ELSEVIER

Carbohydrate Polymers 45 (2001) 135–138

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Synthesis of carbohydrate based polymers

M.J. Carneiro, A. Fernandes, C.M. Figueiredo, A.G. Fortes*, A.M. Freitas

Department of Chemistry, University of Minho, Campus de Gualtar, 4700-320 Braga, Portugal

Received 9 November 1999; revised 2 June 2000

Abstract

The synthesis of a methacrylated D-galactopyranose monomer is described; its copolymerisation reaction with ethyl acrylate using a radical initiator is also discussed; the copolymer obtained has an average molar mass lower than 10 000 g/mol; this and other physico-chemical properties of this copolymer are presented.

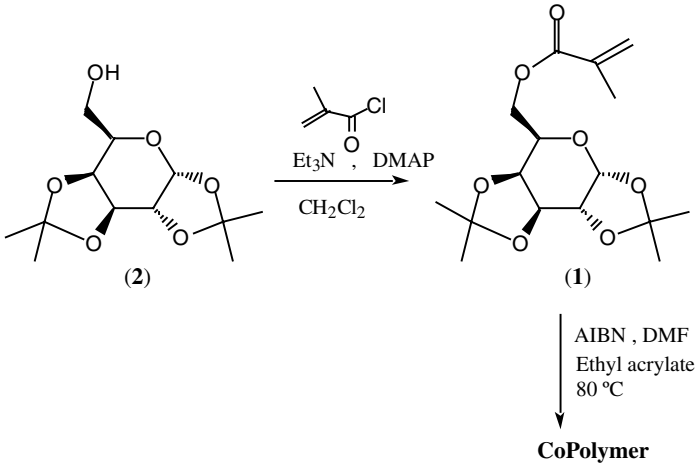
Keywords: Synthesis; Copolymerisation; Carbohydrates

1. Introduction

Sugars are an important resource for development of new materials such as water soluble polymers (Descotes, 1993; Khan, 1984; Roy, 1998; Schiweck, Rapp & Vogel, 1998); owing to their low price, sugars such as sucrose and D-galactose play an important role for this purpose. Some possible applications for these type of polymers are drug delivery systems, dental medicine, bioimplants, contact lenses and tissue engineering (Pachence & Kohn, 1997). Furthermore they have the advantage of being potentially biodegradable.

In this work, the preparation of a D-galactopyranose derivative is described; the copolymerisation study of the monomer obtained with ethyl acrylate and the characterisation of some physico-chemical properties of the copolymer are also presented. The methodology used with D-galactopyranose, has been applied with success to other sugars such as D-mannitol and is being applied also to sucrose and the results will be presented elsewhere.

A monofunctionalised monomer (**1**) containing a D-galactopyranose unit attached through an ester linkage to a vinyl group was synthesised and reacted with ethyl acrylate to form a copolymer. Synthesis of monomer (**1**) was carried out by reacting 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**2**) with methacryloyl chloride (Scheme 1). The



Scheme 1.

* Corresponding author.
E-mail address: gilf@quimica.uminho.pt (A.G. Fortes).

0144-8617/01/$ - see front matter
PII: S0144-8617(00)00322-2

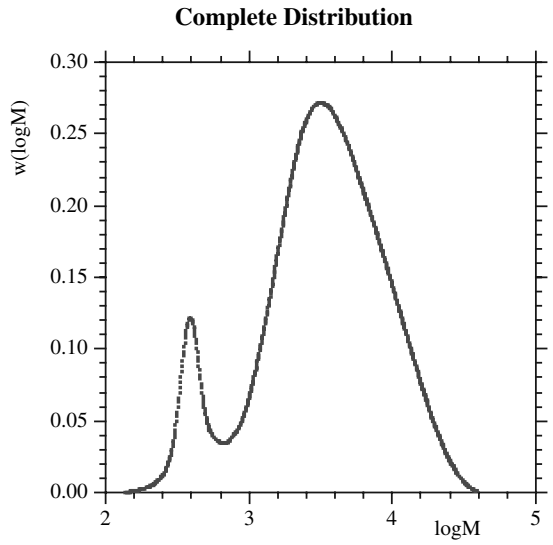


Fig. 1. Graphic showing the complete distribution.

copolymerisation reaction between monomer (**1**) and ethyl acrylate was performed in DMF at 80°C using AIBN as radical initiator. GPC analysis has shown that the average molar mass of the copolymer obtained was lower than 10^3 g/mol (Figs. 1 and 2), which is in agreement with published results (Jhurry, Deffieux, Fontanille, Betremieux, Mentech & Descotes, 1992) for similar copolymers obtained under similar conditions. GPC data was obtained using polystyrene standards in the molar mass range 600–7.7×10^6 g/mol; the chromatogram (Fig. 3) shows that the sample has a bimodal distribution, which could be due to the presence of oligomers. Thermal analysis indicates that the copolymer is thermally stable until about 160°C; thermogravimetric data (TG) show a mass loss of the galactose copolymer of about 25% in the range 160–310°C;

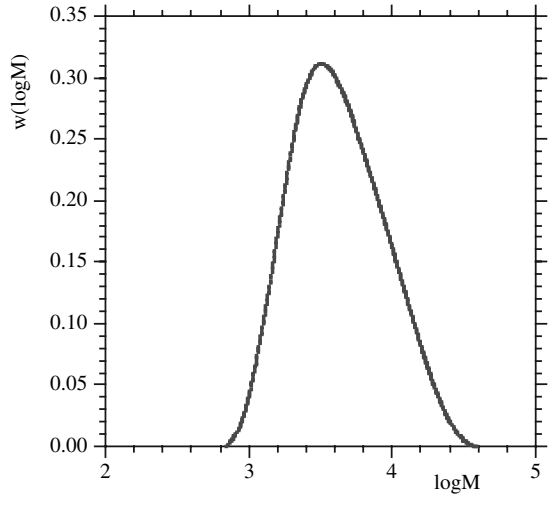


Fig. 2. Graphic showing the higher molecular weight part of the distribution.

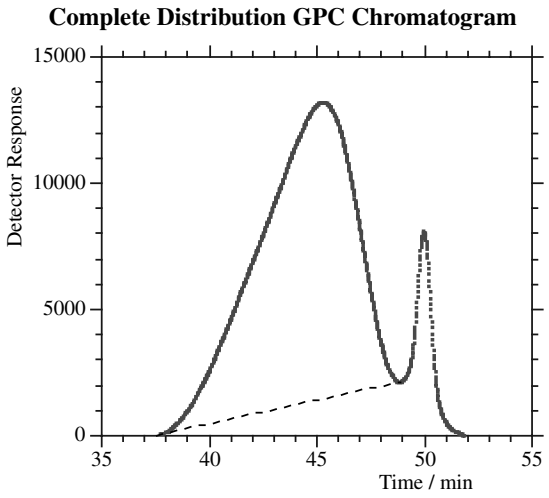


Fig. 3. GPC chromatogram showing a bimodal distribution.

differential thermal analysis (DTA) has revealed that this mass loss occurs in two stages, which are probably due to thermo-oxidative decomposition of the sample (Fig. 4). ^{1}H NMR (Fig. 5) shows typical broad signals around 1–2 ppm (–CH, $-CH_2$ and $-CH_3$ groups) and 4–5 ppm (–CH, $-CH_2$ groups from galactose unit and alkyl ester groups). The copolymer is soluble in organic solvents, such as $CHCl_3$ or CH_2Cl_2 and insoluble in water.

2. Experimental

THF was dried under sodium/benzophenone, refluxed and distilled under nitrogen before use. DMF was purified by distillation under reduced pressure and kept over molecular sieves. Ethyl acrylate and AIBN were used without further purification.

*Synthesis of 1,2:3,4-di-O-isopropylidene-α-D-methacryloylgalactopyranose (**1**).* To a solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (5.017 g; 19.2 mmol) in CH_2Cl_2 (190 ml), was added triethylamine (38.5 ml) and 4-DMAP (0.115 g; 0.94 mmol); the resulting solution was cooled to 0°C and stirred under nitrogen. Methacryloyl chloride (2.8 ml; 28.8 mmol) in CH_2Cl_2 (40 ml) was added, and the reaction was left at room temperature for 4 h. The reaction was monitored by TLC (ethyl acetate/petroleum ether 40–60°C, 1:1); the amine salt was filtered, and the resulting solution was partitioned between water and CH_2Cl_2; the organic phase was washed with 1 N HCl, and then with saturated $NaHCO_3$. The organic phase was collected, dried with magnesium sulphate, filtered and finally concentrated to afford a yellow oil (11.968 g). The oil obtained was eluted from a column of silica gel with ethyl acetate/petroleum ether 40–60°C, 1:1, to give an oil (5.96 g; 94%). ^{1}H NMR($CDCl_3$): δ (ppm) = 6.12 (q, 1H, C=C–Ha, $J = 0.9$ Hz); 5.6 (q, 1H, C=C–Hb, $J = 1.6$ Hz); 5.5 (d, 1H, H-1′, $J = 4.9$ Hz); 4.6 (dd, 1H, Ha-6′, $J_{6,6'} = 7.9$ Hz, $J_{5,6} = 2.5$ Hz), 4.28–4.24 (dd, 1H, Hb-6′,

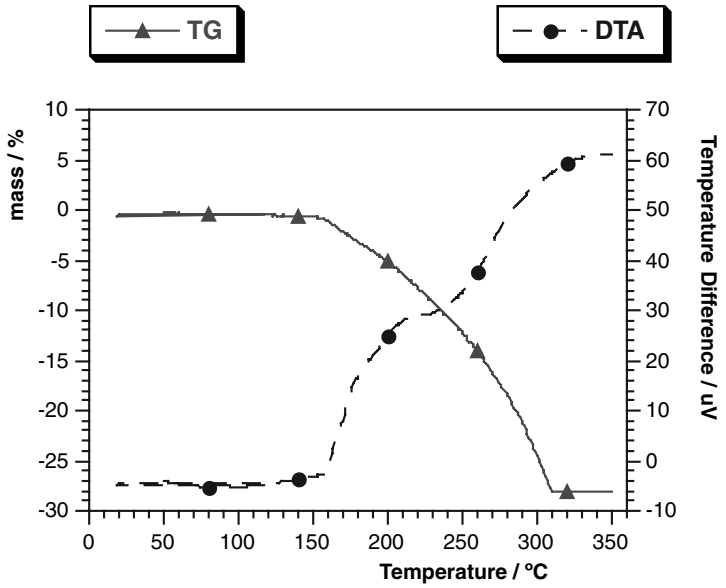


Fig. 4. Thermogravimetric (TG) and differential thermal analysis (DTA) of copolymer (heating rate: 7.5°C/min).

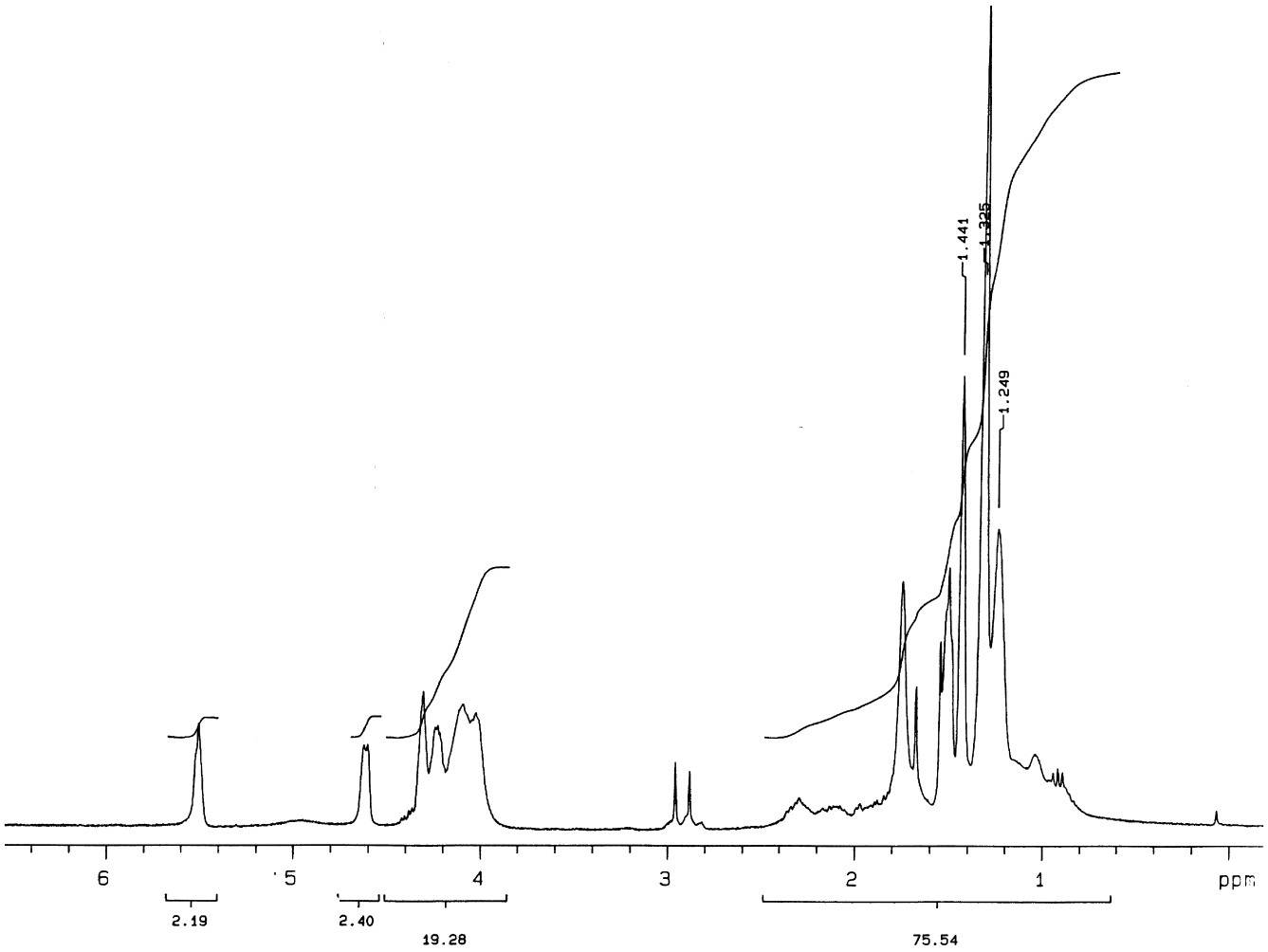


Fig. 5. 300 MHz ^{1}H NMR spectrum of copolymer in $CDCl_3$.

$J_{6,6'} = 7.9$ Hz, $J_{5,6'} = 1.8$ Hz); 4.37–4.21 (m, 3H, H-2′, H-3′, H-4′); 4.06 (m, 1H, H-5′); 1.94 (dd, 3H, CH_3–C=C, $J =$ 0.9 Hz and $J = 1.8$ Hz); 1.5, 1.45, 1.33, 1.32 (4s, 12H, $(CH_3)_2C$).

*Copolymerisation reaction of (**1**) with ethyl acrylate.* The methacrylated monomer (3.23 g; 9.8 mmol) was dissolved in DMF (80 ml), and ethyl acrylate (1.06 ml; 9.78 mmol) was added, followed by AIBN (0.15 g); the solution was flushed with nitrogen and the reaction was kept at 80°C for 24 h. The solution was cooled to room temperature, 1 N HCl (80 ml) was added and a white solid formed, which was filtered and washed several times with water and then with small quantities of acetone; the solid obtained was dried under vacuum to afford the copolymer (4.05 g); m.p. = 72–76°C; IR (neat), ν_{max} (cm^{-1}): 2978 (C–H st), 1732 (C=O), 1210–1125 (C–O–C as); ^{1}H NMR($CDCl_3$): see Fig. 4; GPC (molecular weight averages): $M_z = 9248$, $M_w = 5490$, $M_n = 3226$, $M_v = 5053$ (Figs. 1–3).

GPC method. Solvent: dimethylacetamide containing 0.02% (w/v) lithium nitrate. Sample injection: 70 μl of a 0.3% (w/v) solution in the solvent. Solvent delivery: Knauer Type 64 HPLC pump. Flow rate: 0.6 ml/min. Columns: three 5-μm bead size Phenomenex Styragel-packed columns with porosities of 10^5, 10^3 and 50 nm, respectively, in series. Column oven: Anachem LC oven. Column temperature: 80°C. Detector: Knauer Type 98 differential refractometer. Detector temperature: 30°C. Flow rate marker: diphenyl ether. Calibration: polystyrene standards in the molar mass range 600–7.7×10^6 g/mol. Data analysis: Polymer Laboratories "PL Caliber" version 6.0. Thermal analysis was carried out on a Netzsch Simultan. Thermal Analyser STA 409 EP.

References

Descotes, G. (1993). Carbohydrates as organic raw materials VCH.

Jhurry, D., Deffieux, A., Fontanille, M., Betremieux, I., Mentech, J., & Descotes, G. (1992). Sucrose-based polymers, 1: Linear polymers with sucrose side-chains. *Makromolekulare Chemie*, *193*, 2997–3007.

Khan, R. (1984). Chemistry and new uses of sucrose: how important? *Pure and Applied Chemistry*, *56*, 833–844.

Pachence, J. M., & Kohn, J. (1997). In R. Lanza, R. Langer & W. Chick, *Principles of tissue engineering* (pp. 273–285). Academic Press/R.G. Landes Company (chap. 19).

Roy, R. (1998). In G. -J. Boons, *Carbohydrate chemistry* (pp. 280–320). London: Blackie (chap. 7).

Schiweck, H., Rapp, K., & Vogel, M. (1998). Utilisation of sucrose as an industrial bulk chemical — state of the art and future implications. *Chemistry & Industry (London)*, 228–234.