

Theoretical models for determination of weight percent of PHCS-g-PLLA copolymer using experimental data

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Abstract

The amphiphilic graft copolymer using chitosan (CS) as hydrophilic segment and poly (*L*-lactic acid) (PLLA) as hydrophobic segment, was prepared through a protection-graft-deprotection route. A simple and convenient procedure for chemo selectively protecting the amino groups of CS was developed to provide *N*-phthaloyl-chitosan (PHCS) that is indispensable as a soluble *N*-protected precursor for further controlled modification reaction of CS. The weight percent PHCS-g-PLLA copolymer was determined by the theoretical models based on experimental data. Low error regression in new models was monitored.

Keywords: Chitosan, PHCS-g-PLLA, CS-g-PLLA, graft copolymer

Introduction

Chitosan is a polysaccharide comprising of physicochemical (polycationic, reactive OH and copolymers of glucosamine and *N*-acetyl NH₂ groups) properties, which makes chitosan an glucosamine. Chitosan is the deacetylated excellent material for the biomedical applications derivative of chitin, which is one of the most [2,3]. Considering the unique structure of abundant natural polysaccharides containing chitosan, it is important to maintain the nitrogen [1]. Chitosan has many biological aminosaccharide unit for various specific (bioactive, biocompatible, biodegradable) and functions including biological activities and

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cationic polymer properties [4]. Grafting with synthetic polymers has been explored as a novel hybrid materials of chitosan. A simple and convenient procedure for chemo selectively protecting the amino groups of chitosan has been interesting alternative method for developing developed to provide *N*-phthaluylchitosan that is indispensable as a soluble *N*-protected precursor for further controlled modification reaction of chitosan [5,6]. Poly (*L*-lactic acid) is completely biodegradable and well biocompatible aliphatic polyester [7]. Poly (*L*-lactic acid) has many potential applications in packaging and consumer goods due to excellent mechanical properties, transparency, compatibility and biosafety [8]. There are two ways to synthesize PLLA, ring-opening polymerization and direct polycondensation. Direct melt polycondensation can simplify the synthetic process and reduce the cost of PLLA [9]. The low molecular weight PLLA synthesized by direct melt polycondensation has reactive functional groups such as hydroxyl and carboxyl group, and its molecular weight can be improved through chain extension [10-12]. In this paper, PLLA with viscosity average molecular weight (M_v) of 7.6×10^3 was prepared. PLLA promises to combine chitosan to produce a new biosynthetic polymer hybrid applicable for a variety of purposes. In this article, the hydrophobic PLLA macro monomer was grafted onto the hydrophilic chitosan regions

selectively at the hydroxyl group through a protection-graft-deprotection route [13-15].

Experimental

IR spectra of the compounds were obtained on a Shimadzu IR-435 spectrometer using a KBr disk. The ^1H nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker AQS 400 Advance instrument at 300 MHz in dimethyl sulfoxide (DMSO- d_6) using tetramethylsilane as an internal standard. All the products are known compounds and are characterized by comparing the FTIR, ^1H NMR data.

General procedure preparation phthaloylation of chitosan

Solution of phthalic anhydride in *N,N*-dimethylformamide (DMF) containing 5 % (v/v) water was added deacetylated CS, and the mixture was heated in nitrogen at 120 °C with stirring. After 8 h of reaction, the resultant was cooled at room temperature and poured into ice water. The precipitate washed with methanol for 1h and dried (at 40 °C) to give *N*- phthaloyl chitosan (PHCS).

Preparation synthesis of PLLA

Fifty milliliters solution of 85 wt% aqueous solution *L*-lactic acid (LLA) was dehydrated at 150 °C under the atmospheric pressure for 4 h and then under a reduced pressure of 10 KPa for another 4 h. The above treated solution was heated up to 200 °C under a magneto electric stirring. The

pressure was reduced subsequently stepwise to 300 Pa, at which the reaction continued for 12 h. At the end of the reaction, the product was dissolved in chloroform and subsequently precipitated in ethanol. The resultant were filtered and dried under vacuum for 72 h.

Preparation of graft copolymers

Step 1: The per polymers were prepared by dropping TDI into PLLA solution at the NCO/OH ratio of 2:1 (mol/mol). The reaction in DMF was performed under N₂ at 60 °C for 30 min.

Step 2: Vacuum dried PHCS was dissolved in anhydrous DMF, and then added into per polymers solution. The reaction continued with stirring at different temperature (90 °C) for different time (1) h under a nitrogen atmosphere. The obtained product was poured in to ice water and separated by filtration. The unreacted was removed by Soxhlet, extraction with acetone for 24 h.

Consequently, transmission copolymers, theoretical weight (W₄) and weight percent theoretical (G%) PHCS-g-PLLA copolymer are calculated from initial weight copolymers (W₁). The graft percent (G %) was calculated as follows: $G\% = (W_g - W_i) / W_i \times 100$ Where W_g and W_i are the weight of graft copolymers and PHCS, respectively, there are recorded in Table 1 and Table 2.

Deportation of the graft copolymers

CS-g-PLLA amphiphilic copolymer is prepared from effect hydrazine monohydrate on the PHCS-g-PLLA copolymer.

Results and discussion

Effect of temperature on percentage of PLLA-g-PHCS copolymer under the terms of time 3 h and PLLA/PHCS feed ratio 4:1 (w/w) was investigated.

Table 1. The graft percent and graft weight relative to temperature

G ₂ % ^f	w ₄ ^e (g)	G ₁ % ^d	w ₃ ^c (g)	w ₂ ^b (g)	w ₁ ^a (g)	T(°C)
271	1.3874	223	1.2074	1.7846	2.0507	70
284	1.4373	237	1.2614	1.6543	1.8850	80
320	1.5683	257	1.3330	1.7221	2.0261	90
323	1.5854	260	1.3475	1.7623	2.0734	100

^aThe weight of initial precipitate copolymer; ^bthe weight of copolymer before extraction.

^cThe weight of copolymer after extraction. ^dThe weight percent experimental copolymer.

^eThe weight of computed copolymer after extraction. ^fThe weight percent theoretical copolymer

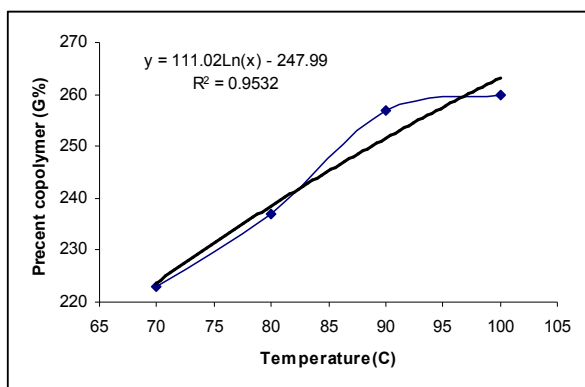


Figure 1. Logarithmic graph theoretical percent of PHCS-g-PLLA copolymer according to the temperature

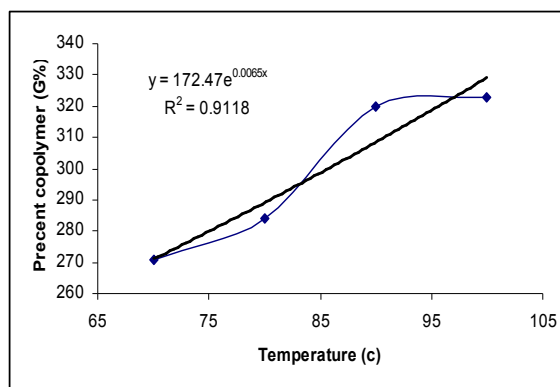


Figure 4. Exponential graph empirical percent of PHCS-g-PLLA copolymer according to the temperature

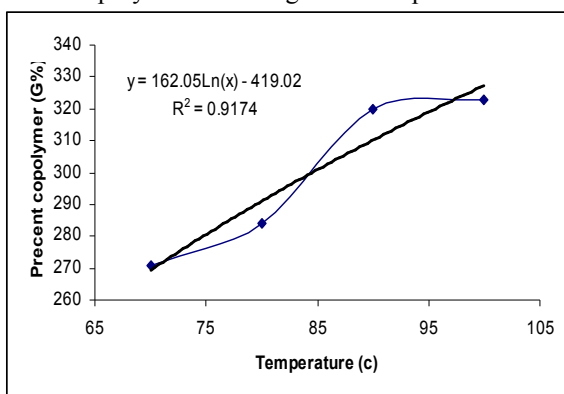


Figure 2. Logarithmic graph empirical percent of PHCS-g-PLLA copolymer according to the temperature

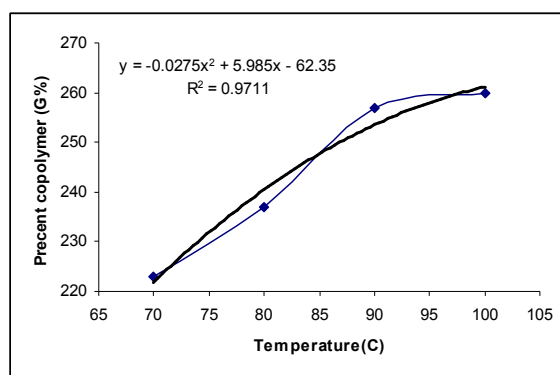


Figure 5. Quadratic graph theoretical percent of PHCS-g-PLLA copolymer according to the temperature

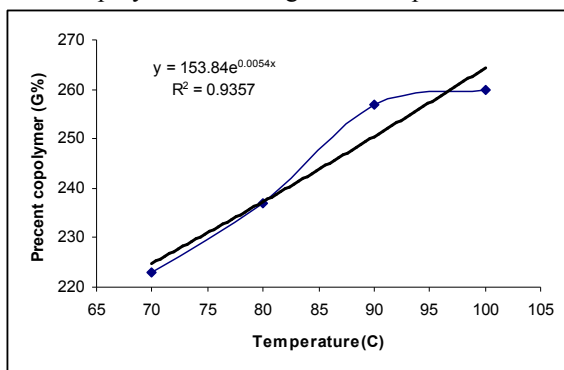


Figure 3. Exponential graph theoretical percent of PHCS-g-PLLA copolymer according to the temperature

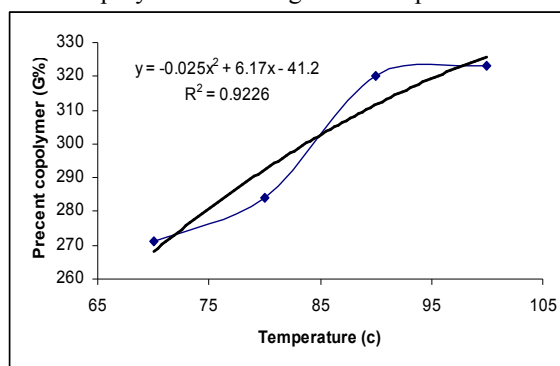


Figure 6. Quadratic graph empirical percent of PHCS-g-PLLA copolymer according to the temperature

Table 2. The regression coefficients equations and error percent

Equation	R(theoretical)	R(experimental)	Error percent
Logarithmic	0.9174	0.9532	3.90
Exponential	0.9118	0.9357	2.62
Quadratic	0.9225	0.9711	5.27

Respect to the figures (Figures 1-6) and table (2) empirical equations (Table 3), and the equation is determined by the regression error theoretical for innovational are used for determining weight and experimental quadratics is less than other percent PLLA-g-PHCS copolymer. equations, therefore, the integration of theory and

Table 3. The coefficients quadratics

Equation	A	b	C
Theoretical	-0.0250	6.1700	-41.2000
Experimental	-0.0275	5.9850	-62.3500
Innovation	-0.0263	6.0775	-51.7750

Innovation model weight percent PHCS-g- PLLA copolymer that is shown in equation 1. (Figure7).

In the model proposed, innovation is temperature(x) and graft percent PHCS-g- PLLA(y).

$$y = -0.0066x^3 + 1.6525x^2 - 135.2685x + 3876.5$$

$$R=1.00 \quad (\text{eq. 1})$$

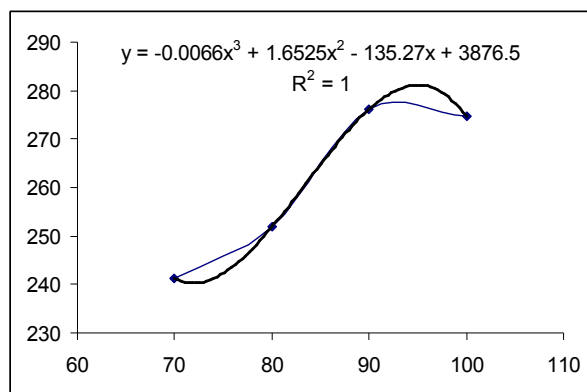


Figure 7. Quadratic graph theoretical weight percent PHCS-g-PLLA copolymer

Effect of time on percentage of PLLA-g-PHCS copolymer under the terms of temperature 90 °C and PLLA/PHCS feed ratio 4:1 (w/w) was investigated.

Table 4. The graft percent and graft weight relative to time

$G_2\%^f$	w_4^e (g)	$G_1\%^d$	w_3^c (g)	w_2^b (g)	w_1^a (g)	t(h)
214	1.1756	165	0.9919	1.6974	2.0118	1
264	1.3647	213	1.1716	1.7887	2.0835	3
319	1.5685	262	1.3550	1.7010	2.6680	7
325	1.5908	275	1.4036	1.8701	2.1195	9

^aThe weight of initial precipitate copolymer.

^bThe weight of copolymer before extraction.

^cThe weight of copolymer after extraction.

^dThe weight percent experimental copolymer.

^eThe weight of computed copolymer after extraction.

^fThe weight percent theoretical copolymer.

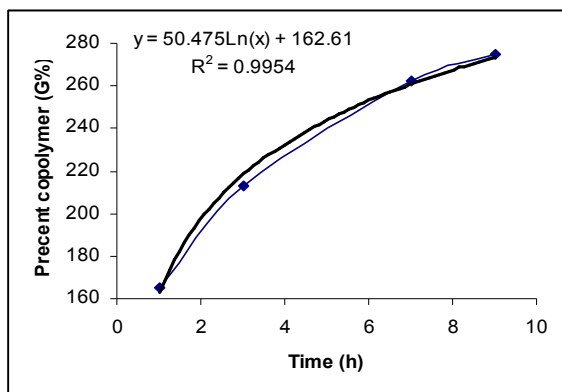


Figure 8. Logarithmic graph theoretical percent of PHCS-g-PLLA copolymer according to the time.

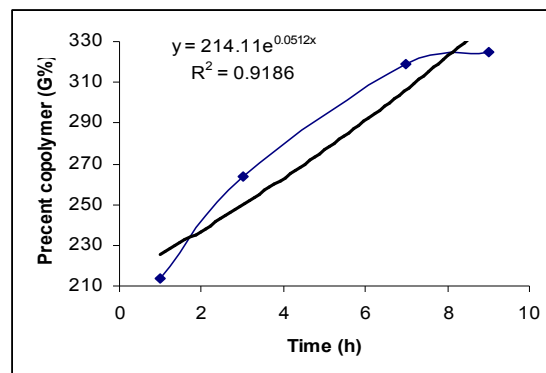


Figure 10. Exponential graph theoretical percent of PHCS-g-PLLA copolymer according to the time

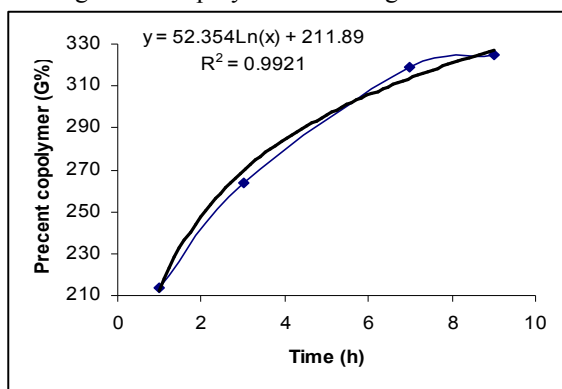


Figure 9. Logarithmic graph empirical percent of PHCS-g-PLLA copolymer according to the time.

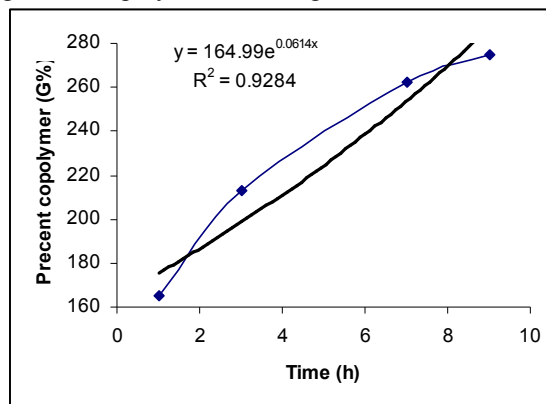


Figure 11. Exponential graph empirical percent of PHCS-g-PLLA copolymer according to the time.

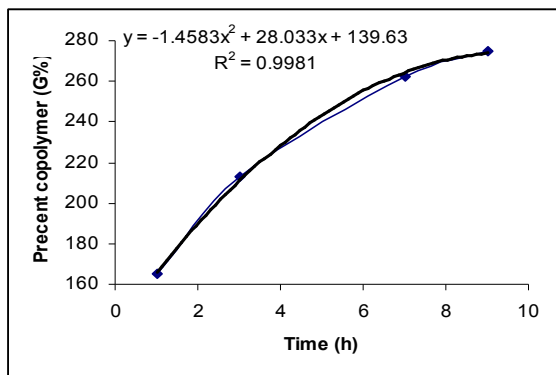


Figure 12. Quadratic graph theoretical percent of PHCS-g-PLLA copolymer according to the time.

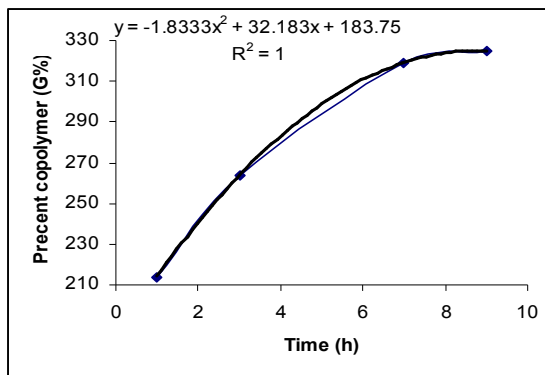


Figure 13. Quadratic graph empirical percent of PHCS-g-PLLA copolymer according to the time

Table 5. The regression degree equations and error percent

Equation	R(theoretical)	R(experimental)	Error percent
Logarithmic	0.9921	0.9954	0.33
Exponential	0.9186	0.9284	1.07
Quadratic	1.0000	0.9981	0.19

Respect to the Figures 8-13 and Table 5 is determined by the regression error theoretical and experimental quadratics is less than other equations, therefore, the integration of theory and

empirical equations (Table 6), and the equation for innovational is used for determining weight percent PLLA-g-PHCS copolymer.

Table 6. The coefficients quadratics

Equation	A	b	c
Theoretical	-1.833	32.183	183.750
Experimental	-1.458	28.033	139.600
Innovational	-1.645	30.105	161.650

Innovation model weight percent PHCS-g-PLLA copolymer that is shown in equation 2.

$$y = -1.645 x^2 + 30.105 x + 161.650 \quad R=1.00$$

(eq. 2)

In the model proposed, innovation is time(x) and graft percent PHCS-g-PLLA(y).

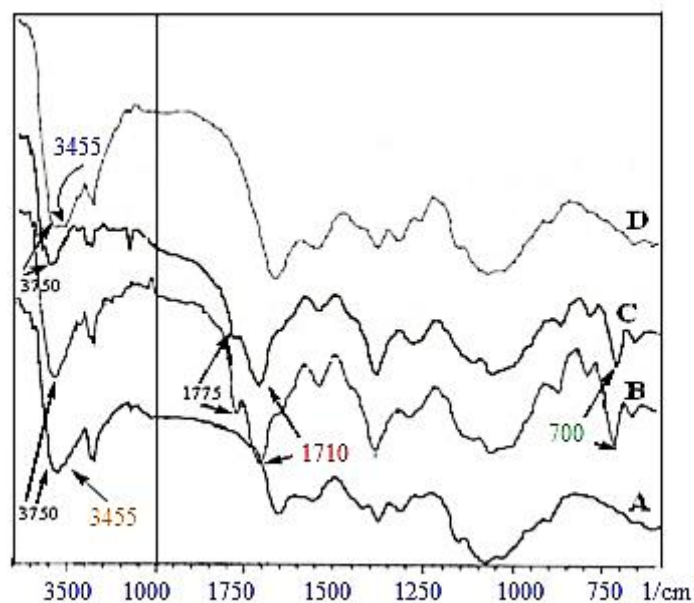


Figure 14. (A), (B), (C) & (D) are FT-IR spectra of CS, PHCS, and PHCS-g-PLLA&CS-g-PLLA respectively.

Figure 14 depicts the FT-IR spectra of CS, PHCS, PHCS-g-PLLA and CS-g-PLLA. The FT-IR Spectra of CS show some characteristic absorption bonds at about 3455 and 3750 cm^{-1} ($\nu_{\text{N-H}}$ and $\nu_{\text{O-H}}$), 1060 cm^{-1} ($\nu_{\text{C-O-C}}$) and 890 cm^{-1} (ν_{NH_2}). Compared with the spectrum of CS, the additional existence of phenyl groups in the spectrum of PHCS was evidenced by peaks at about 1710 and 1775 cm^{-1} , referring to the carbonyl anhydride, and 700 cm^{-1} ($\gamma_{\text{arom.ring}}$). Compared with the spectrum of PHCS, new peaks at about 1635 (ν_{CONH}) and 1538 and 1758 cm^{-1} come out in the spectrum of PHCS-g-PLLA, which indicates the formation of amide ester

linkage (-OCONH-) and the ester groups of PLLA branches. In spectrums PHCS and PHCS-g-PLLA, the peak about 3455 cm^{-1} ($\nu_{\text{N-H}}$) is disappeared. After the deportation of phthaloyl groups in PHCS-g-PLLA, in spectrum of CS-g-PLLA, the peaks at 1710 and 1775 cm^{-1} are almost disappeared that indicate the carbonyl anhydride is deleted whereas the peaks at 1538 and 1758 cm^{-1} still exist in the final grafted product and again the peak about 3455 cm^{-1} ($\nu_{\text{N-H}}$) has been seen. As a result, it can be concluded that the final product was obviously a titled graft copolymer of chitosan and PLLA.

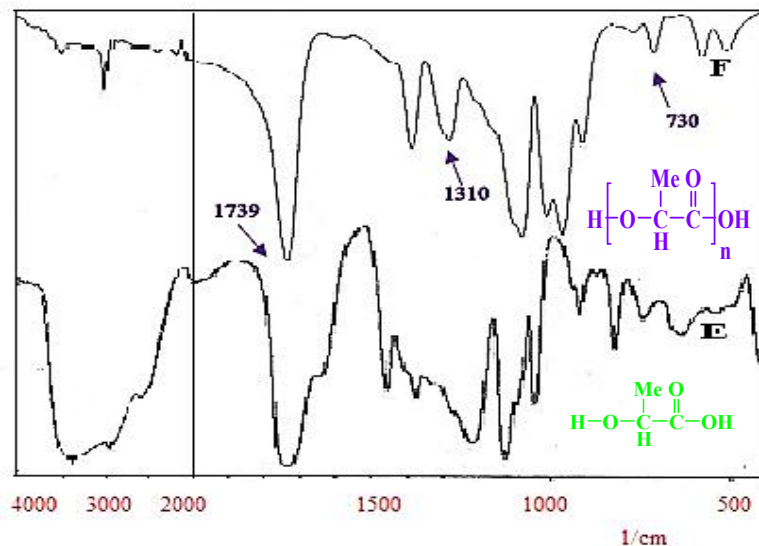


Figure 15. (E) & (F) are IR spectra of LLA and FT-IR spectra of PLLA respectively.

As indicated in FT-IR (F) and IR (E) (Figure.15), this constituency had completely fit them together, and only board peak in spectrum (E) is related to OH factors of acid. Moreover, alcohol in the monomer cannot be seen in spectrum (F); for this reason, water molecules are removed and we have the synthesis of PLLA. ¹H-NMR spectra of CS-g-PLLA copolymer are shown in Figure 16.

The spectrum ¹H-NMR (DMSO δ ppm) CS-g-PLLA is represented: Yellow solid oil, FT-IR (KBr): 3450cm⁻¹ (-NH), 1710 cm⁻¹ (stretching C=O); ¹H-NMR (FT-400 MHz, DMSO): δ; 2.0 (d, 2H, a), 2.8 (t, 6H, b), 3.1 (d, 4H, c), 4.0-5.2 (m, 10H, d), 7.3-7.8(s, 6H, e, f), 8.5 (d, 1H, g), 9.4 (s, 1H, i), 10.7 (s, 1H, j).

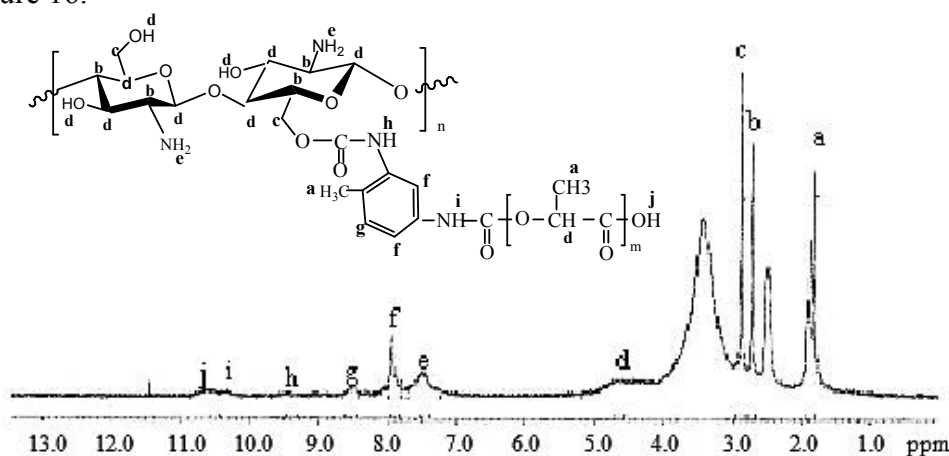


Figure 16. ¹H-NMR spectra of CS-g-PLLA copolymer

Conclusion

Weight percent of PLLA-g-PHCS copolymer without using test models of innovation in the bases set temperature (70-100) °C and time (1-9) h, can be calculated by equations 1 and 2.

We obtained different weight percent (W%) graft copolymer of PLLA-g-PHCS in width of temperatures at 100 °C by theoretical models and helped to anticipate and determinate weight percent macromolecule.

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