Novel Sugar Based Acrylate: Synthesis, Characterization and Polymerization

MERYEM KORUYUCU[a], FEHMi SALTAN[a,b], GÖKHAN KÖK[a], HAKAN AKAT[a] AND YEŞIM SALMAN[a*]

[a]*Ege University, Faculty of Science, Chemistry of Department, 35100, Izmir*
[b]*Çankiri Karatekin University, Faculty of Science, Chemistry of Department, 18100, Çankiri*

ABSTRACT

The present study has demonstrated that novel acrylic glycopolymers are successfully prepared by using monosaccharides containing an acrylate group (9-12). For this purpose, sugar based acrylate monomers were synthesized via ring opening method (Method B) and homopolymerization of this sugar oxypropylacrylates was performed using free radical polymerization. The characterization of all the monomers and polymers were verified by ^{1}HNMR, ^{13}CNMR, FTIR and GPC techniques. The Glass transition temperatures and thermal characteristics of the polymers were also analyzed by using DSC and TG techniques. The thermal stability of prepared polymers have changed with the stereochemistry of the carbohydrate moiety. Also, the molecular weight of the polymers has affected the thermal stability.

KEYWORDS: *Acrylic glycopolymers, Polysaccharides, Epoxy sugar, Radical polymerization, Thermal properties*

INTRODUCTION

Carbohydrates are the most abundant group of natural products. Every year 127 billion tons of carbohydrates are produced by photosynthesis in plants and microorganisms. The first work from Emil Fischer at the beginning of the 20th century has put the basics of the carbohydrate chemistry and opened the door to a great development in this field. In the early 20th century, many attempts were undertaken to utilize the carbohydrates as raw materials for the chemical industry especially for polymer production. In spite of all the difficulties in this way, researchers from many fields have been doing the best efforts to reach this goal.

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Correspondence author e-mail:yesim.salman@ege.edu.tr
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Nowadays, millions of tons of low molecular-weight carbohydrates such as D-glucose, D-fructose, sucrose, lactose, maltose and others are industrially available with high purity and that enhances the activities for the chemical utilization of such materials in non-food applications.

It has long been known that carbohydrates play an important role in biological processes [1-3]. Significant incorporation of carbohydrates into various cellular processes makes them very useful in the building up of synthetic carbohydrate-based systems for therapeutic needs. Carbohydrate based monomers and polymers confer high hydrophilicity and water solubility [4], they are studied immensely for a variety of applications such as drug delivery systems [5], hydrogels[6], surfactants[7], and extracellular matrices [8] as controlled cell culture, chromatography supports[9-12]. Also, in the last decade, carbohydrates as renewable resources [13-15] for the chemical industry as synthetic polymers have attracted attention because they many be considered as an alternative to the traditional petroleum based-plastics. In the synthesis of basic raw materials, products have been used carbohydrate polymers whose number has increased by sugars such as acrylate such as methacrylate based monomers. Synthetic polymers with pendant saccharide residues are called glycopolymers [16-17]. Glycopolymers, [18-20] synthetic polymers featuring pendant and/or terminal carbohydrate moieties, have been of particular interest to the field of drug delivery and therapeutics. This interest is derived from the complex roles that carbohydrates play in vivo, particularly in recognition events with carbohydrate- binding proteins known as lectins [21,22].

Most of the synthetic glycopolymers (poly vinylsaccharides) were prepared by radical polymerization of acrylic and methacrylate components added to the sugar structures by flexible extenders [23,24].

Here, we have described the preparation and characterization of the novel glycopolymers which are poly-Glu-OPA, poly-Gal-OPA, poly-Fru-OPA and poly-Man-OPA. It is expected that this study will contribute literature and application areas for synthetic glycopolymers. Low irritation and compatibility with skin and other biological surfaces of the synthesized sugar based monomers enable for their use in the domain of polymer synthesis to prepare biocompatible materials with favourable pharmacological and cosmetic properties.

MATERIALS AND METHODS

Materials

Epichlorohydrin, 2,2-azobis(isobutyronitrile) (AIBN), acrylic acid, D-glucose, D-galactose, D-mannose, D-fructose and solvents were obtained from Merck. All chemicals were used as received unless specified otherwise.

Instrumentation

Perkin-Elmer Spectrum 100 was used for analyses of the FTIR spectra. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian 400 MHz NMR spectrometer. The thermal analyses were carried out using a Perkin Elmer TG and DSC in both N_2 and air with a flow rate with 100 mL/min and with a heating rate of 10 °C/min. The polymers were dried at 35 °C under 10 mbar vacuum before the thermal analysis. Analysis of molecular weights of the polymers were performed using a gel permeation chromatography (GPC) instrument; viscotek GPC max. auto sampler system, consisting of a pump, three visco GEL GPC columns (G2000HHR, G3000HHR and G4000HHR), a viscotek differential refractive index (RI) detector with a THF flow rate of 1.0 mL/min at 30 °C.

Method

General Procedure for Epoxy Sugar (Method A)

Firstly, Isopropylidene protected sugars (1-4) were synthesized according to the literature [25,26]. Epichlorohydrin (10 mL, 128 mmol) was stirred with aq. NaOH (50 %, 20 mL) and tetrabutylammonium bromide (1.00 g, 3.10 mmol) for 30 min. Then the mixture was added slowly into a flask containing the protected sugar (4 g, 15.38 mmol) at approx. 5 °C under stirring. The reaction carried out for 1 h at 5 °C and then 12 h. at rt. After that, the reaction mixture was poured over crushed ice and extracted with ethyl acetate (4x20 mL). The organic layer was washed with aq. NH_4Cl (10 %, 2x5 mL) and water (2x10 mL), dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated to give a syrupy product. The epoxy sugars (5-8) were obtained as colorless syrup after column chromatography with Hexane-EtOAc; (2/1).

General procedure for the ring opening of epoxy sugars with acrylic acid (Method B)

To a solution of epoxy sugar (5-8) (4.0 g, 12.64 mmol) in DMF (20 mL) was added acrylic acid (6.94 mL, 7.30 g, 101.18 mmol). Then triethylamine (1.4 mL, 0.102 g, 10.12 mmol) was added slowly to the mixture. The mixture was stirred vigorously while being heated to 65 °C. The mixture was cooled by adding water after 24 h. The obtained product was extracted with CH_2Cl_2 and washed with cold water and dried by using Na_2SO_4. The products were passed through an open silica gel column (Hexane/EtOAc; 7/3). All the acrylic compounds (9-12) were obtained as light yellow transparent gels (67-72.3 % yield).

General procedure for the polymerization of sugar based acrylate monomers (Method C)

AIBN (typically 0.03 g, ~2 mol %) was added to the functional sugar acrylate monomers (9-12) (0.5 mg, 1.242 mmol) in 2 mL of anhydrous DMF under argon. The mixture was stirred at 70 °C and the polymerizations were accomplished in over 22 h. FT-IR spectroscopy was used in order to checking whether the reaction completed. After cooling down, the reaction mixtures were added dropwise to methanol to precipitate the polymer products (13-16), which were filtered off and dried in vacuum oven at 35 °C (66-75 % yield).

Spectral data for synthesized compounds

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2′3′-epoxypropan-1′-yl)-α-D-glucofuranose (5): Compound 5 was synthesized from 1 according to Method A. The product is a colorless syrup; 1.84 g, 76 %, $[\alpha]^{19}_D$ -0,26 (c=1 in CH_2Cl_2), ^{1}H-NMR (δ , ppm): 5.89 (d, J=3.6, H-1′), 5.88 (d, J=3.6, H-1), 4.60 (d, J=3.6, H-22), 4.55 (d, J=3.6, H-2), 4.31 (m, H-5), 4.11 (H-4, H-6a, H-6a′), 4.00 (H-6b′, H-6b', H-3), 3.95 (dd, H-13a′), 3.89 (dd, H-13a), 3.64 (dd, J=11.8, 5.0, 0.6 1H, H-13b), 3.48 (dd, J=11.6, 6.4, 0.37H, H-13b′), 3.15 (m, H-14, H-14′), 2.82 (t, J=4.6, H-15a′), 2.80 (t, J=4.6, H-15a), 2.65 (dd, J=5.0, 2.6, H-15b), 2.62 (dd, J=4.8, 2.8, H-15b′), 1.50 (s, 3H, H-11, H-11′), 1.43 (s, 3H, H-9, H-9′), 1.35 (s, 3H, H-10, H-10), 1.32 (s, 3H, H-12, H-1′), ^{13}C-NMR (δ, ppm): 111.8 (C-8), 109.1(C-7,), 105.2 (C-1), 82.9 (C-3), 82.6 (C-2), 81.1 (C-4), 72.4 (C-5), 72.1 (C-13′), 70.6 (C-13), 67.4 (C-6), 50.7 (C-14′), 50.5 (C-14), 44.4 (C-15′), 44.1 (C-15′), 26.9 (C-11), 26.8 (C-9), 26.2 (C-12), 25.4 (C-10), FTIR (cm^{-1}): 3055, 2987, 2934, 1374, 1079, 1020.

1,2:3,4-Di-*O*-isopropylidene-6-*O*-(2′,3′ -epoxypropan-1′-yl)-α-D-galactopyranose (6): Compound 6 was synthesized from 2 according to Method A. The product is colorless syrup1.59 g, 70 %. $[\delta]^{22}_D$-25 (c=1 in CH_2Cl_2), ^{1}H NMR ($CDCl_3$, ppm): δ 5.50 (d, 1H, J= 5.2, H-1), 4.58 (dd, 1 H, J=7.6, 2, H-3), 4.28 (dd, 1 H, J=7.5, 2.4, H-2), 4.22 (dd, 1 H, J=5.2, 4, H-4), 3.85 (m,1H, H-5), 3.80 (m,1H, H-6b), 3.70 (m, 1H, H-6a), 3.53 (dd, J=11.6, 5.6, H-13b2), 3.52 (dd, 1H, J=11.6, 5.6, H-13b′), 3.48 (dd, J=12, 5.6, H-13a′), 3.40 (dd, 1H, J=12, 5.6 , H-13a), 3.25 (m, H-14′), 3.22 (m, 1H, H-14), 2.74 (t, J=4.48, H-15a′), 2.72 (t, 1H, J=4.48, H-15a), 2.60 (dd, 1H, J=5.2, 2.8, H-15b), 2.58 (dd, J=5.2, 2.8, H-15b′), 1.51 (s, 3H, H-11), 1.41 (s, 3H, H-9), 1,33 (s, 3H, H-10), 1.30 (s, 3H, H-12), ^{13}C NMR ($CDCl_3$, ppm): δ 109.2 (C-7), 108.5 (C-8), 96.3 (C-1), 71.1 (C-4), 70.6 (C-3), 70.4 (C-2), 70.0 (C-5), 66.9 (C-6), 66.7 (C-13), 50.6 (C-14), 44.3 (C-15), 26.1 (C-11), 26.0 (C-9), 24.9 (C-12), 24.4 (C-10), FTIR (cm^{-1}):3054, 2988, 2934, 1382, 1070.

2,3:5,6-Di-*O*-isopropylidene-1-*O*-(2′,3′-epoxypropan-12 -yl)-α-D-mannofuranose (7): Compound 7 was synthesized from 3 according to Method A. The product is a colorless syrup1.59 g, (yield 70%) was obtained,

$[\delta]^{19}_{D}$ 0.60 (c=1 in CH_2Cl_2).^{1}H NMR ($CDCl_3$, ppm): 2.80 (dd, 1H, J=4.4 and 5.2, H-15a), 2.60 (dd, 1H, J=2.8 and 4.8, H-15b), 5.13 (m, 1H, H-14), 3.76 (dd, 1H, J=3.2 and 11.6, H-13a), 3.48 (dd, 1H, J=6.8 and 11.6, H-13b), 1.32 (s, 3H, H-12), 1.38 (s, 3H, H-11), 1.45 (s, 3H, H-10), 1.46 (s, 3H, H-9), 4.40 (m, 1H, H-5), 4.11 (dd, 1H, J= 6.4 and 8.8, H-4), δ 5.03 (d, 1H, J= 3.6, H-1), 4.78 (dd, 1H, J=3.6, H-2), 4.63 (t, 1H, J=6.0, 2, H-3), FTIR (cm^{-1}): 3049(), 2988-2937 (C-H), 1372 ($C(CH_3)_2$), 1086 (C-O-C).

2,3:4,5-Di-*O*-isopropylidene-1-*O*-(2′,3′-epoxypropan-12 -yl)-α-D-fructopyranose (8): Compound 8 was synthesized from 4 according to Method A. The product is colorless syrup 1.68 g, 73.96 %. $[\alpha]^{21}_{D}$ -46 (c=1 in CH_2Cl_2), ^{1}H NMR ($CDCl_3$, ppm): δ 4.53 (dd, 1H, J=8, 2.4, H-4), 4.32 (dd, 1H, J=5.2, 2.4, H-3), 4.15 (dd, 1H, J=7.6, 1.2, H-5), 3.84 (d, 1H, J=11.2, H-1a), 3.70 (dd, 1H, J=1.6, 1.2, H-6a), 3.65 (d, 1H, J=13.2, H-6b), 3.56 (d, 1H, J=3.55, H-1b), 3.54 (dd, 1 H, J=11.6, 5.6, H-13a), 3.38 (dd, 1H, J=12, 5.6, H-13b), 3.08 (m, 1H, H-14), 2.70 (t, 1H, J=4.8, H-15a), 2.55 (dd, 1H, J=5.2, 2.8, H-15b), 1.47 (s, 3H, H-11), 1.40 (s, 3H, H-9), 1.37 (s, 3H, H-12), 1.28 (s, 3H, H-10), ^{13}C NMR ($CDCl_3$, ppm): α 109.1 (C-7), 108.7 (C-8), 102.7 (C-2), 73.0 (C-3), 71.1 (C-4), 70.3 (C-5), 70.2 (C-1), 61.2 (C-6), 59.2 (C-13), 50.8, 50.7 (C-14, C-14′), 44.5, 44. 3 (C-15, C-15′), 26.7 (C-11), 26.0 (C-9), 25.4 (C-12), 24.3 (C-10), FTIR (cm^{-1}): 3056 (), 2989-2936 (C-H), 1381 ($C(CH_3)_2$), 1070 (C-O-C).

3-*O*-(2′ -hydroxy-3′-acryloyloxypropyl)-1,2:5,6-di-*O*-isopropylidene-α-D glucofuranose (9): Compound 9 was synthesized from 5 according to Method B. The product was obtained as a light yellow transparent gel, 1.65 g, 67 %. ^{1}H NMR ($CDCl_3$, ppm): δ 6.45 (dd, 1H, J=17.2, 1.6, H-18a), 6.15 (dd, 1H, J=17.2, 10.4, H-17), 5.90 (d, 1H, J=3.2, H-1), 5.84 (dd, 1H, J=10.4, 1.6, H-18b), 4.55 (dd, 1H, J=5.0, 3.6, H-2),, 4.32 (m, 1H, H-5), 4.22 (dd, 1H, J=7.4, 5.0, H-3), 4.18 (m, 1H, H-15a), 4.16 (m, 1H, H-15b), 4.12 (dd, 1H, J=8.6, 6.4, H-4), 4.05 (m, 1H, H-14), 4.00 (dd, 1H, J=8.6, 7.2, H-6b), 3.98 (dd, 1H, J=9.8, 7.4, H-6a), 3.88, 3.62, (dd, 1H, J=10.4, 4.2, J′ =11.6, 4.2, H-13a, H-13a′), 3.78, 3.44 (dd, 1H, J=10.4, 4.2, J′ =11.6, 4.2, H-13b, H-13b′), 1.49 (s, 3H, H-11), 1.44 (s, 3H, H-9), 1.36 (s, 3H, H-10), 1.32 (s, 3H, H-12), ^{13}C NMR ($CDCl_3$, ppm): α 128.2 (C-18), 131.5 (C-17), 166.2 (C-16), 65.2 (C-15), 65.0 (C-152), 69.6 (C-14), 71.2 (C-13), 26.4 (C-12), 27.1 (C-11), 25.3 (C-10), 27.0 (C-9), 112, 2 (C-8), 109.7 (C-7), 68.1 (C-6), 73.1 (C-5), 81.5 (C-4), 84.7 (C-3), 82.7 (C-2), 105.8 (C-1), FTIR (cm^{-1}):3456 (OH), 1727 (C=O), 1635 (C=C), 1073 (C-O-C), 2987-2937 (C-H), Anal. Found for $C_{18}H_{28}O_9$: H, 7.49; C, 54.66; O, 38.01, Calcd: H, 7.27; C, 55.66; O, 37.07.

6-*O*-(2′-hydroxy-3′-acryloyloxypropyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose(10): Compound 10 was synthesized from 6 according to Method B. The product is light yellow transparent gel, 1.65 g., 67 % yield. ^{1}H NMR ($CDCl_3$, ppm): δ 5.53 (d, 1H, J=5.2, H-1), 6.42 (dd, 1H, J=17, 1.2, H-18a), 5.84 (dd, 1H, J=10.4, 1.2, H-18b), 6.15 (dd, 1H, J=17, 10.4, H-17), 4.62 (dd, 1H, J=7.5-2.4, H-3), 4.34 (dd, 1H, J=5,2.4, H-2), 4.26 (d, 1H, J=7.5, H-4), 4.23 (m, H-14′), 4.22 (m, 1H, H-14), 4.06 (m, 1H, H-6a), 3.90 (m, 1H, H-5), 3.71 (m, 1H, H-6b), 3.70 (m, 1H, H-15b), 3.62 (m, 1H, H-15a), 3.60 (dd, 1H, J=12, 5.6, H-13b), 3.50 (dd, 1H, J=12, 5.6, H-13a), 1.54 (s, 3H, H-11), 1.44 (s, 3H, H-9) , 1.34 (s, 3H, H-10), 1.33 (s, 3H, H-12), ^{13}C NMR ($CDCl_3$, ppm): δ 128.3 (C-18), 131.3 (C-17), 166.3 (C-16), 65.6 (C-15), 66.9 (C-14), 70.2 (C-13), 25.1 (C-12), 26.2 (C-11), 24,6 (C-10), 26.1 (C-9), 108.9 (C-8), 109.6 (C-7), 68.7 (C-6), 70.6 (C-5), 72.6 (C-4), 71.3 (C-3), 70.8 (C-2), 96.5 (C-1), FTIR (cm^{-1}): 3482 (OH), 1635 (C=C), 2987-2937 (C-H), 1725 (C=O), 1069 (C-O-C), Anal. Found for $C_{18}H_{28}O_9$: H, 7.49; C, 54.66; O, 38.01, Calcd: H, 7.57; C, 55.98; O, 36.26.

1-*O*-(2′-hydroxy-3′-acryloyloxypropyl)-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (11): Compound 11 was synthesized from 7 according to Method B. The product was obtained as a light yellow transparent gel 1.68 g., 68 % yield. ^{1}H NMR ($CDCl_3$, ppm): δ 6.45 (dd, 1H, J=17.6, 1.2, H-18a), 5.86 (dd, 1H, J=10.4, 1.2, H-18b), 6.15 (dd, 1H, J=17.6, 10.4, H-17), 4.22 (m, 1H, H-15a), 4.23 (m, 1H, H-15b), 4.00 (m, 1H, H-14), 3.68 (dd, 1 H , J=10.4, 4.4, H-13a), 3.50 (dd, 1H, J2 = 10.4, 5.2, H-13a2), 3.72 (dd, 1H, J=10.4, 4.4, H-13b), 3.60 (dd, 1H, J′ =10.4, 5.2, H-13b′), 1.32 (s, 3H, H-12), 1.46 (s, 3H, H-11), 1.38 (s, 3H, H-10), 1.44 (s, 3H, H-9), 3.98 (dd, 1H, J=8.7, 4.4, H-6a), 5.10 (d, 1H, J=2.1. H-1), 4.61 (dd, 1H, J=6, 3.2, H-2), 4.80 (dd, 1H, J=6, 3.2, H-3), 4.10 (dd, 1H, J=3.6, 7.6, H-4), 4.40 (ddd, 1H, J=7.2, 6.4, 5.2, H-5),

3.96 (dd, 1H. J=8.7, 5.0, H-6b),^{13}C NMR ($CDCl_3$, ppm): 128.1 (C-18), 131.6 (C-17), δ 166.4 (C-16), 66.9 (C-14), 69.0(C-13), 68.8 (C-13′), 24.7 (C-12), 26.0 (C-11), 25.4 (C-10), 26.9 (C-9), 109,3 (C-8), 112.9 (C-7), 107.2 (C-1), 65.6 (C-15), 65.5 (C-6), 73.3 (C-5), 85.2 (C-4), 80.8 (C-3), 79.6 (C-2), FTIR (cm^{-1}): 1722 (C=O), 1632 (C=C), 1160 (C-O-C), 2987-2935 (C-H), 3472 (OH), Anal. Found for $C_{18}H_{28}O_9$: H, 7.45; O, 36.47; C, 56.02, Calcd: H, 7.27; O, 37.07; C, 55.66.

1-*O*-(2′-hydroxy-3′-acryloyloxypropyl)-2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose(12): Compound 12 light yellow transparent gel 1.78 g (72.3 % yield) was obtained, ^{1}H NMR ($CDCl_3$, ppm): δ 3.89 (d, 1H, J=11.2, H-1a), 3.54 (d, 1H, J=11.2, H-1b), 6.43 (dd, 1H, J=17.6, 1.2, H-18a), 5.85 (dd, 1H, J=10.4, 1.2, H-18b, 6.15 (dd, 1H, J=17.6, 10.4, H-17), 4.60 (dd, 1H, J=8, 2.4, H-4), 4.35 (dd, 1H, J=5.2, 2.7, H-3), 4.25 (dd, 1H, J=7.6, 1.2, H-5), 4.23 (m, 1H, H-15a), 4.21 (m, 1H, H-15b), 4.09 (m, 1H, , H-14), 4.07 (m, 1H, H-14′), 3.78 (dd,1H, J=13.2, H-6a), 3.70 (dd, 1H, J=12, 3.2, H-6b), 3.65 (dd, 1H, J=12, 5.6, H-13a), 3.60 (dd, 1H, J=12, 5.6, H-13b), 1.54 (s, 3H, H-11), 1.48 (s, 3H, H-9), 1.41 (s, 3H, H-12), 1.34 (s, 3H, H-10), ^{13}CNMR ($CDCl_3$, ppm): δ 128.2 (C-18), 131.5 (C-17), 166.3 (C-16), 65.5 (C-15), 65.8 C-15′), 68.8 (C-14), 68.7 (C-14′), 70.5 (C-13), 70.8 (C-13′), 25.5 (C-12), 26.7 (C-11), 24.1 (C-10), 26.0 (C-9), 108.7 (C-8), 109.2 (C-7), 61.2 (C-6), 70.4 (C-5), 71.0 (C-4), 73.5 (C-3), 102.5 (C-2), 71.1 (C-1), FTIR (cm^{-1}): 3483 (OH), 1635 (C=C), 2989-2936 (C-H), 1726 (C=O), 1069 (C-O-C), Anal. Found for $C_{18}H_{28}O_9$: H, 7.29; C, 55.63; O, 37.06, Calcd: H, 7.27; C, 55.66; O, 37.07.

Poly-3-*O*-(2′ -hydroxy-3′ -acryloyloxypropyl)-1,2:5,6-di-*O*-isopropylidene-α-D glucopyranose polymer (Poly-Glu-OPA) (13): Polymer 13 was synthesized from 9 according to Method C with 66 % yield. FTIR (cm^{-1}): 3408 (OH), 2983-2935 (C-H), 1731 (C=O), 1067 (C-O-C).

Poly-6-*O*-(2′ -hydroxy-3′-acryloyloxypropyl)-1,2:3,4- di-*O*-isopropylidene-α-D galactopyranose polymer (Poly-Gal-OPA) (14):Polymer 14 was synthesized from 10 according to Method C with 72 % yield. FTIR (cm^{-1}): 3357 (OH), 2978-2928 (C-H), 1731 (C=O), 1069 (C-O-C).

Poly-1-*O*-(2′-hydroxy-3′-acryloyloxypropyl)-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose polymer (**Poly-Man-OPA**) (**15):** Polymer **15** was synthesized from **11** according to Method C with 62 % yield, **FTIR** (cm^{-1}): 3408 (OH), 2978-2935 (C-H), 1731 (C=O), 1067 (C-O-C).

Poly-1-*O*-(2′-hydroxy-3′-acryloyloxypropyl)-2,3:4,5-di-*O*-isopropylidene-α-D-fructopyranose polymer (**Poly-Fru-OPA**) (**16):** Polymer **16** was synthesized from **12** according to Method C with 75 % yield. FTIR (cm^{-1}): 3448 (OH), 2982-2929 (C-H), 1729 (C=O), 1065 (C-O-C).

RESULTS AND DISCUSSION

Starting compounds **1-4** which have only one hydroxyl group were synthesized according to the literature. Thus, we synthesized "-O-[2′,3′ -epoxypropane-1′ -yl] ether derivatives (**5-8**) of these free hydroxyl groups using epichlorohydrin (1-chloro-2,3-epoxypropane). The crucial point of the present study is that polymers have a spacer between sugar parts and acrylate parts, which decreases the steric effect in the polymerization of acrylic moieties. Furthermore, by opening the epoxide ring the hydrophilicity of the side chain is increased. Thus, four new sugar based acrylic monomers (9-12) have been obtained by opening epoxide ring of sugars (5-8) by acrylic acid in DMF. Polymerizations were carried out using AIBN (as an initiator) at 70 °C, with DMF to afford **13-16**. By this means, acrylic glycopolymers (**Poly-SOPA**s): poly(glucooxypropylacrylate) (Poly-Glu-OPA), poly(mannooxypropylacrylate) (Poly-Man-OPA), poly(galactooxypropylacrylate) (Poly-Gal-OPA), poly(fructooxypropylacrylate) (Poly-Fru-OPA) were obtained. The synthetic strategy is presented in figure 1.

The number of average molecular weight (M_n), mass average molecular weight (M_w) and

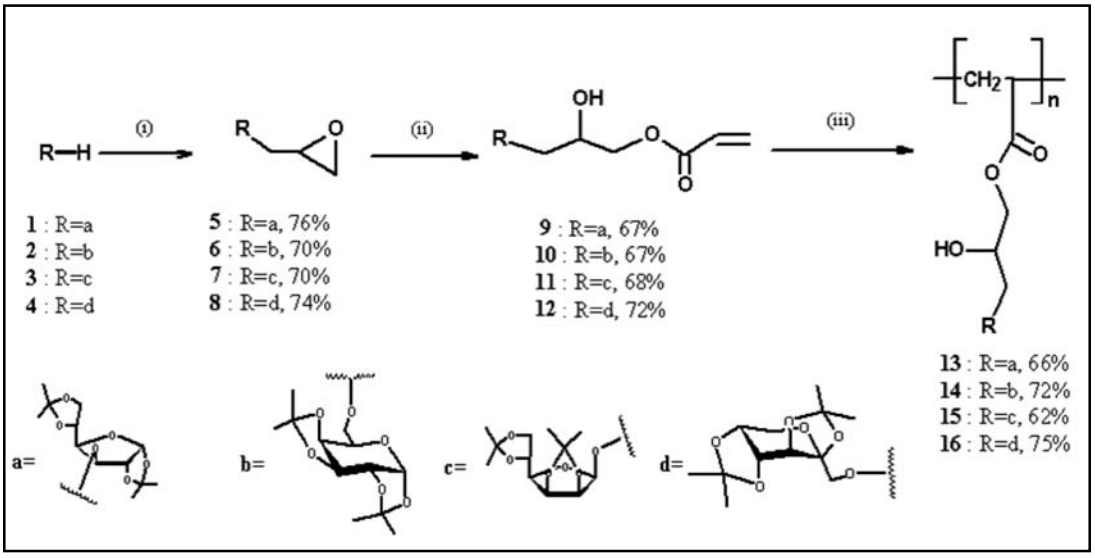

Fig. 1. Synthesis of sugars based on oxypropylacrylate monomers and polymers. (i) NaOH 50 %, $(Bu)_4NBr$, epichlorohydrin; (ii) acrylic acid, $(Et)_3N$, DMF, 65 °C; (iii) AIBN, DMF, 70 °C.

polydispersity index (PDI) of all sugar oxypropylacrylate polymers **(Poly-SOPA**s) were determined (Table 1). When Poly- Glu-OPA (**13**) was compared with the other **Poly-SOPA**s, **13** had the highest M_n and M_w values (M_n: 60.600 and M_w: 102.500).

The thermal properties of the **Poly-SOPA**s were studied using the TGA technique at

TABLE 1. Molecular weights and PDI ratios of Poly-SOPAs

Sample	$M_{n\,g/mol}$	$M_{w\,s/mol}$	PDI
Poly-Glu-OPA	60,600	102,500	3.7
Poly-Gal-OPA	17,500	27,700	1.59
Poly-Man-OPA	8,600	15,900	1.84
Poly-Fru-OPA	7,300	21,500	2.94

temperatures from ambient temperature to 1000 °C under a nitrogen atmosphere. The TGA curves for the **Poly-SOPA**s in N_2 are given in figure 2. The initial (5% loss) and final temperatures and total mass losses in the thermal decomposition of polymers were determined.

The first degradation step which corresponds to 5 % weight loss started at 200, 268, 164, and 290 °C and continued up to 430, 419, 434, 410 °C (90 % loss) for Poly-Gal-OPA, Poly-

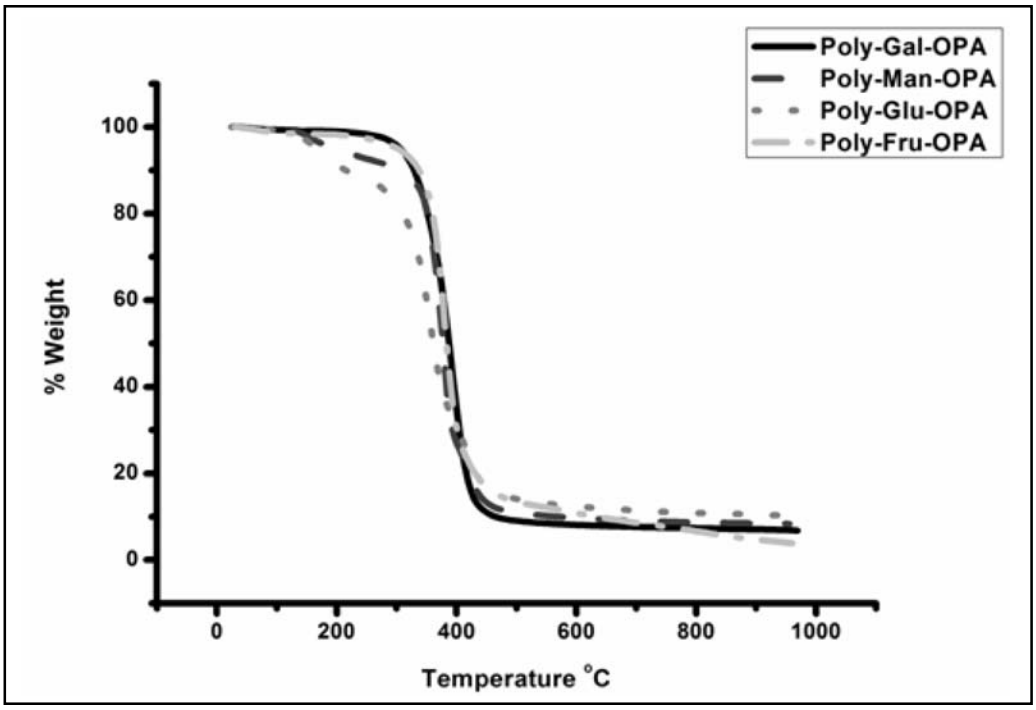

Fig. 2. TGA curves of synthesized polymers (Poly-SOPAs).

Man-OPA, Poly-Glu-OPA, and Poly-Fru-OPA, respectively. The temperatures for maximum weight loss of Poly-Gal-OPA, Poly-Man-OPA, Poly-Glu-OPA and Poly-Fru-OPA were 380, 393, 359 and 380 °C, respectively. When analyzing the **Poly-SOPA**s TG curves and data, Poly-Man-OPA, which had the lowest M_n and M_w, was stable up to 298°C and also the degradation of Poly-Glu-OPA, which had the highest molecular weight (Mn: 60, 600), began to degrade at the lowest temperature.

Differential scanning calorimetry (DSC) was also used to analyzed the thermal characteristics of **Poly-SOPA**s. According to DSC data, none of the acrylic glycopolymers have significant glass transition temperature (Tg) which might have resulted from amorphous structures of the polymers. When the DSC curves are examined in detail, it is seen that the Poly-Glu-OPA polymer has the highest glass transition temperature (136°C). The reason for this is that Poly-Glu-OPA has a higher molecular weight than the other synthesized sugar-based polymer [27].

NMR study

NMR spectra confirmed the assigned structures of the ring-opened monomers 9, 10, 11, and 12. The NMR spectrum for compound 12 (Figure 3 and Figure 4) is discussed below as an example for all monomers:

TABLE 2. Glass transition temperature(Tg) of Poly-SOPAs.

Polymer	T_g(°C)
Poly-Glu-OPA	136
Poly-Gal-OPA	134
Poly-Man-OPA	132
Poly-Fru-OPA	130

The characteristic vinlyic protons (H-18a, H-18b and H-17) observed at δ 5.86, δ 6.45 and β 6.15 ppm,respectively. The proton on C-17 which is adjacent to the esther group, observed as a double doublet at δ 6.15 (J=17.2, 10.4 Hz). H-18a and H-18b protons also both observed as double doublets. Trans proton (H-18a) and cis proton (H-18b) adjacent to H-17 observed at 6.43 ppm (J=17.2, 1.2 Hz) and δ 5.85 ppm (J=10.4, 1.2 Hz), respectively. H-1a gave signal at 3.89 ppm as a doublet (J=11.2 Hz) and H-1b at 3.54 ppm as a doublet (J=11.2 Hz).

The carbon atoms of vinyl group (C-17 and C-18) signals observed at δ 131.5, 128.2 ppm. The ester carbonyl atom, which has the specific signal, gave a signal at δ 166.3 ppm.

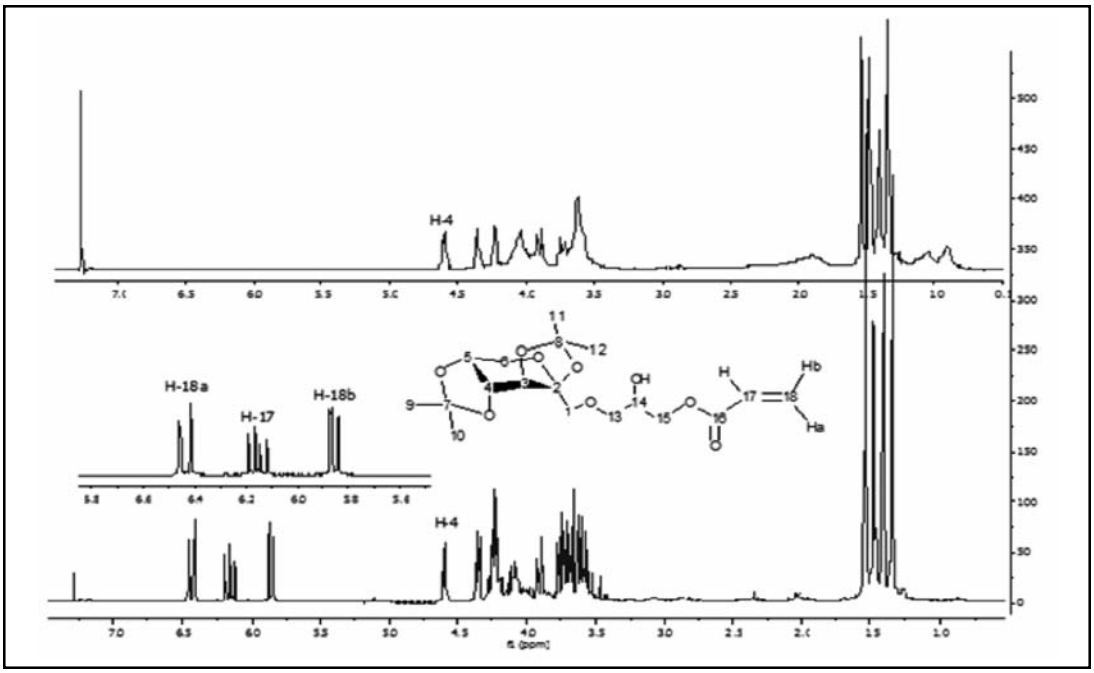

Fig. 3. The comparison of ^{1}H-NMR of 1-*O*-(2′ -hydroxy-3′ -acryloyloxypropyl)-2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**12**) and Poly-Fru-OPA (**16**).

Homopolymers 13, 14, 15, and 16 were prepared by radical polymerization reactions of sugar based acrylate monomers 9, 10, 11 and 12 using AIBN at 70 °C as an initiator in DMF. Comparison of the Poly-Fru-OPA (16) ^{1}H NMR spectrum with its precursor sugar based acrylate monomer's (12) spectrum showed that the signals related to the vinylic protons (H-17, H-18a and H-18b) of the monomer disappeared and this indicated that the polymerization was accomplished (Figure 3).

CONCLUSION

In conclusion, carbohydrate containing polymers were synthesized by using a shorter synthetic route compared to the literature. Free radical polymerization was used for the synthesis of polymers and all synthesis of monomers Poly-Glu-OPA has the highest molecular weight. It is thought that molecular weights of these polymers can affect their thermal behavior. Also, TG curves showed that

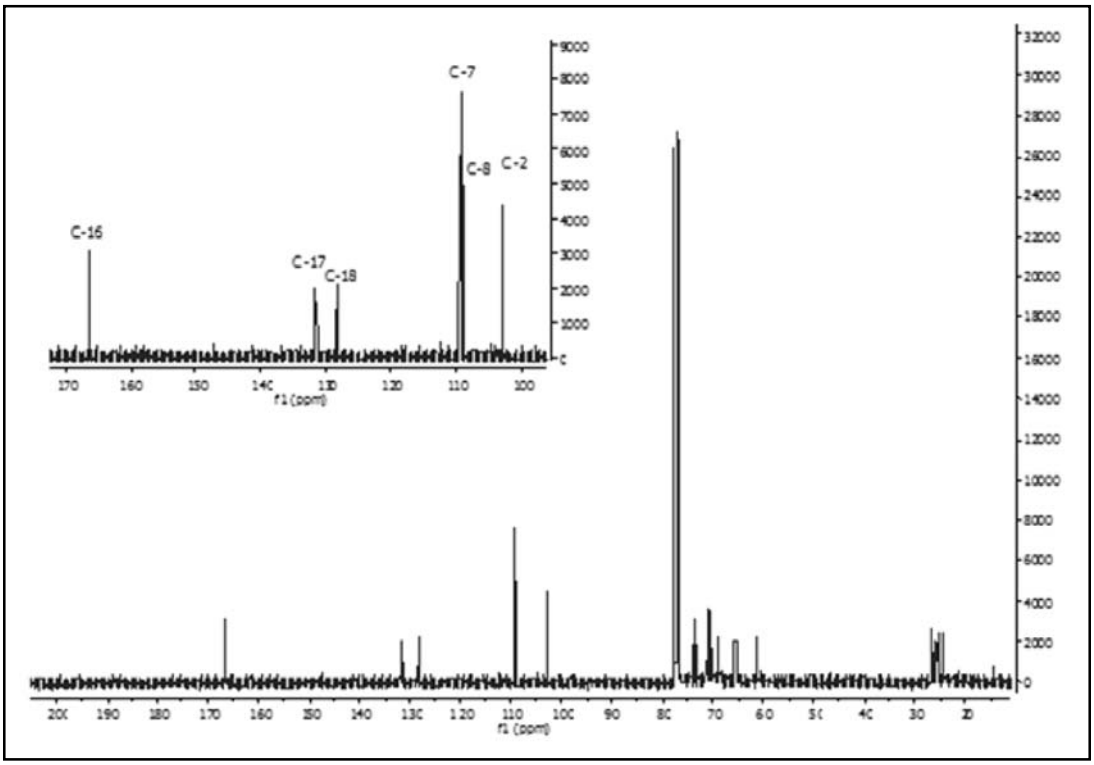

Fig. 4. ^{13}C-NMR of 1-*O*-(2′ -hydroxy-3′ -acryloyloxypropyl)-2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**12**).

the decomposition of Poly-Glu-OPA is faster than the other polymers (Poly-Gal-OPA, Poly-Man-OPA, Poly-Fru-OPA), reason of that it can be earlier fracture of long chains of Poly-Glu-OPA.

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