

Synthesis and Thermal Degradation Kinetics of D-(+)-Galactose Containing Polymers

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Abstract: In this study, it is investigated the synthesis and characterizations of polymerizable vinyl sugars. Carbohydrate containing polymers were synthesized via free radical polymerization. Thermal behavior of polymer derivatives was analyzed by using DSC and TG. Molecular weight dispersion of polymer derivatives was also analyzed with GPC. Molecular structures were analyzed by FT-IR and ¹H-NMR spectrophotometer. We found that molecular weight of copolymers could effect to the thermal stability. According to TG data related to the copolymers, molecular weight of polymers increased while the thermal stability decreased. Thermogravimetric analysis of polymers also investigated. The apparent activation energies for thermal degradation of carbohydrate containing polymers were obtained by integral methods (Flynn–Wall–Ozawa, Kissinger–Akahira–Sunose, and Tang).

Keywords: Copolymers, carbohydrates, radical polymerization, thermal properties, kinetics.

Introduction

Large amounts of carbohydrates are commercially available and a substantial part of the surplus of their agricultural production may be spent in this way. One possibility to prepare macromolecules from sugars makes use of the preparation of vinyl sugars and their polymerization. Unlike polysaccharides, such polymers have an all-carbon backbone and pendant saccharide units. They can be tailor-made for many purposes. The polymers are water-soluble unless the sugars still carry protecting groups which make them more hydrophobic. Possible applications can be seen for water-soluble non-ionic polymers, which are hydrophilic due to their large number of hydroxyl groups. The polymers might then find use as thickeners (e. g. in the tertiary oil recovery), as flocculating agents, as polymeric detergents, or for surface modification of standard polymers. They might also be of interest as models for intercellular recognition processes^[1-5]. Crosslinked poly(vinyl saccharides) form water-swallowable gels which have potential as superabsorbers. They can also be used as stable dextran analogues for the immobilization of enzymes and as gel-permeation chromatography (GPC) materials for the separation of water soluble substances. Polymers that still have protecting groups (such as isopropylidene) are interesting polymers of medium polarity.

Many natural polysaccharides possess a complex branched backbone architecture and undoubtedly this feature plays an important part in their biological activity, whether the latter is primarily a physical function or a biochemical one^[6]. Significant research has now been published on various synthetic macromolecules that attempt to mimic glycopolymers^[7-10]. Well-defined synthetic glycopolymers have been prepared by using techniques such as ring-opening metathesis polymerization (ROMP)^[11,12] reversible addition-fragmentation chain transfer (RAFT) polymerization^[13-15], atom transfer radical polymerization (ATRP)^[16-20]

cyanoxyl-mediated free-radical polymerization^[21,22] or 'click chemistry' for the preparation of saccharide terminated dendritic structures^[23,24].

The O-isopropylidene acetal group is a common protecting group extensively used in carbohydrate chemistry for the preparation of valuable building blocks^[25,26]. Especially, acetonation of an aldohexose results in the formation of an O-isopropylidene derivative with a selective unmasked hydroxyl group, depending upon the nature of the sugar.

In this study, a major requirement was to prepare a polymerizable derivative of galactose. Although the copolymerization of polymerizable galactose derivatives with styrene was seen at the literature reports, we could not find any detailed of thermal behaviour of these polymers and so we are worthful to research thermal behaviour of synthesized of polymers. Thermal degradation kinetics of the poly(galactomonomethacrylate) (P(G_aMA)) and poly(galactomethacrylate-co-styrene) (P(gm-co-st)⁵) were also studied to compare their thermal properties. The apparent activation energies for thermal degradation of the polymers were obtained by using Flynn-Wall-Ozawa, KAS and Tang methods.

Kinetic Analysis^[27-29]

Thermogravimetric analysis can be used for determination of degradation kinetic a lot of polymer. In general, the thermal degradation reaction of a solid polymer can be shown as:



where A is the starting material, B_{solid} and C_{gas} are the solid residue and the gas product, respectively.

The kinetic of thermal degradation of polymers is generally expressed by the following typical kinetic equation

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

Where T is the absolute temperature (in K); r is the rate of change conversion or composition per unit time (t) and f(α) is the conversion function (reaction model). The conversion degree (α) was calculated with Equation 2, where mo, mt and mf are the weights of sample before degradation, at time t and after complete degradation, respectively.

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

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

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

where A is the pre-exponential factor, E_a is activation energy and R is the gas constant.⁸⁸

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

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

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

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

Equation 4 is modified as follows:

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

Equation 4 and Equation 6 are the basis for the many equations derived to evaluate thermal analysis data.

Integral Methods

Flynn-Wall-Ozawa method^[28-31]

This method is one of the integral methods that can be determined the activation energy without knowledge of reaction mechanism. Pre-exponential factor (A) and activation energy (E_a) do not depend on degradation fraction, but they depend on the temperature. This method uses Equation 7.

$$\log g(\alpha) = \log(AE_a/R) - \log \beta + \log p(E/RT) \quad (7)$$

Doyle approximation is used and Equation 7 can be obtained.

$$\log \beta = \log(AE_a/R) - \log g(\alpha) - 2.315 - 0.4567(E/RT) \quad (8)$$

the plot of $\log \beta$ versus $1000/T$ should be linear with the slope E_a/R , from which E_a can be obtained.

Kissinger-Akahira-Sunose(KAS) method^[29,30]

The activation energy can be determined by KAS method, using the following equation

$$\ln(\beta/T^2) = \ln AR/E_a g(\alpha) - (E_a/RT) \quad (9)$$

According to this method, the plots of $\ln(\beta/T^2)$ versus $1000/T$ at same α value give straight lines with slope equal to $-E_a/R$.

Tang method^[32,33]

The Tang method is based on the following equation:

$$\ln(\beta/T^{1.894661}) = \ln AE_a/Rg(\alpha) + 3.635041 - 1.894661 \ln E_a - (1.001450E_a/RT) \quad (10)$$

the plot of $\ln(\beta/T^{1.894661})$ versus $1000/T$ can give E_a from slope

Experimental

Materials

All chemicals and solvents used in this study were analytical grade. Main chemicals used in this study were as follow: D-(+)- galactopyranose, G_a , (%98, BDH), zinc chloride (pure exsiccated, Riedel-de Haën), Phosphorus pentoxide (%99.95, Sigma-Aldrich), Phosphoric acid (%85, Merck), acetone (%99, Riedel-de Haën), dichloromethane (%99, Sigma-Aldrich), toluene (%99.5, Riedel-de Haën), styrene (min. %99, Sigma-Aldrich), sodium carbonate (anhydrous %99.5, Merck), magnesium sulfate (anhydrous %99.5, Sigma-Aldrich), diethyl ether (%99.5, Riedel-de Haën), triethylamine (min %99, Sigma-Aldrich), methacryloyl chloride (%97, Fluka), Methanol (%99.9, Elkim), AIBN (%98, Merck).

Measurement and characterization

Fourier-transformed infrared (FT-IR) spectra were recorded with a Perkin-Elmer Spectrum 100 FT-IR spectrometer. ¹H NMR spectra were recorded with a Varian 400 MHz NMR spectrometer in chloroform as solvents at room temperature. The thermal analysis was performed in both N_2 and air (flow rate 100ml/min) with a heating rate of 10 °C/min using a Perkin Elmer TG and Perkin Elmer DSC. All of the products were dried in vacuum oven at 40 °C on 10 mbar pressure before the thermal analyses. Molecular weights were determined by a gel permeation chromatography (GPC) instrument, viscotek GPC max. 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⁻¹ at 30 °C. Both detectors were calibrated with PS standarts having narrow molecular weight distribution data were analyzed using viscotek OmniSEC Omni-01 software.

Synthesis of isopropylidene-protected D-(+)-galactose: pG_a^[34,35]

To a solution of D-(+)-galactopyranose G_a (10 g, 55 mmol) in acetone (200 ml) were added zinc chloride (10.2 g), phosphorus pentoxide (2 g) and phosphoric acid (4 g). The reaction mixture was stirred overnight at room temperature to ensure reaction completion (TLC system, chloroform/methanol/water 70:30:3). The solution was made alkaline by the addition of an aqueous suspension

of sodium carbonate. The inorganic salts formed were then filtered off and washed with acetone. The filtrate and solution were combined and acetone removed by rotary evaporation. The remaining aqueous solution was then extracted with three 150 ml portions of diethyl ether after which the combined organics were dried over magnesium sulfate. After filtration, to remove the hydrated magnesium sulfate, the solution was evaporated to dryness, leaving the protected D-(+)-galactopyranose pGa (quantitative yield) as an oil. ¹H-NMR (CDCl₃ δ:ppm): 1.25-1.30(6H), 1.40-1.45(3H), 1.50-1.55(3H), 2.15-2.20(H), 3.85-3.90(2H), 4.25-4.30(1H), 4.30-4.35(1H), 4.60-4.70(2H), 5.55-5.60(1H).

Synthesis isopropylidene-protected D-(+)-galactosemonomethacrylate: pG_aMA^[36]

To a 0.1 M solution of protected D-(+)-galactopyranose pGa (7.0 g, 26.8 mmol) in anhydrous dichloromethane (DCM) (275 ml) were added triethyl amine (Et₃N) (6.8 g, 67.4 mmol) and a catalytic amount of 4-dimethylaminopyridine (DMAP) (0.350 g, 2.86 mmol) under nitrogen. The reaction mixture was cooled to 0 °C for 1 h and then a 0.5 M solution of methacryloyl chloride (3.37 g, 32.2 mmol, 1.2 eq) in anhydrous DCM (65 ml) was added. The reaction mixture was allowed to reach room temperature and left for 36 h to ensure reaction completion (TLC system, toluene/methanol 9:1). Three 150 ml portions of DCM were added to the mixture, which was then extracted with two 100 ml portions of saturated sodium carbonate and two 100 ml portions of distilled water. The resulting organic phase was dried with magnesium sulfate and the solvent was removed under vacuum to give pG_aMA as a yellow oil (%75 yield). ¹H-NMR (CDCl₃ δ:ppm): 1.25-1.30(6H), 1.40-1.45(3H), 1.50-1.55(3H), 1.85-1.90(3H), 3.80-3.85(1H), 4.05-4.10(1H), 4.25-4.35(2H), 4.60-4.65(2H), 5.50-5.55(1H), 5.60-5.65(1H), 6.10-6.15(1H).

General procedure for free radical polymerizations

The functional monomer pG_aMA with the styrene (1 ml for all experiments) was dissolved in anhydrous toluene (2 ml), followed by the addition of AIBN (typically 0.03 g, ~2 mol% wt styrene). The reaction vessels were sealed and degassed individually with four nitrogen-vacuum purge cycles. The temperature was then set at 70 °C and the polymerizations were accomplished for 22 h. To check for reaction completion, small samples were taken for analysis by FT-IR spectroscopy. After cooling down, the reaction mixtures were added dropwise into methanol to precipitate the polymer product, which was filtered off and vacuum-dried at 40 °C to constant mass. (yield higher than 85%). Also, other polymerization reactions were carried out to obtain different mole ratios of copolymers using the same procedure. ¹H-NMR, P(pG_aMA), (CDCl₃ δ:ppm): 1.25-1.30(6H), 1.40-1.45(3H), 1.50-1.55(3H), 1.85-1.90(3H), 3.80-3.85(1H), 4.05-4.10(1H), 4.25-4.35(2H), 4.60-4.65(2H), 5.60-

5.65(1H). ¹H-NMR, P(pgm-co-st)⁶, (CDCl₃ δ:ppm): 6,60-7.20(6H).

General procedure for the deprotection of (co)polymers

Typically the copolymers (100 mg) were dissolved in THF (2 ml) and then 0.5 ml hydrochloric acid was added to the reaction mixture. After one hour, 0.5 ml distillate water was added dropwise. The reaction mixture was allowed to reach room temperature and left for overnight. The solvent was removed under vacuum. Purification of the product was carried out by washed with water. Over all processes can be seen in Scheme 1.

Results and Discussions

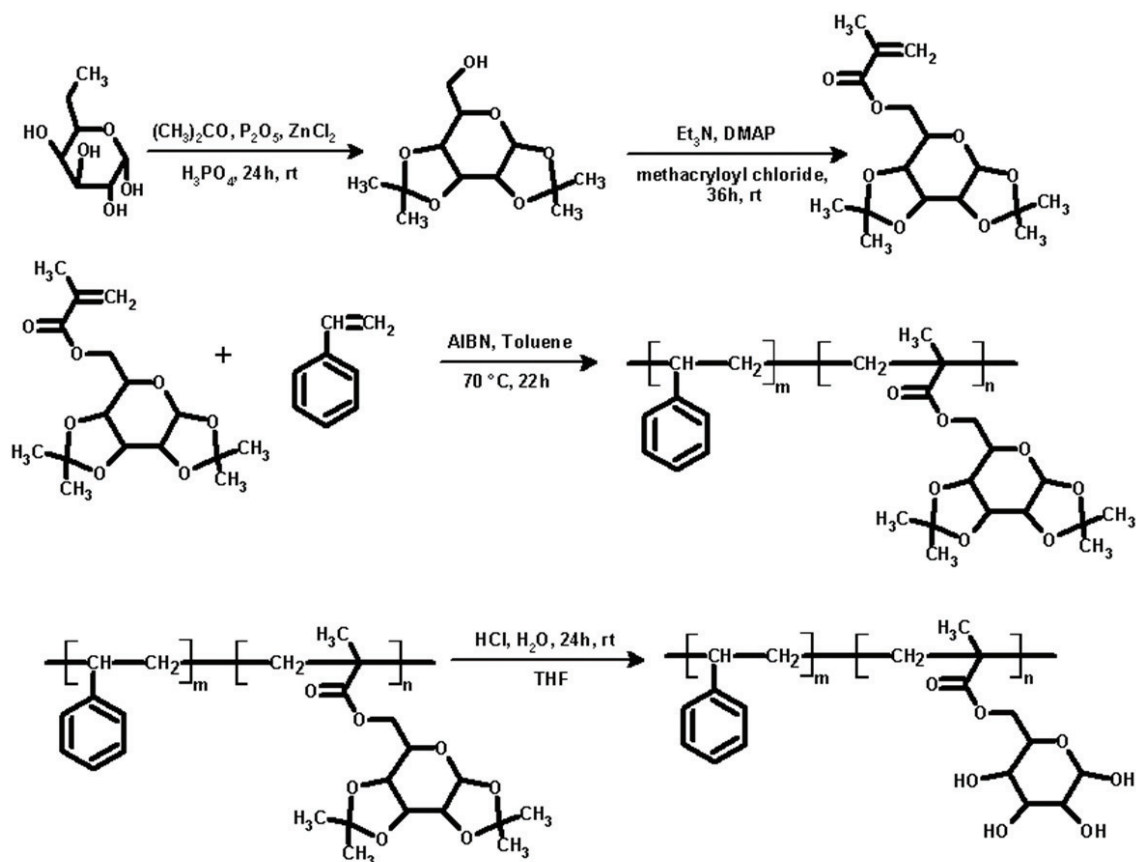
Characterization of synthesis polymers

In our study, we first synthesized pG_a and pG_aMA. Following experiment was carried out for different protected copolymer compositions and homopolymers. Deprotection copolymers and homopolymers was used to obtain P(gm-co-st) copolymers and P(G_aMA) polymers. Chemical structure of both homopolymers and copolymers were identified several techniques which are FT-IR, NMR, GPC, TG and DSC.

Firstly, G_a was reacted with acetone for obtaining protected Ga (pG_a). The FT-IR spectrums of G_a, pG_a, pG_aMA, PS, P(pgm-co-st)⁵, P(gm-co-st)⁵ and P(G_aMA)⁵ are shown in Figure 1. This figure shows that after protection of G_a, the appearance of a broad -OH stretch belong to -CH₂- in Ga is clear at around 3450 cm⁻¹. As well as, this is also supported by the appearance of the -CH- stretching between 2950 and 3000 cm⁻¹ and the C-O stretching are seen between 1000 and 1500 cm⁻¹. Secondly, pGa was reacted with methacryloylchloride to get pG_aMA. The appearance of C=O and C=C stretching of pG_aMA can be seen at around 1716 cm⁻¹ and 1637 cm⁻¹ in the spectra respectively. On the other hand, it is also supported by disappearance of a broad -OH stretch around 3450 cm⁻¹. This shows successful of the synthesis of pG_aMA.

The homopolymers and random copolymers were synthesized using free radical polymerization. The polymerization reactions were performed in toluene. AIBN was used as an initiator. The FT-IR spectra of these homopolymers and copolymers can be seen in Figure 1. Stretching vibrations of ν (C=C) in PS unit are observed around 1800-1900 cm⁻¹. CH stretching of aromatic ring is observed at around 3000 cm⁻¹ for PS and copolymers. The bands around 1490 cm⁻¹ may be also attributed to stretching vibrations of the carbons in the aromatic rings. Otherwise, when we look at the spectrum in Figure 1, it can be seen disappearance of C=C stretch at around 1637 cm⁻¹ for P(pG_aMA) and copolymer. According to data obtained from FT-IR spectrum, it is clear that success of the polymerization.

Figure 1 also shows the comparison between the protected polymers (P(pgm-co-st)⁶) and deprotected polymers (P(gm-co-st)⁶) using their FT-IR spectra. After deprotection of P(pgm-co-st)⁶, the appearance of a broad -OH stretch is clear at around 3450 cm⁻¹.



Scheme 1. Synthesis of D-(+)-Galactose Containing Polymers.

We have also supported these results by ^1H NMR. Figure 2 is belong to the ^1H NMR spectrum of pG_a , pG_aMA , $\text{P}(\text{pG}_a\text{MA})$. From the ^1H NMR spectrum of pG_a , it can be seen that the $-\text{CH}_3$, $-\text{OH}$, $-\text{CH}_2$ and galactose signals. After reaction of pG_a with methacryloyl chloride, two new signals were observed. One of them is a singlet at 1.95 ppm, this signal assigned to $-\text{C}=\text{C}-\text{CH}_3$ protons. The second signals are assigned to $-\text{C}=\text{CH}_2-$ protons which are Ha and Hb. Ha is observed at 5.5 ppm and Hb signal is observed at 6.15 ppm. The Figure 2 also shows NMR spectrum of $\text{P}(\text{pG}_a\text{MA})$. $-\text{C}=\text{CH}_2-$ protons at 5.5 ppm - 6.15 ppm are disappeared after polymerization of pG_aMA . From the ^1H NMR spectrum of $\text{P}(\text{pG}_a\text{MA})$, it can be seen that the aromatic CH, galactose and CH_2- signals. The signals of galactose protons are observed at between 4.25-5.5 ppm. CH_2- signals are seen at between 1.5-2.25 ppm. The Figure 3 is belong to an example NMR spectrum of deprotected copolymer ($\text{p}(\text{gm-co-st})^*$). It shows the appearance of the $-\text{OH}$ signal at 3.75 ppm. According to data obtained from NMR spectrum (Figure 3), it is clear that success of the deprotection of polymer. Similar results are also obtained for other copolymers.

Molecular weights of the synthesized polymers are shown in Table 1. According to these results, molecular weight of PS is lower than the others. Molecular weight of $\text{P}(\text{G}_a\text{MA})$ is higher than PS. When mole feed ratio of sugar in the copolymer composition ($\text{p}(\text{gm-co-st})^*$) is

raised, molecular weight of polymer increases. Reason of this increasing may be rising of methacrylate group in the copolymer composition. Polydispersity (PDI) ratios of polymers give similar results for all polymers.

TG measurements were obtained to study the thermal behavior and thermal stability of the prepared PS, $\text{P}(\text{G}_a\text{MA})$ and carbohydrate containing copolymers. TG curves of the polymers are shown in Figure 4. TG thermograms under N_2 atmosphere revealed that polystyrene degradation takes place in two stages the first being at a temperature around 180 °C that corresponds to a very small mass loss about 4%. The second occurs at about 360 °C that corresponds to mass loss about 100% and it is the main degradation stage^[37]. TG curves of copolymers are similar to PS curves but when mole fraction of sugar in the copolymer is enhanced, TG curves of copolymers ($\text{p}(\text{gm-co-st})^*$) start to neat $\text{P}(\text{G}_a\text{MA})$ curve. According to data obtained from TG studies, it is clear that char yield of the copolymers is enhanced when compared with PS.

Glass temperature of polymers is also investigated by DSC. In the DSC curves, (Figure 5) the glass transitions of the PS, $\text{P}(\text{G}_a\text{MA})$ and copolymer compositions are detected between 95 °C and 128 °C. These values are ranged in Table 2. T_g of PS was found to be 95 °C and the T_g of $\text{P}(\text{G}_a\text{MA})$ was found to be 128 °C. T_g values of copolymer compositions was also obtained to between 95 °C and 128 °C as expected. When the mole fraction of

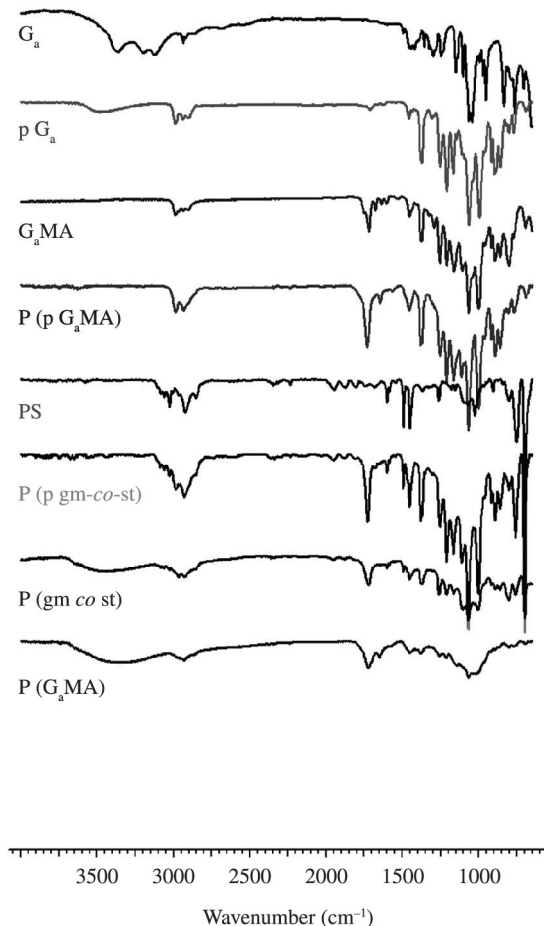


Figure 1. Comparison of FT-IR spectra of G_a , pG_a , pG_aMA , PS, $P(pG_aMA)$, $P(pgm-co-st)^5$, $P(gm-co-st)^5$ and $P(G_aMA)^5$.

sugar was enhanced at the copolymer composition, the T_g values of copolymers regularly increased.

Thermal Degradation Study

Figure 6 shows the respective TG and DTG curves of for $P(G_aMA)$ and $P(G_aMA-co-st)$ under N_2 atmosphere over a temperature range 30 to 600 °C with heating rate of 10 °C min⁻¹. The TG thermogram of $P(G_aMA)$ shows that homopolymer includes three decomposition stages. The T_{max} for the first, second, and third stages are about 180, 368 and 554 °C, respectively. As far as thermal decomposition of $P(G_aMA-co-st)^5$ is concerned, two main decomposition stage is observed. First one appears to begin around 265 °C and stop around 388 °C with maximum rate at 363 °C for heating rate 10 °Cmin⁻¹. Second one appears to begin around 390 °C and stop around 468 °C with maximum rate at 402 °C for heating rate 10 °Cmin⁻¹. There are also two small peaks which can be seen between 100 °C and 300 °C for $P(G_aMA-co-st)^5$ in the thermogram. The first and second decomposition stages may due to degradation from the MMA in the copolymer backbone. The PMMA obtained by radical polymerization may contain some head to head (H-H) linkages and some early decompositions which occur around 110-150 °C is due to breakage at these linkages

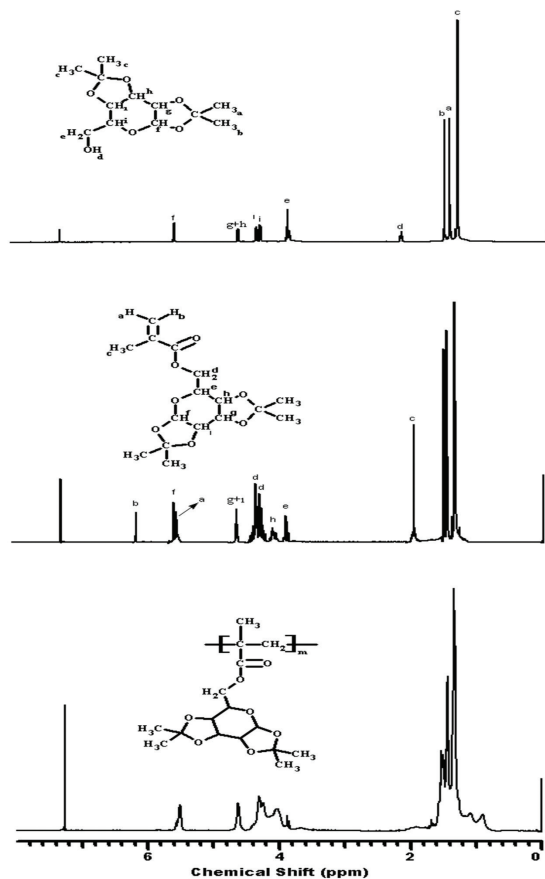


Figure 2. ¹H-NMR spectra of pG_a , pG_aMA , $P(pG_aMA)$.

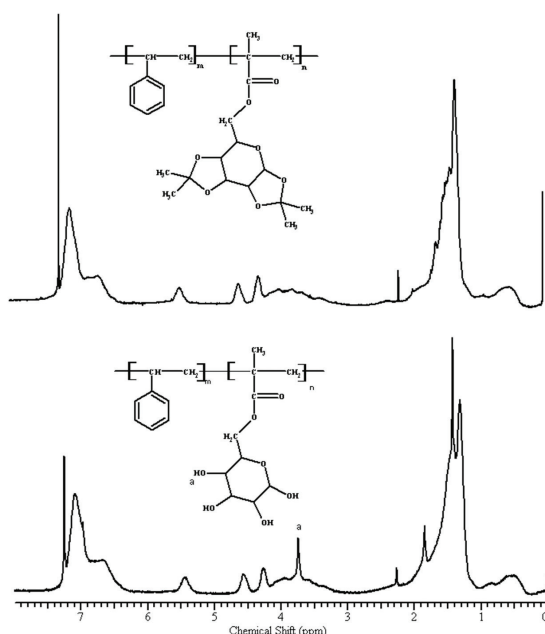


Figure 3. ¹H-NMR spectra of $P(pgm-co-st)^5$ and $P(gm-co-st)^5$.

Table 1. Mole feed ratio and GPC results of synthesized polymers.

Experiment	Composition (mole feed ratio)		Yield %	GPC analysis		
	pG _a MA	Styrene		M _w (gmol ⁻¹)	M _n (gmol ⁻¹)	PDI
PS	-	8.6×10 ⁻³	60	9500	6400	1.49
P(G _a MA)	1.5×10 ⁻³	-	58	11300	7300	1.54
P(gm-co-st) ¹	0.7×10 ⁻³	8.6×10 ⁻³	64	11400	7500	1.5
P(gm-co-st) ²	1.4×10 ⁻³	8.6×10 ⁻³	65	11700	7700	1.51
P(gm-co-st) ³	2.8×10 ⁻³	8.6×10 ⁻³	62	13200	8200	1.62
P(gm-co-st) ⁴	4.3×10 ⁻³	8.6×10 ⁻³	63	14400	8700	1.65

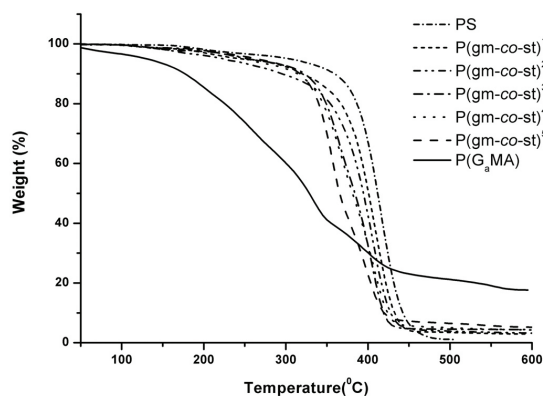


Figure 4. Comparison of TG curves of synthesized polymers.

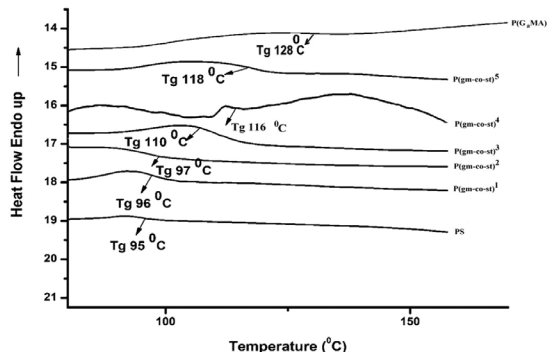


Figure 5. DSC curves for the studied homopolymers and copolymers.

Table 2. The glass transitions of synthesized homopolymers and copolymers.

Experiments	Mole ratio (sugar monomer/styrene)	T _g (°C)
PS	-	95
P(G _a MA)	-	128
P(gm-co-st) ¹	1/12	96
P(gm-co-st) ²	1/6	97
P(gm-co-st) ³	1/3	110
P(gm-co-st) ⁴	1/2	115
P(gm-co-st) ⁵	1/1	118

as the bond dissociation energy of such bonds is less than the C-C bonds mainly due to steric and inductive effects of vicinal ester groups. The second degradation stage which occurs around 230-280 °C seems due to the

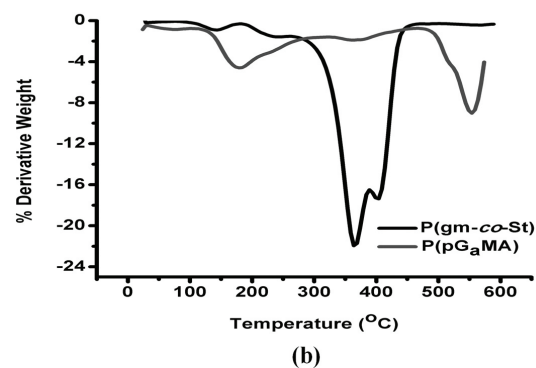
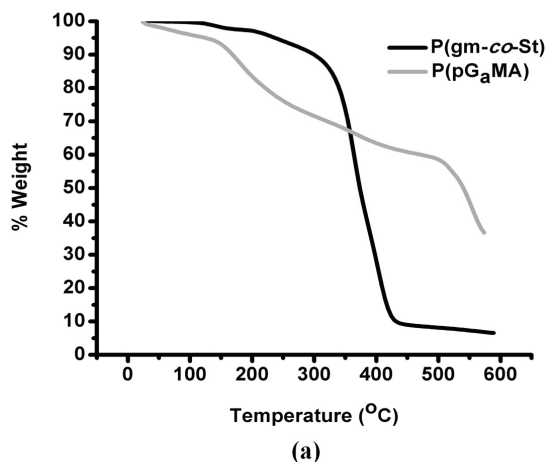


Figure 6. a-b: Typical TG and DTG curves for P(G_aMA-co-st)⁵ and P(G_aMA) samples in N₂ atmosphere at heating rate of 10 °C/min.

unsaturated chain ends resulting from the termination by disproportionation^[38]. When compared to P(G_aMA), P(G_aMA-co-st) is stable up to 400 °C but this situation reverses above 400 °C.

Thermal degradation kinetics of P(gm-co-st)⁵ and P(G_aMA)

To estimate the apparent activation energies of P(G_aMA) and P(G_aMA-co-st)⁵, the TG measurement of the polymers were performed under various heating rates 5, 10, 15, and 20 °C/min in the range 30 to 600 °C. When compared to all copolymers, P(G_aMA-co-st)⁵ is chosen for thermal degradation kinetic analysis because it is more shifted to PS. The decomposition behavior at all heating rates of the polymers were analogous to each other at

Table 3. The degradation activation energies of P(G_aMA-co-st) calculated by Flynn–Wall–Ozawa, TANG, and KAS methods.

α	Flynn-Wall-Ozawa		TANG		KAS	
	first stage					
	E(kJ/mol)	r ²	E(kJ/mol)	r ²	E(kJ/mol)	r ²
0.1	360	0.960	322	0.990	341	0.950
0.2	251	0.950	250	0.950	230	0.940
0.3	251	0.950	250	0.950	230	0.940
0.4	251	0.950	250	0.950	230	0.940
0.5	179	0.990	165	0.900	144	0.970
0.6	179	0.990	160	0.800	139	0.940
Mean	246±23		233±18		219±24	
second stage						
0.7	213	0.990	199	0.890	177	0.940
0.8	218	0.990	182	0.950	160	0.940
0.9	123	0.950	181	0.950	186	0.950
Mean	185±28		187±11		174±12	

Table 4. The degradation activation energies of P(G_aMA) calculated by Flynn–Wall–Ozawa, TANG, and KAS methods.

α	Flynn-Wall-Ozawa		TANG		KAS	
	first stage					
	E(kJ/mol)	r ²	E(kJ/mol)	r ²	E(kJ/mol)	r ²
0.1	101	0.990	107	0.990	92	0.950
0.2	76	0.980	83	0.960	67	0.950
Mean	89±12		95±12		80±13	
second stage						
0.3	260	0.970	241	0.950	261	0.950
0.4	361	0.960	319	0.990	344	0.960
Mean	310±51		280±39		303±41	
third stage						
0.5	362	0.960	345	0.950	319	0.990
0.6	361	0.960	344	0.960	318	0.990
Mean	361±1		344±1		318±1	

different heating rates. The apparent activation energies for thermal degradation of polymers were obtained differential (Kissenger) and Integral methods (Flynn–Wall–Ozawa, Kissenger-Akahira- Sunose(KAS)). These methods are most widely used of the integral methods that can be determined the activation energy without knowledge of reaction mechanism. Pre-exponential factor (A) and activation energy (E_a) do not depend on degradation fraction, but they depend on the temperature. The apparent activation energies (E_a) of the polymers were estimated by Flynn–Wall–Ozawa, TANG, and KAS. The calculated values are shown in Table 3 and Table 4. Flynn–Wall–Ozawa, TANG, and KAS methods were first employed to analyze the TG data of P(G_aMA) and P(G_aMA-co-st)⁵ because they were independent of any thermal degradation mechanism.

Plotting log β and 1000/T as a function of conversation according to the Flynn-Wall- Ozawa method is calculated for P(G_aMA) and P(G_aMA-co-st)⁵. The mean value activation energies obtained by Tang method were calculated from the slope of the ln (β/T^{1.894661}) versus 1000/T as 95±12 kJ/mol (first stage), 280±39 kJ/mol (second stage) and 344±1kJ/mol (third stage) for P(G_aMA)

and they have found 233±18 kJ/mol (first stage) and 187±11 kJ/mol (second stage) for P(G_aMA-co-st). Finally, KAS method is based on Equation 9 and requires several thermograms (at least four) at different heating rates. The values of activation energies were determined from plots of ln(β/T²) versus 1000/T at same a value. The Table 3 and Table 4 summarize the activation energies of all stage obtained by the Flynn-Wall-Ozawa, TANG and KAS methods for two polymers.

Conclusion

In conclusion, molecular weight of copolymers could affect to the thermal stability. According to TG data related to the copolymers, molecular weight of polymers increased while the thermal stability decreased. The reason can be lower thermal stability of galactose. DSC curves showed us that when mole feed ratio of sugar was increased the glass transition temperature was also increased. T_g values of copolymer composition were seen between P(G_aMA) and PS. The thermal degradations of P(G_aMA) and P(G_aMA-co-st)⁵ were evaluated by using Flynn–Wall–Ozawa, KAS and Tang methods. When the thermal stabilities of P(G_aMA) and P(G_aMA-co-st) are

compared, the calculated activation energies indicate that P(G_aMA) is thermally more stable than P(G_aMA-co-st)⁵.

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