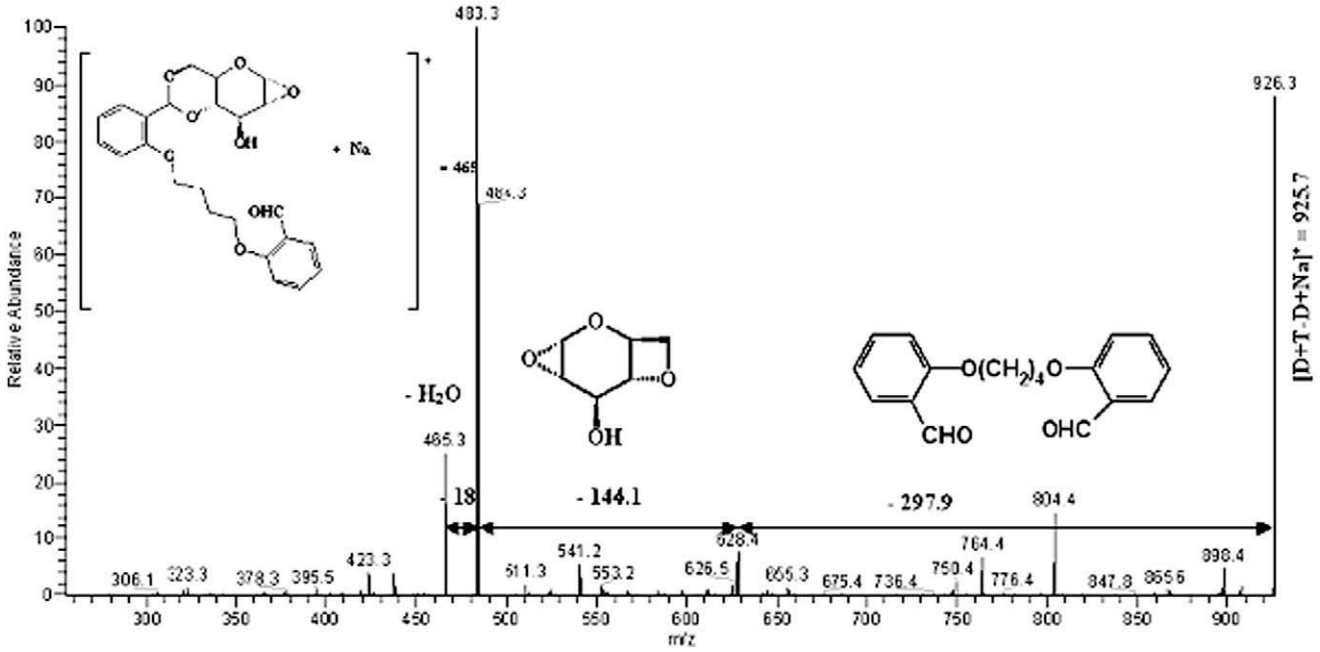


Fig. 3. ESI-MS^2 of the product polycondensation of **4** with **1**.

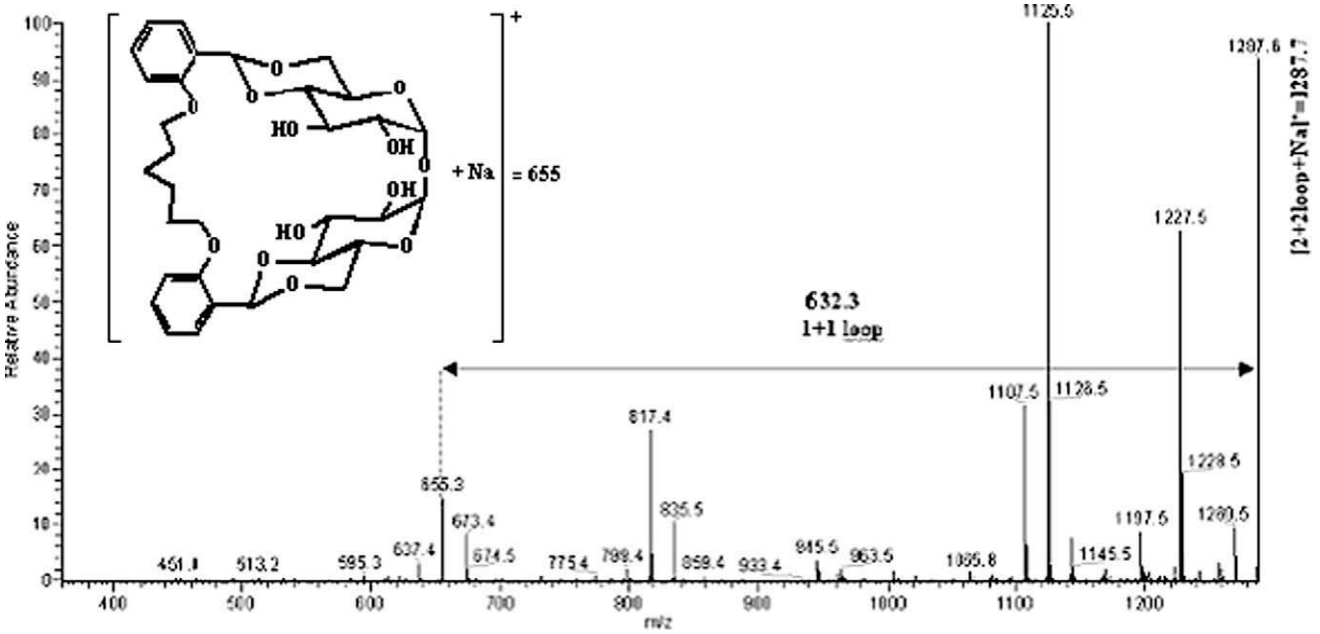


Fig. 4. ESI-MS^2 of the macrocyclic compound [2 + 2loop].

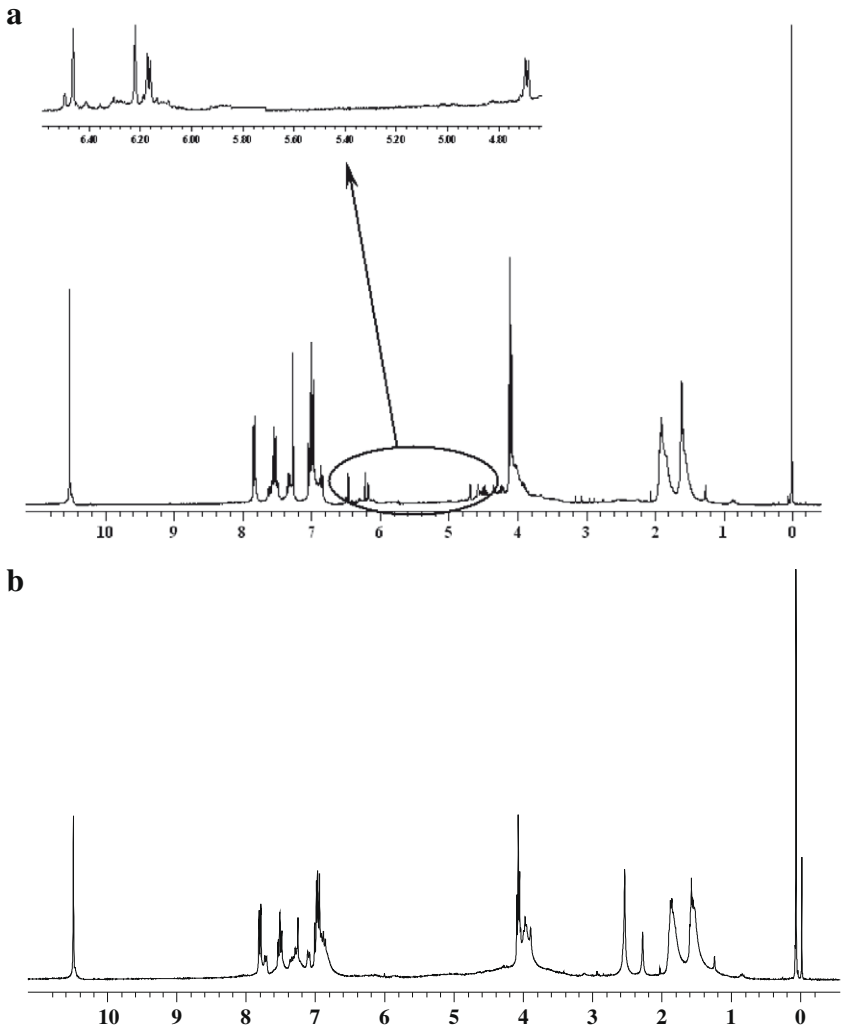


Fig. 5. (a) ^{1}H NMR (300 MHz, $CDCl_3$) spectra of polycondensation products of **2**with **6** after 10 h; (b) ^{1}H NMR (300 MHz, $CDCl_3$) spectra of polycondensation products of **2** with **6** after 24 h.

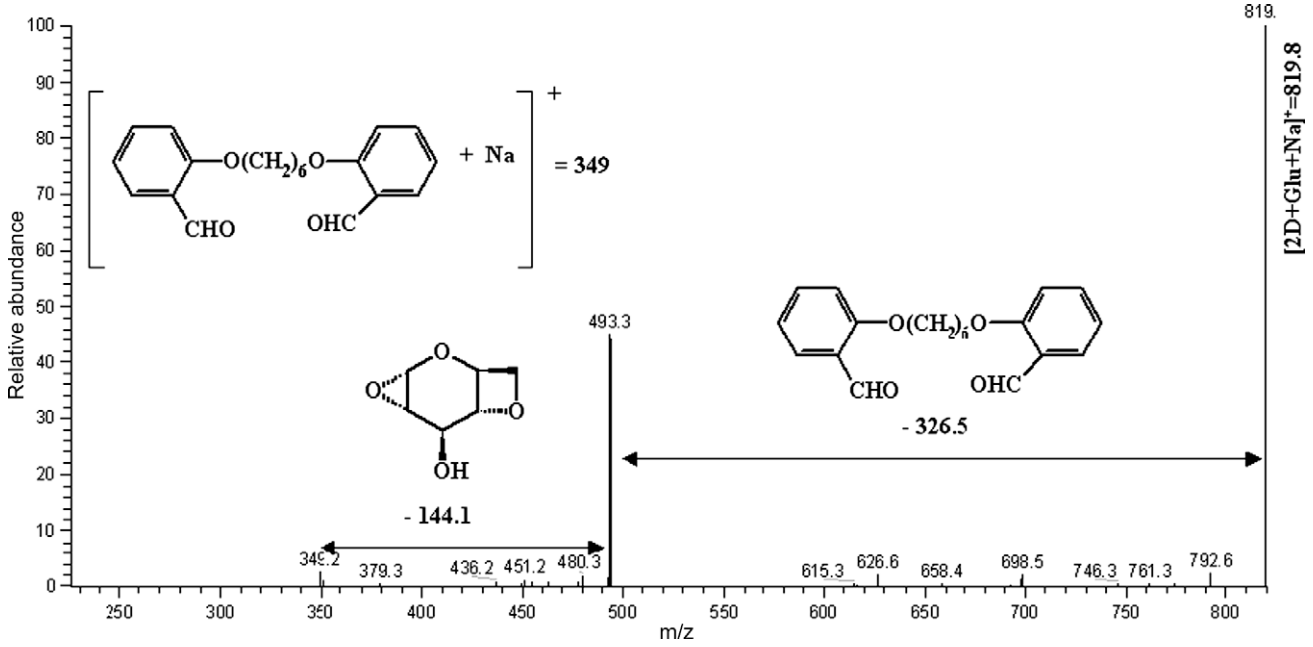


Fig. 6. ESI-MS^2 of the product polycondensation of **2** with **6**.

T+Na]$^+$ = 1143.6, [D-Glc-D-T-D+Na]$^+$ = 1451.7 (see Table 3) too. It was possible that the acidic hydrolysis of α,α-trehalose into D-glucose molecules during polycondensation of **1** with **3** could cause the formation of oligomers with glucose units. It is known in the literature that D-glucose reacts with aldehyde to form a diacetal under the acidic conditions. Thus hydrolytic cleavage of α,α-trehalose unit does not cause its termination of the growing chain in step reaction. On the basis of chemical and spectral evidence Wood, Diehl, and Fletcher (1957) found that the reaction product of D-glucose with benzaldehyde was 1,2:4,6-di-*O*-benzylidene-α-D-glucopyranose.

Therefore, the reaction of **2** with **6** was carried out (as a model reaction) under the same reaction conditions**.** After 10 h ^{1}H NMR analyze (Fig. 5a) of this compound exhibits several sets of bands concerning acetal at 4.69 ppm – doublet – due to anomeric protons; 6.17 ppm – doublet – H^2 dioxan-2-yl; 6.22 ppm (H^2 dioxolan-2-yl, exo) and 6.46 ppm (H^2 dioxolan-2-yl, endo). The relative intensities of *endo*-H and *exo*-H in 1,3-dioxolane rings were 1:1. On the basis of NMR data one can consider that 5- and 6-membered acetal rings at C-1,2 and C-4,6 carbons of glucose unit are present in the trimer D-Glc-D product. It was experimentally proved that the formyl end groups of the trimer do not react with other molecules of D-glucose. However, prolonged time of polycondensation of **2** with **6** probably leads to the auto-oxidation of acetal rings of glucose. ^{1}H and ^{13}C NMR spectra (Fig 5b) demonstrate the disappearance of acetal protons signals at 6.17–6.46 ppm and acetal carbons at 99.0–100.0 ppm and the presence of a new signal at 161.4 ppm characteristic of the carbon in ester groups.

To test this proposal of the product polycondensation of **6** with **2** was subjected to ESI-MS^2 fragmentation. The ESI-MS^2 fragmentation pattern of the mass-selected molecular ion *m*/*z* 819.8 of the trimer [D-Glc-D+Na]$^+$ (Fig. 6) confirmed its structure. The fragment ion at *m*/*z* = 493.3 was formed due to the loss of 326.5 (dialdehyde) followed by elimination of dehydrated D-glucose (minus two molecules of water) *m*/*z* = 144.1 in the next step.

The question whether D-Glc-D sequences exist in the macromolecules at higher molar mass was resolved by MALDI analysis. Fig. 7 shows the MALDI-TOF mass spectrum of 10 where *x* = 4 (after 24 h of polycondensation). The spectrum revealed the presence of sodium adduct ions with *m*/*z* values corresponding to three kinds of macromolecules terminated with phenylidene-formyl (D) or α,α-trehalose (T) end groups. Only one signal located at *m*/*z* = 1231 reveals the precence of macrocyclic compound [2 + 2loop + Na]$^+$. The third series of peaks correspond to polyacetals with one glucose [D-Glc-D] sequence in macromolecules, which consist of the α,α-trehalose-dial repeating units. It confirms the occurrence of hydrolytic degradation of α,α-trehalose into glucose at the first stage of polycondensation, but does not interfere in the step growth of **1** with **4**. No oxidation product in which the acetals would be transformed into ester has been found.

4. Conclusion

ESI-MS and MALDI-TOF analyses have been successfully used to characterize the polyacetal of α,α-trehalose prepared by its polycondensation with dialdehydes catalysed by *p*-toluenesulfonic acid. The mass spectrum shows evidence of polyacetal chains with the small content of glucose-dialdehyde units. The small amount of Glc-D sequence is due to the low reactivity of **2** as compared to **1** with dialdehydes during the polyacetalization. The spectra also showed the presence of macrocyclic compounds as minor products of polyreaction.

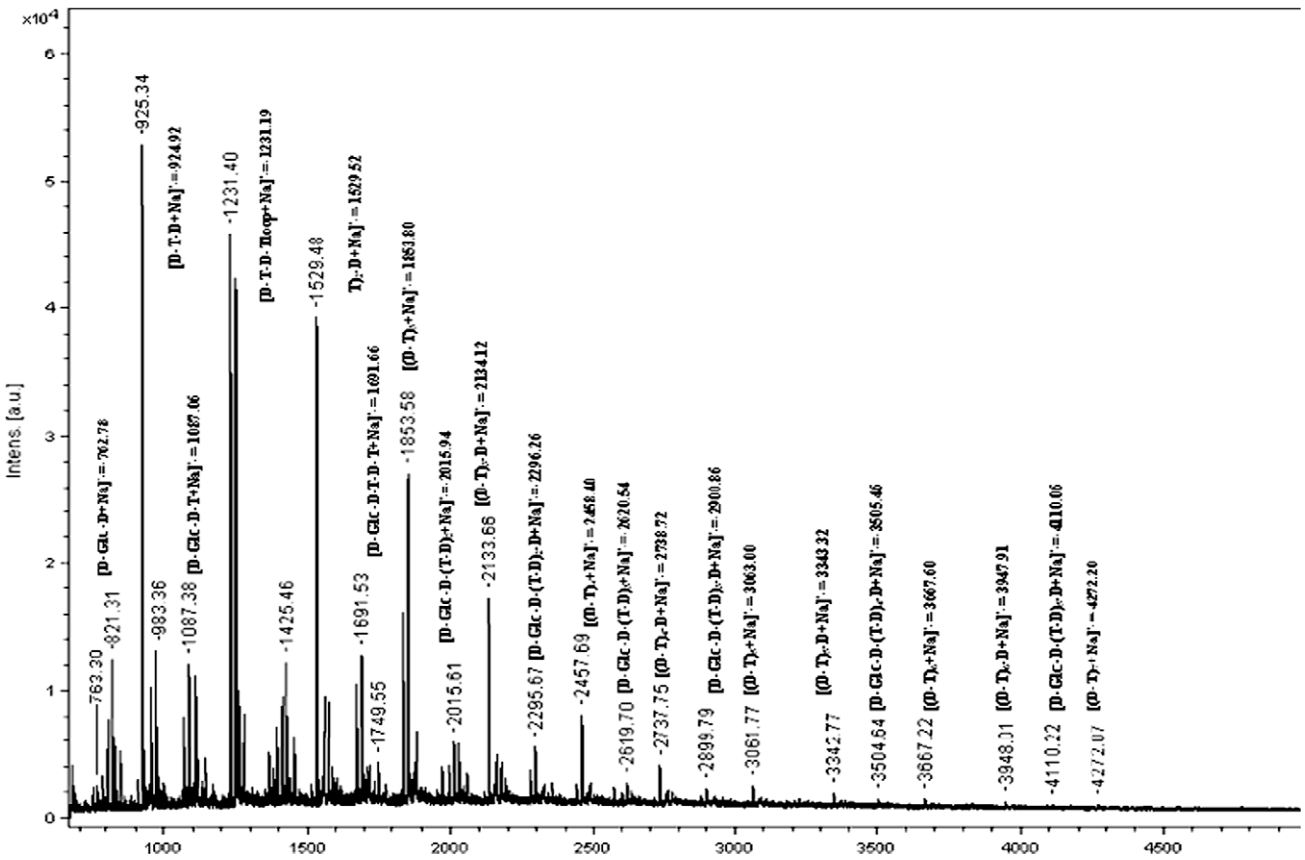


Fig. 7. MALDI-TOF spectrum of polycondensation products of **1** with **4** after 24 h; D, the molecular weight of 1,4-*o*-dial ($C_{18}H_{18}O_4$ = 298.3); T, the molecular weight of α,α-trehalose ($C_{12}H_{22}O_{11}$ = 342.3); Glc, represents the molecular weight of glucose ($C_6H_{12}O_6$ = 180.1).

Acknowledgement

The work was partly supported by the Committee for Scientific Research (Poland) in the framework of project no. N N205 017834.

References

Barker, S. A., & Bourne, E. J. (1952). Favoured ring forms in acetals of the polyhydrics alcohols. *Journal of Chemical Society, 905*, 909.

Besson, J., Fayet, C., & Gelas, J. (1997). The introduction of an hydrophobic chain on α, α-α, α-trehalose via the synthesis of acetals. The detergent properties of these derivatives. *Carbohydrate Research, 303*, 159–164.

Carbonnel, S., Fayet, C., & Gelas, J. (1999). Introduction of a carboxyl group through an acetal as a new route to carboxylic acid derivatives of sugars. *Carbohydrate Research, 319*, 63–73.

Choi, E.-J., Ahn, H.-K., Lee, J. K., & Jin, J.-I. (2000). Liquid crystalline twin epoxy monomers based on azomethine mesogen: Synthesis and curing with aromatic diamines. *Polymer, 41*, 7617–7625.

Crowe, J. H., Carpenter, J. F., & Crowe, L. M. (1998). The role of vitrification in anhydrobiosis. *Annual Review of Physiology, 60*, 73–103.

Fanton, E., Fayet, C., & Gelas, J. (1997). Long-chain acetals derived from sucrose as a new class of surfactants. *Carbohydrate Research, 298*, 85–92.

Higashiyama, Takanobu. (2002). Novel functions and applications of trehalose. *Pure and Applied Chemistry, 74*, 1263–1269.

Madonna, G. S., Ledney, G. D., Elliott, T. B., Brook, I., Ulrich, J. T., Myers, K. R., et al. (1989). Trehalose dimycolate enhances resistance to infection in neutropenic animals. *American Society for Microbiology, 57*, 2495–2501.

Maślińska-Solich, J. (2001). Condensation and polycondensation of terephthaldehyde with methyl D-hexopyranosides. *Macromolecular Bioscience, 1*, 312–321.

Maślińska-Solich, J., & Kukowka, S. (2004a). Chiral polymers containing a carbohydrate moiety: Synthesis. *Macromolecular Bioscience, 4*, 421–430.

Maślińska-Solich, J., & Kukowka, S. (2004b). Synthesis of functional polymers with acetal – monosaccharide moieties. *Macromolecular Symposia, 210*, 67–75.

Maślińska-Solich, J., Kuźnik, N., Kubicki, M., & Kukowka, S. (2002). The formation of a cyclic diacetal of methyl α-D-mannopyranoside with a 16-membered macrocyclic loop. *Chemical Communication, 984*, 985.

Richards, A. B. et al. (2002). Trehalose: A review of properties, history of use and human tolerance and results of multiple safety studies. *Food and Chemical Toxicology, 40*, 871–898.

Sampedro, J. G., & Uribe, S. (2004). Trehalose-enzyme interactions result in structure stabilization and activity inhibition. *Molecular and Cellular Biochemistry, 256*(257), 319–327.

Teramoto, N., Arai, Y., Shibasaki, Y., & Shibata, M. (2003). A facile synthesis of a novel polyacetal containing trehalose residue in the main chain. *Carbohydrate Polymers, 56*, 1–6.

Varma, A. J., Kennedy, J. F., & Galgali, P. (2004). Synthetic polymers functionalized by carbohydrates: A reviews. *Carbohydrate Polymers, 56*, 429–445.

Wiemken, A. (1990). Trehalose in yeast, stress protectant rather than reserve carbohydrate. *Antonie van Leeuwenhoek, 58*, 209–217.

Wood, H. B., Diehl, H. W., & Fletcher, H. G. (1957). 1, 2:4, 6-di-*O*-benzylidene-α-D-glucopyranose and improvements in the preparation of 4, 6-*O*-benzylidene-D-glucopyranose. *Journal of the American Chemical Society, 79*, 1986–1988.