

Synthesis, characterization and thermokinetic analysis of the novel sugar based styrene co-polymer

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Abstract

A new α -chloralose (1,2-*O*-(*R*)-trichloroethylidene- α -D-glucofuranose)-based copolymer of styrene (PSVTEG) (**2**) was synthesized from vinyl (hydroxyl) furan monomer (**1**) and styrene by a conventional free radical polymerization reaction. The thermal decomposition kinetics of polymer were investigated by means of thermogravimetric analysis in dynamic nitrogen atmosphere at different heating rates. The apparent activation energy for the main stage thermal decomposition of the copolymer PSVTEG (**2**) was calculated using the Flynn-Wall-Ozawa and found to be 159.0 ± 3 kJ/mol. In addition, the activation energy value was calculated according to Coats-Redfern method and found to be compatible with the obtained result. The thermogram of the glycopolymer (PSVTEG) (**2**) has two decomposition stages and the calculated activation energy indicated that the main degradation stage is a nonspontaneous process (integral form $1/(1-\alpha)^2$ for F_3).

Keywords: glycopolymers, carbohydrate based vinyl copolymer, α -chloralose, thermal analysis, decomposition kinetic.

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1. Introduction

Glycopolymer is synthetic polymer with pendant carbohydrates^[1]. Carbohydrates are important natural sources of building blocks for the synthesis of biodegradable polymers. They are also easily accessible and some are even coming from agricultural wastes^[2]. Furthermore, they are found in different kinds of chemical structures with great stereochemical diversity and constituted as renewable sources as being more sustainable than fossil fuels^[3,4]. Recently, the basic raw materials used for polymers have expanded by sugars including glucose, galactose, fructose and sucrose. Therefore, carbohydrates are excellent substitutes for products of fossil origin for industrial developments^[5]. Chemically containing sugar moieties onto synthetic polymers are individual methods for the functionalization of synthetic polymers. With these use of these methods, the polymer is not only functionalized, but also other desirable properties such as biodegradability, biocompatibility and biorenewability can be achieved^[6]. Thus, these could be available alternatives for developing environmental friendly products. Synthetic carbohydrate polymers were investigated as biodegradable, biocompatible, biorenewable materials as water absorbents, chromatographic supports, drug delivery systems and medical devices^[7,8], in dental medicine, bioimplants, contact lenses, tissue engineering and electrochemical applications^[9-12]. Moreover, polymers with pendant carbohydrate moieties have been useful in clinical diagnostic trials and targeted gene therapies. The use of these polymers are essential in surgery, prosthetic systems and pharmacology^[6,13-16]. In addition, using sugar functionalized petrochemical polymers of polystyrene for use as biodegradable polymers is a newly discovered application of a sugar linked synthetic polymer^[17,18].

During the last three decades, the synthesis of glycopolymers became popular with an effort towards biomimics and most of the attempts were based on the polymerization of monomers containing carbohydrate moieties^[15-25]. These glycomonomers (sugar carrying monomers) were reported to be polymerized by controlled/living radical polymerisation, radical, anionic, cationic ring-opening polymerization, ring-opening metathesis polymerization and post-functionalization techniques^[19,24,25]. Until the last decade, there had been limited attempts to react a functional polymeric backbone with a carbohydrate to obtain a glycopolymer. A significant reason for this was the difficulty of introducing sufficiently reactive pendant groups onto the polymer backbone to react with carbohydrates. With respect to a sustainable chemistry, unsaturated sugar monomers are useful building blocks for copolymers with special properties like biocompatibility, biodegradability, hydrophilicity/hydrophobicity balance and skin compatibility. These properties are of major importance in many fields such as pharmaceuticals, drugs and cosmetics. Up to now; several saccharide monomers have been investigated in free radical polymerization with a wide range of commercially available co-monomers. Vinylsaccharides give rise to polymers bearing sugar appendages in the side chains^[26]. For example, sugar-containing vinyl monomers were synthesized from isopropylidene^[27], chloralosed^[28] and other protected sugars^[6,29]. Additionally, poly(vinyl saccharide)s attracted much attention since vinyl sugars can easily be copolymerized with various comonomers. Thus, the resulting copolymers have a chemically stable C-C backbone and hydrophilic side chains. Klein and coworkers have studied the synthesis and solubility of poly(vinyl saccharide)^[30,31].

Nakamae et. al have copolymerized 2-(glycosyloxy)ethyl methacrylate with methyl methacrylate or styrene and investigated the surface properties of cast films^[32,33]. Wulff and coworkers have investigated the synthesis of *C*-glycosyl compounds containing polymerizable double bonds without protecting groups. They have used poly(vinyl saccharide)s with *N,N*-dimethylbarbituric acid as linkers between sugar and styrene^[34,35]. Other types of vinyl sugar monomers and polymers have been reviewed elsewhere^[36,37]. Since poly(vinyl sugar)s constitute polymers of a new structural type, they may have high potentials in modifying the surface of conventional polymer materials and improve the antistatic property, dyeability, adhesion, printability, and biocompatibility of bulk polymers^[38].

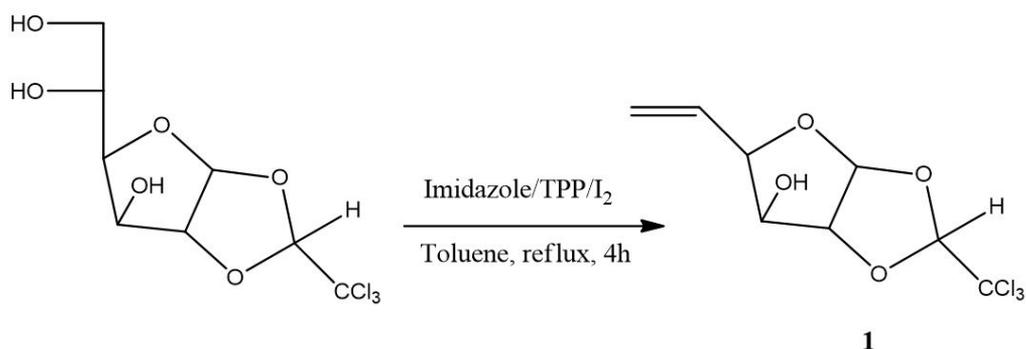
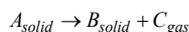
Monosaccharides mostly react in their furanose forms with chloral to give trichloroethylidene acetals. Chloraloses (β -chloralose or α -chloralose) have been prepared by the simple reaction of chloral and glucose^[39]. 1,2-*O*-(*R*)-trichloroethylidene-D-glucofuranose is a commercially available compound, also known as α -chloralose, which is used as an anesthetic for animals^[40,41]. Unlike most acetals, 1,2-*O*-trichloroethylidene acetals are very stable as protecting groups under acidic conditions due to the inductive effect of the trichloromethyl group. In addition, this protecting group is stable under mildly basic conditions. However, they are converted to the more reactive ketene acetals in the presence of strong bases such as potassium *tert*-butoxide. The only reported method for the removal of this protecting group is a Raney Nickel procedure^[42]. Additionally,

trichloroethylidene acetals are suitable protecting groups for the synthesis of some biologically important compounds such as amines^[43], orthoesters^[44], *spiro*endoperoxides^[45], *spiro*difuranose^[46], oxetanes^[47], NHC ligands^[48], Schiff base^[49], glyconanoconjugates^[50], etc.

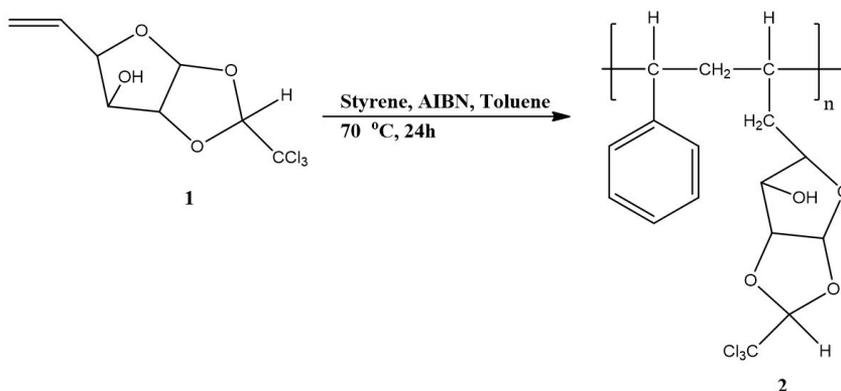
In this work, new vinyl (hydroxyl) furan monomer (**1**) of α -chloralose has been synthesized (Scheme 1) and characterized by Fourier transform infrared spectroscopy (FTIR), elemental analysis and optical rotation. In addition, it is used for the preparation of copolymer styrene (**2**) (Scheme 2). The thermal degradation kinetics of the copolymer was studied to compare its thermal properties. The apparent activation energies for thermal degradation of the copolymer were obtained by using Flynn-Wall-Ozawa and Coats-Redfern methods. Accordingly, in the further studies, the new carbohydrate-based copolymer of styrene will be a good candidate to prepare the metacomposites with negative electromagnetic parameters by a biomass conversion method^[51-53].

1.1 Kinetic Analysis^[54-56]

Thermogravimetric analysis can be used for the determination of the degradation kinetics of many polymers. In general, the thermal degradation reaction of a solid polymer is shown as:



Scheme 1. Synthesis of new vinyl (hydroxyl) furan monomer (**1**) from α -chloralose.



Scheme 2. Synthesis of the new copolymer styrene (**2**) from vinyl (hydroxyl) furan monomer (**1**).

where A is the starting material, B_{solid} and C_{gas} are the solid residue and the gas product, respectively. The following typical kinetic equation is generally expressed by the thermal degradation kinetics of the polymers.

$$r = d\alpha / dt = k(T) \times f(\alpha) \quad (1)$$

where T is the absolute temperature (K); r is the conversion per f(α) unit time (t) is the conversion function which represents the reaction model. The degree of conversion (α) is calculated by Equation 2 where m_o , m_i and m_f are the weights of sample before degradation, after complete degradation and at time t, respectively.

$$\alpha = m_o - m_i / m_o - m_f \quad (2)$$

The Arrhenius equation is the reaction constant which can be expressed by calculating k

$$k(T) = A_o e^{-(E / RT)} \quad (3)$$

where A is called pre-exponential factor, R is the gas constant and E is the activation energy

By combining Equation 1 and Equation 3 the following equation is obtained

$$d\alpha / dt = A_o e^{-(E / RT)} x f(\alpha) \quad (4)$$

According to the kinetic theory for the non-isothermal decomposition reactions, the fractional conversion α is expressed as a function of temperature which depends on the time of heating. Therefore, the heating rate (β) can be described as:

$$\beta = dT / dt \quad (5)$$

that Equation 6 is modified as follows:

$$d\alpha / dT = (1 / \beta) A_o e^{-(E / RT)} x f(\alpha) \quad (6)$$

Equation 5 and Equation 6 are the basis for the many equations derived to evaluate thermal analysis data.

1.1.1. Coats-Redfern Method^[57]

This method is based on the following equation

$$\ln(g(\alpha) / T^2) = \ln(AR / E\beta(1 - 2RT / E)) - (E / RT) \quad (7)$$

as E is calculated from the slope $-E/R$ of the plot $\ln(g(\alpha)/T^2)$ versus $1000/T$ which is a straight line. The most commonly used reaction models can be estimated for the solid-state processes by calculating the possible thermal degradation mechanism. The activation energy calculated by using this method was found to be as 159.2±3 kJ/mol.

1.1.2. Flynn-Wall-Ozawa (FWO) Method^[58,59]

In this method, there is no need of any knowledge for the reaction mechanism for the calculation of the activation energy. The activation energy (E) and pre-exponential factor (A) are not dependent on the fraction of degradation while they depend on temperature. This method uses Equation 8.

$$\log g(\alpha) = \log(AE / R) - \log \beta + \log p(E / RT) \quad (8)$$

Equation 9 is obtained by means of the Doyle approximation.

$$\log \beta = \log(AE / R) - \log g(\alpha) - 2.315 - 0.4567(E / RT) \quad (9)$$

Thus, from the slope $-E/R$ of the linear plot of $\log \beta$ versus $1000/T$, E is readily obtained. The activation energies calculated by using this method was found to be 159.0±3 kJ/mol.

2. Experimental

2.1 Materials

1,2-*O*-(*R*)-trichloroethylidene- α -D-glucofuranose (α - chloralose) (stated purity $\geq 98\%$), triphenylphosphine (TPP) (stated purity $\geq 99\%$), imidazole (stated purity, 99%), iodine (I_2) (stated purity 99%), toluene (stated purity 99%), sodium thiosulphate ($Na_2S_2O_3$) toluene (stated purity 99%), diethyl ether (stated purity $\geq 99\%$), ethyl acetate (EtOAc) (stated purity 99%), n-hexane (stated purity 99%), sodium hydrogen carbonate ($NaHCO_3$) (stated purity 98%), Na_2SO_4 (stated purity 98%), styrene, ABIN, toluene were purchased from Merck A.G and Sigma-Aldrich. The materials and chemicals were used without any further purification.

2.2 Instrumentation

All 1H NMR and ^{13}C NMR spectra were recorded using a Varian AS 400+ Mercury FT NMR spectrometer at ambient temperature. FTIR spectra were recorded on a Perkin Elmer 100 FTIR spectrometer. The test wavenumber range of FTIR spectra were 400-4000 cm^{-1} . Optical rotations were determined using a Rudolph Research Analytical Autopol I automatic polarimeter with a wavelength of 589 nm. The concentration 'c' has units of g/100 mL. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer. TLC and column chromatography were performed on precoated aluminum plates (Merck 5554) and silica gel G-60 (Merck 7734), respectively.

The TG (Thermogravimetric Analysis) curves were recorded using a Perkin Elmer, Diamond TG/DTA. The samples were heated under a N_2 atmosphere over a temperature range of 30 to 600 $^{\circ}C$ with a heating rate of 10 $^{\circ}C min^{-1}$. The weight loss (TG curve) and its first derivative according to the temperature (DTG curve) were recorded simultaneously.

Molecular weights were determined by a gel permeation chromatography (GPC), viscotek GPC(UK)-max an instrument Autosampler system, consisting of a pump, three visco GEL GPC columns (G2000HHR, G3000HHR and G4000HHR) a viscotek UV detector and a viscotek differential refractive index (RI) detector with a THF flow rate of 1.0 mL/min at 30 $^{\circ}C$ were employed.

2.3 Synthesis of the 5,6-dideoxy-1,2-*O*-(*R*)-trichloroethylidene- α -D-xylo-*hekso*-5-enofuranose (1)

A solution of α - chloralose (3.1 g, 10 mmol), triphenylphosphine (TPP) (10.8 g, 40 mmol) and imidazole (3.1 g, 10 mmol) in dry toluene (100 mL) was stirred and warmed to 50 $^{\circ}C$. Iodine (10.2 g, 40 mmol) was added to above reaction mixture in small lots during 30 min with the temperature of the reactants being maintained approximately 60 $^{\circ}C$. The reaction mixture was heated

to reflux for 4 h, cooled room temperature and solvent removed on a rotary evaporator to produce a dark brown syrupy. The purification of the residue is well documented in the literature^[60]. After this process, the white crystal of the title product was synthesized %86 yield (2.4 g). m.p. 102-103 °C, $[\alpha]_D^{23}$ -14.3 (*c* 0.7, MeOH). ¹H NMR (DMSO, 400 MHz): δ 6.05 (d, 1H, $J_{1,2}$ =4.0 Hz, H-1), 5.85 (m, 1H, H-5), 5.41 (s, 1H, HCCl₃), 5.34 (dd, 1H, $J_{5,6a}$ =0.8, $J_{5,6a}$ =16.8 Hz, H-6a), 5.23 (dd, $J_{6a,6b}$ =0.8, $J_{5,6b}$ =14.8 Hz, H-6b), 4.79 (dd, 1H, $J_{4,5}$ =2.8 Hz, $J_{3,4}$ =3.2 Hz, H-4), 4.51 (d, 1H, $J_{2,3}$ =4.0 Hz, H-2), 4.07 (t, 1H, $J_{3,4}$ =3.2 Hz, H-3), 2.50 (br s, 1H, OH). ¹³C NMR: 133.3 (C-5), 119.2 (C-6), 106.2, 105.7 (HC-CCl₃, C-1), 97.6 (HC-CCl₃), 87.8, 83.7, 75.2(C-2, C-3, C-4).

Anal. Calc. for C₈H₉Cl₃O₄: C, 34.88; H, 3.29. Found: C, 34.55; H, 3.34.

2.4 Synthesis of the new glyco-polymer (PSVTEG) (2) from vinyl (hydroxyl) furan monomer (1)

The new copolymer (PSVTEG) (2) from vinyl (hydroxyl) furan monomer (1) (2.4 g, 8.7 mmol) and styrene (1 mL, 8.7 mmol) (1:1 mol monomer rate) were obtained through a conventional free radical polymerization using 2,2-azobisisobutyronitrile (AIBN) (2%, based on the total weight of the monomer) as initiator in 10 mL of toluene at 70 °C in an all glass Schlenk flask under inert atmosphere. After 24 hours, copolymer 2 was obtained with approximately 90% conversion. The resulting polymer was precipitated in methanol and dried under vacuum at 40 °C for overnight. The polymer was then characterized using FTIR and NMR spectroscopy. The synthetic route is presented in Scheme 2. The apparent activation energies for the main degradation stage of the copolymer were calculated from the TG data by using Flynn-Wall-Ozawa (FWO) and Coats-Redfern methods. The activation energies calculated by these methods were found to be 159.0±3 kJ/mol and 159.2±3 kJ/mol, respectively. ¹H NMR (DMSO, 400 MHz): δ 7.05-6.55 (d, 5H, aromatic H), 6.05 (d, 1H, $J_{1,2}$ =4.0 Hz, H-1), 5.40 (s, 1H, HCCl₃), 4.78 (dd, 1H, H-4), 4.52 (d, 1H, H-2), 4.10 (t, 1H, H-3), 2.62 (m, 1H, CH-), 2.50 (br s, 1H, OH), 1.62-1.25 (m, 5H, CH₂-, CH-). ¹³C NMR: 142.0-128.2 (aromatic carbons), 106.2, 105.7 (HC-CCl₃, C-1), 97.6 (HC-CCl₃), 87.8, 83.7, 75.2(C-2, C-3, C-4), 40.4-21.6 (alifatic carbons).

3. Results and Discussion

3.1 Characterization Studies

3.1.1 The FTIR spectra of the monomer 1 and copolymer PSVTEG (2)

The FTIR spectra of compound 1 and copolymer PSVTEG (2) are shown in Figure 1. The peak assignments in the FTIR spectrum of compound 1 are as follows: C-H in CH₃ and C-H in CH₂ at 2925 cm⁻¹; vinyl C=CH₂ at 1505 cm⁻¹; C-O-C peak in the sugar ring at 1162 cm⁻¹; C-Cl peaks of trichloroethylidene protective group at 854 and 823 cm⁻¹. Finally, the absorption band at 3294 cm⁻¹ corresponds to the presence of the C-3 OH group.

The FTIR spectrum of copolymer 2 (Figure 1) is as follows: C-H in CH₃ and C-H in CH₂ at 2800-3000 cm⁻¹; C=C double bond peaks in the benzene ring at 1493 and 1452 cm⁻¹;

C-O-C peak in the sugar ring at 1107 cm⁻¹; C-Cl peaks of trichloroethylidene protective group at 832 and 812 cm⁻¹. Finally, the absorption band at 3440 cm⁻¹ corresponds to the presence of the C-3 OH group. Instead of the vinyl C=CH₂ at 1505 cm⁻¹ peak observed in the FTIR spectrum of new vinyl (hydroxyl) furan monomer (1), the mono substitute benzene ring peak at 698 cm⁻¹ was observed in the FTIR spectrum of the copolymer PSVTEG (2).

3.1.2 The ¹H and ¹³C NMR spectra of the monomer 1 and copolymer PSVTEG (2)

In the ¹H-NMR spectrum of the monomer 1 the anomeric H-1 proton usually appears at a low field and is a very characteristic and distinct signal. Two doublets are observed in this ¹H-NMR spectrum. One is the H-1 doublet at δ 6.05 and another is the H-2 doublet at δ 4.51. The coupling constant between H-1 and H-2 is 4.0 Hz which is typical for an α -D-furanose derivative. Due to the twisted conformation of the furanose rings, the dihedral angle between the H-2 and H-3 protons are usually 90°. Hence, in the ¹H NMR spectrum of compound 1, the coupling constant between H-2 and H-3 is 0 Hz. The H-5 protons give a complex multiplet at δ 5.85. One of the H-6 signals obtained is H-6a which is resolved into add at δ 4.34 with one of the coupling constant between H-6a and H-5 of 16.8 Hz. The another of the coupling constant between H-6a and H-6b of 0.8 Hz and H-6b signal is observed at δ 5.23 with one of the coupling constant between H-5 and H-6b of 14.8 H. The H-4 signals are resolved giving a triplet signal at δ 4.79 with a coupling constant between H-4 and H-5 of 3.2 Hz. The H-3 signals are resolved giving a triplet signal at δ 4.07 with a coupling constant between H-3 and H-4 of 3.2 Hz. The hydroxyl proton is resolved giving a br singlet at δ 2.50. Finally, the trichloroethylidene acetal proton (HCCl₃) gives a signal at δ 5.41. Also, the ¹³C NMR peak performance of the monomer 1 was described and similarly, the expected indications were observed. In the ¹³C NMR spectrum of monomer 1, the peaks at 133.3 and 119.2 ppm (C-5 and C-6) assigned the vinyl carbon. In addition, trichloroethylidene acetal carbon (HC-CCl₃) was observed at 106.2 ppm. ¹³C NMR peak of the sugar moiety for the monomer 1 was observed as predicted from C-1 at 105.7 ppm.

In the ¹H NMR spectrum of the copolymer PSVTEG (2), disappearance of characteristic vinyl peaks for the the monomer is observed. And also, the acetal proton, the

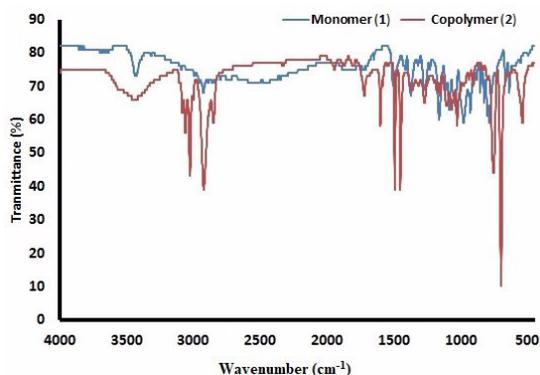


Figure 1. The FTIR spectra of new vinyl (hydroxyl) furan monomer (1) and the copolymer PSVTEG (2).

trichloroethylidene acetal proton (HCCL_2) and other sugar protons give a signal at δ 6.05, 5.40, 4.78-4.10, respectively. Besides, the appearance of the aromatic proton peaks for the styrene are observed as multiplet at δ 7.05 and 6.55 in the ^1H NMR spectrum of the copolymer PSVTEG (2).

In the case of the polymer, it is observed that alkyl group carbon peaks of the copolymer PSVTEG (2) appeared in the range from 40.4 to 21.6 ppm in the ^{13}C NMR spectrum. Therefore, vinyl carbons of glycopolymer shifted to a higher field as a result of increased electron intensity. ^{13}C NMR peaks of the sugar moiety of the copolymer 2 are observed from C-1 to C-4, as predicted. Furthermore, the appearance of the aromatic carbon peaks for the styrene appeared in the range from 142.0 to 128.2 ppm in ^{13}C NMR spectrum of the glycopolymer 2.

3.2 Thermogravimetric analysis of the copolymer PSVTEG (2)

Thermal properties of glycopolymer (PSVTEG) (2) were investigated by TG and DTG under argon atmosphere over a temperature range 30 to 600 °C with a heating rate of 10°C/min. The thermogram of the glycopolymer (PSVTEG) (2) shows two decomposition stages (Figure 2). The thermal decomposition in the first stage is in a weight loss of nearly 10%. The main degrading process involving random scission starts around 350 °C.

According to the literature data, using the TG/DTG-DTA-FTIR analysis, the following releasing gases after pyrolysis could be seen u.a: H_2O , $\text{C}=\text{O}$, CH_4 , C_2H_2 , and $\text{C}_2\text{H}_4\text{O}_2$ ^[61]. The degradation reactions began at the temperature of circa 200 °C, when the thermal condensation between hydroxyl groups of copolymer chains started the formation of ether fragments, and the release of water molecules was obtained. When dehydration was located in the neighborhood of itself, hydroxyl groups in the glycosidic ring cause the formation of the $\text{C}=\text{C}$ bond or degradation of the glycosidic ring. All of aldehyde groups were formed at the same time as terminal groups, while the monosaccharide ring was damaged. The main degradation reactions began at the temperature of circa 350 °C, aromatic rings such as substituted benzene and furan structures with groups such as $-\text{CH}_2-$ or $-\text{CH}_2-\text{O}-\text{CH}_2-$ as main binders between the aromatic rings could be seen^[62].

3.3 Thermal degradation kinetics of the copolymer (PSVTEG) (2)

The glycopolymer (PSVTEG) (2) was heated thermogravimetrically under various heating rates such as 5, 10, 15, and 20 °C/min in a temperature range of 30 to 600 °C to determine their thermal degradation mechanisms and the activation energies. The TG curves obtained for the copolymer is shown in Figure 3 and 4, respectively. The individual degradation behavior of the glycopolymer (PSVTEG) (2) was analogous at all heating rates as seen from these figures. The apparent activation energies and thermal degradation models for the copolymer was estimated by FWO and Coats-Redfern.

The thermal degradation mechanism of the copolymer (PSVTEG) (2) for the main degradation stage is confirmed by comparing the mean activation energy value (E_{FWO})

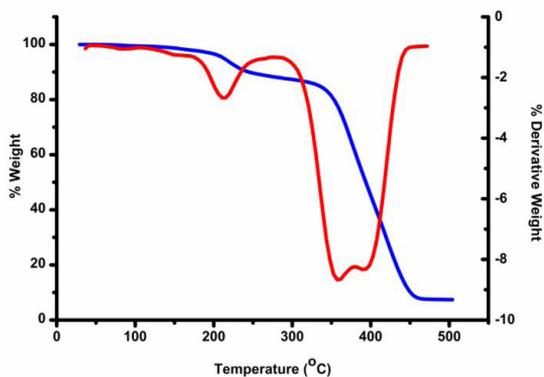


Figure 2. DTG curves of glycopolymer PSVTEG (2).

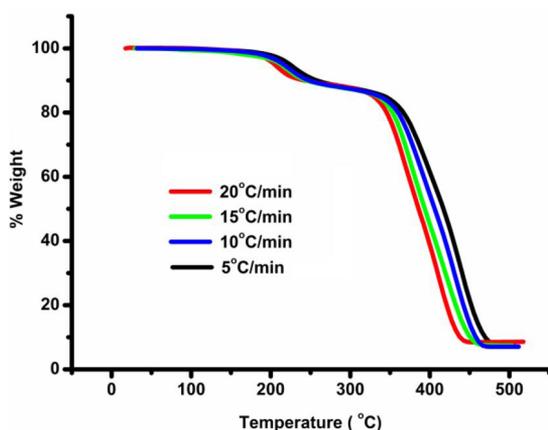


Figure 3. TG curves of glycopolymer PSVTEG (2).

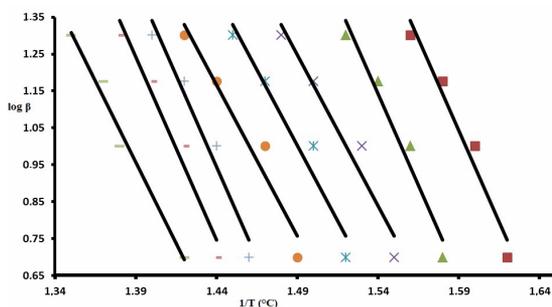


Figure 4. FWO plots for the thermal decomposition of glycopolymer PSVTEG (2) at varying conversion in N_2 .

with those calculated by the Coats-Redfern method for different models. The activation energies and correlations obtained from Coats-Redfern method at different heating rates are represented in Table 1. The E calculated from the F_3 model is nearly the same with E_{FWO} for PSVTEG (2) and found as 159.0 ± 3 kJ/mol leading to a conclusion that the most probable mechanism for the thermal degradation of PSVTEG (2) is the third-order. Therefore, the calculated activation energy indicates that the main degradation stage is a nonspontaneous process (integral form $1/(1-\alpha)^2$ for F_3). In literature, the activation energy value of polystyrene homopolymer and vinyl sugar- carrying copolymer viz.,

Table 1. Algebraic expressions of $f(\alpha)$ and $g(\alpha)$ for the reaction models considered in the present work.

Symbol	Reaction model	$f(\alpha)$	$g(\alpha)$
Sigmoidal curves			
A2	Avrami–Erofeev ($n = 2$) (Nucleation and growth)	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
A3	Avrami–Erofeev ($n = 3$) (Nucleation and growth)	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
A4	Avrami–Erofeev ($n = 4$) (Nucleation and growth)	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$
An	Avrami–Erofeev ($n = n$) (Nucleation and growth)	$n(1-\alpha)[- \ln(1-\alpha)]^{(n-1)/n}$	$[- \ln(1-\alpha)]^{1/n}$
Deceleration curves			
R1	Zero-order (Polanyi–Winger equation) Phase-boundary controlled reaction (one dimensional movement)	1	α
R2	Phase-boundary controlled reaction (contracting area, i.e., bidimensional shape)	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
R3	Phase-boundary controlled reaction (contracting area, i.e., bidimensional shape)	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$
F1	First-order (Mampel) (Random nucleation with two nucleus on the individual particle)	$(1-\alpha)$	$-\ln(1-\alpha)$
F2	Second-order (Random nucleation with two nucleus on the individual particle)	$(1-\alpha)^2$	$1/(1-\alpha)$
F3	Third-order (Random nucleation with two nucleus on the individual particle)	$(1-\alpha)^3$	$1/(1-\alpha)^2$
D1	One-dimensional diffusion	$1/2\alpha$	α^2
D2	Two-dimensional diffusion (bidimensional particle shape) Valensi equation	$1/[- \ln(1-\alpha)]$	$(1-\alpha)\ln(1-\alpha) + \alpha$
D3	Three-dimensional diffusion (tridimensional particle shape) Jander equation	$3(1-\alpha)^{1/3}/2[(1-\alpha)^{-1/3} - 1]$	$[1-(1-\alpha)^{1/3}]^2$
D4	Three-dimensional diffusion (tridimensional particle shape) Ginstling–Brounshtein	$3/2[(1-\alpha)^{-1/3} - 1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

poly(galactomethacrylate-*co*-styrene) (P(gm-*co*-st)) were stated as circa 50 ± 5 kJ/mol and 185 ± 28 kJ/mol, respectively^[63,64]. In addition, Paně et al. have indicated the average activation energy value of a glycopolymer derived from a D-mannose oligomer with maleic backbone and 2-hydroxypropyl acrylate inside as 105.98 kJ/mol by using Flynn–Wall–Ozawa method^[65]. When these values in the literature was compared with the activation energy value of the copolymer PSVTEG (2), it was concluded that the copolymer was a sugar-based styrene copolymer.

3.4 Molecular weight study of the copolymer (PSVTEG) (2)

The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) for glyco-polymer (PSVTEG) (2) was analysed by GPC. The number average molecular weight (M_n), mass average molecular weight (M_w) and polydispersity index (PDI) of glyco-polymer (PSVTEG) (2) were found to be 14000 g/mol, 18900 g/mol and 1.35, respectively.

4. Conclusions

A new carbohydrate-based the copolymer of styrene (2) from vinyl (hydroxyl) furan monomer (1) were synthesized by a conventional free radical polymerization reaction using AIBN as an initiator in toluene. The thermal degradation of the copolymer of styrene (2) from vinyl (hydroxyl) furan monomer (1) under nitrogen atmosphere is a one-stage reaction. The thermal degradation kinetics of the compounds

was evaluated using the Flynn–Wall–Ozawa (FWO) and Coats–Redfern methods. The activation energies calculated by these methods were found to be 159.0 ± 3 kJ/mol and 159.2 ± 3 kJ/mol, respectively. Consequently, the calculated activation energy shows that the main degradation stage is a nonspontaneous process (integral form $1/(1-\alpha)^2$ for F_3).

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