CHAPTER IV
POLYSTYRENE GRAFTED WITH BIOCOMPATIBLE POLYMER

ABSTRACT

Polystyrene, densely grafted with poly(DL-lactide), poly(ε-caprolactone) or poly(ε-caprolactam) in the benzene ring; i.e. PS-g-PLA, PS-g-PCL, and PS-g-Nylon6 respectively, was synthesized by a "grafting-from" method using polystyrene-hydroxylated precursors as macroinitiators for ring-opening polymerization of DL-lactide, ε-caprolactone, and ε-caprolactam. The wt% monomer feed ratios (PS:comonomer) were 1:1, 1:2, 1:3. All synthesized graft copolymers were structurally characterized by ^{1}H and ^{13}C NMR, HATR/FTIR, UV-Vis spectroscopy and GPC. PS-g-PLA had the highest molecular weight followed by PS-g-PCL, and PS-g-Nylon6, respectively. Grafting percentage was studied by ^{1}H NMR, weighing and TGA-DTA. The average grafting length was calculated from ^{1}H NMR results. Furthermore, thermal properties were detected by TG-DTA, DMA and DSC. Solubility of the copolymers in various solvents, water, acetic acid (pH 4), and 0.1 wt% aqueous salt solution was also determined. Higher monomer feed ratio enhanced molecular weight, degradation content, glass transition temperature and melting temperature but lowered the crystallinity and thus the copolymers became softer.

INTRODUCTION

Amphiphilic graft copolymers are conveniently prepared in solution or dispersed media by the functional copolymerization of a hydrophobic macromonomer and hydrophilic comonomer. These materials are of great interest because of their surface-active properties.

Polylactide and poly(ε-caprolactone) are family of biodegradable and biocompatible polymers that have been widely used in biomedical applications, such as absorbable sutures, sustained drug delivery systems, implants for orthopedic devices and absorbable fibers. Slomkowski *et al.* (1998) showed that ε-caprolactone can polymerization via cationic, anionic or pseudoanionic. For polymerizations of DL-lactide, the most widely used initiator was tin(II) 2-ethylhexanoate (stannous octoate), in order to obtain high molecular weight polymer. Side reaction (intermolecular and intramolecular) can occur and result in a broadening of the molecular weight distribution.

By "grafting-from" method, different polymerized mechanisms can be applied to build-up of the grafts; among them, anionic, controlled/ "living" radical, coordination-insertion ring opening and cationic mechanisms have been mostly applied.

Polymer grafting on PS can be carried out by several methods. Janata *et al.* (2001 and 2003) use the Friedel-Crafts acetylation of PS as the first step for functionalization acetyl group to benzene ring. In the second step, they accomplished reduction of carbonyl groups to secondary hydroxyl groups followed by grafting of polymers via ring opening polymerization. Li *et al.* (2001) described that starting Friedel-Crafts acetylation of polystyrene led to the polymer ring substituted with acetyl group. In the second step, polymer anion (polystyrene) attacked at carbon position of carbonyl group. Kee *et al.* (2002) showed grafting poly(2-vinylpyridene) on polystyrene via chloromethylation reaction. This reaction is danger because dichloromethyl caused cancer disease.

In this work, PS-g-biocompatible polymers were synthesized from Friedel-Crafts acetylation to the benzene ring of polystyrene backbone. Friedel-Crafts acylation of PS has been mostly used for the preparation of acylated polystyrene resins. Thus in this work, propionyl chloride was chosen as acylating agent along with $AlCl_3$ complexed with nitrobenzene, $[AlCl_2(RNO_2)m]^+AlCl^-_4$ which were discovered in the 1:1, 2:1, and 1:2 molecular complexes of aluminium chloride with nitrobenzene (Perlovskaya, *et al.*, 2001), as catalyst and dichloromethane as diluent. The catalyst and acylating agent were allowed to react prior to addition of substrate (PS). In the first step, Friedel-Crafts acylation of polystyrene led to the polymer ring-substituted with propionyl groups. The ring-acetylated polystyrene was reduced to hydroxyl substituted which was situated along the polymer chain, as multifunctional reactive sites; i.e. introducing 1-hydroxypropyl functionality into the benzene rings of PS. Then at these reactive sites, the "grafting from" reaction via ring opening (ROP) polymerization of DL-lactide or ε-caprolactone or caprolactam was followed (Janata *et al.*, 2001, 2003). Moreover, the characterization, thermal properties, and solubility of the synthesized "grafting from" copolymers having various feed monomer ratios were described.

EXPERIMENTAL

Reagent

Propionyl chloride (98%, Merck), $AlCl_3$ (97%, Fluka), Nitrobenzene (98%, Merck), Tin(II) 2-ethylhexanoate (stannous octoate, $SnOct_2$, Aldrich), $LiAlH_4$ (99%, Aldrich), Dichloromethane (99.8%, Lab Scan), Tetrahydrofuran (99.8%, Lab Scan), Toluene (99.5%, Lab Scan), Ethanol (99.9%, Aldrich), Dicumyl peroxide (98%, Aldrich), ε-caprolactone (99%, MW= 114.144, Fluka), DL-lactide (MW= 116.072, Aldrich), Caprolactam (MW= 112.152, Thai Caprolactam Public Company Limited), Polystyrene (TPI POLENE) were used as received. All syntheses were carried out under out under purified nitrogen gas.

Starting Polymers

Polystyrene chain (MW=238,272.54 in **Table 1** and **Figure A2**) was cut by dicumyl peroxide 0.5% (w/w) in dichloromethane at room temperature, 10 min and terminated by frozen. The final MW detected by GPC was 77,810.64 in **Table 1** and **Figure A3**. (**Figure A1** for GPC Calibration curve used to determine molecular weight of PS).

Synthesis of Ring-Acylated Polystyrene (polymer A)

A dichloromethane solution (180 mi) of polystyrene which was cut (12 g, MW=77,810.64, 1.53 mol) was added under nitrogen to a stirred solution of propionyl chloride (10 ml, 0.576 mol), $AlCl_3$ (12 g) in nitrobenzene (20 ml) (0.09 mol of $AlCl_3$) and dichloromethane (140 ml). The mixture was stirred for 5 h. at room temperature and then precipitated into acidified 80% ethanol (v/v, 1000 ml; 15 ml of HCl). The resulting yellowish product was reprecipitated from THF into 80% ethanol and dried at 40 °C under vacuum.

Synthesis of Polystyrene Ring Substituted with 1-Hydroxypropyl Group (polymer B)

A solution of polymer A (10 g, 1.22 mol) in dry THF (160 ml) was added to a suspension of $LiAlH_4$ (10 g, 0.26 mol) in dry THF (340 ml) under nitrogen gas. The mixture was refluxed for 5 h and, after that water (5 ml) was gently added to decompose residual $LiAlH_4$. The mixture was then precipitated into acidified water (1350 ml; 150 ml of HCl), filtered, washed with water and dried. The product was reprecipitated from THF into water and finally dried at 40 °C under vacuum.

Synthesis of Polystyrene-Graft-Poly(ε-caprolactone)

A mixture of polymer B, ring-substituted with 1-hydroxypropyl groups (1 g, 1.20 mol), and ε-caprolactone (1 g, 2 g, and 3 g; weight ratio 1:1, 1:2 and 1:3 or mole ratio 1:724.6, 1:1449.3, 1:2173.9, respectively) in toluene (10, 20 and 30 ml respectively) was heated at 90 °C under nitrogen gas to dissolve all components and a solution of stannous octoate in toluene (1 ml, 0.3 mmol or 0.12153 g of $SnOct_2$, MW = 405.10) was then added. The clear solution was then stirred at 90 °C for 24 h, precipitated into cold (-10 °C) hexane and the product was dried at room temperature under vacuum.

Synthesis of Polystyrene-Graft-Poly(DL-lactide)

A mixture of polymer B, ring-substituted with 1-hydroxypropyl groups (1 g, 1.20 mol), and DL-lactide (1 g, 2 g, and 3 g; weight ratio 1:1, 1:2 and 1:3 or mole ratio 1:712.6, 1:1425.2, 1:2137.8, respectively) in toluene (10, 20 and 30 ml, respectively) was heated at 90 °C under nitrogen gas to dissolve all components and a solution of stannous octoate in toluene (1 ml, 0.3mmol or 0.12153 g of $SnOct_2$, MW = 405.10) was then added. The clear solution was then stirred at 90 °C for 24 h, precipitated into cold (-10 °C) hexane and the product was dried at room temperature under vacuum.

Synthesis of Polystyrene-Graft-Polycaprolactam

A mixture of polymer B, ring-substituted with 1-hydroxypropyl groups (1 g, 1.20 mol), and caprolactam (1 g, 2 g, and 3 g; weight ratio 1:1, 1:2 and 1:3 or mole ratio 1:737.5, 1:1475, 1:2212.5, respectively) in toluene (10, 20 and 30 ml, respectively) was heated at 90 °C under nitrogen gas to dissolve all components and a solution of stannous octoate in toluene (1 ml, 0.3 mmol or 0.12153 g of $SnOct_2$, MW = 405.10) was then added. The clear solution was then stirred at 90 °C for 24 h, precipitated into cold (-10 °C) hexane and the product was dried at room temperature under vacuum.

Equipment and Characterization

NMR

^{13}C and ^{1}H NMR spectra were used to analyze the resulting polymers that were dissolved in $CDCl_3$ in 5-mm glass tubes using a Bruker DPX 300 spectrometer at frequencies 75.4 and 300.1 MHz, respectively, with an internal deuterium lock. The number of data points was 32,000, repetition delay 5-10 s, temperature 297 K and the number of FID accumulations was 32-12,000 to obtain a good signal-to-noise ratio. ^{13}C NMR spectra were measured using a standard pulse sequence with inverse gated decoupling. Hexamethyldisiloxane was used as an internal standard for calibration of the ^{13}C and ^{1}H NMR scale, the chemical shifts of the nuclei being 2.0 and 0.05 ppm, respectively, referred to tetramethylsilane.

FTIR/HATR Spectroscopy

FTIR spectra were obtained with a Thermo Nicolet spectrometer (NEXUS 670 FT-IR). The spectra were collected in the wave number ranging from 4000-400 cm^{-1} and using sample-KBr pellets. For HATR (spectra-Tech) measurements, a ZnSe crystal ($\theta = 45°$, $n_p = 2.4$) was used. All spectra were recorded at a resolution of 2 cm^{-1}. The samples for HATR were dissolved in THF. A few drop of the solution was allowed to spread out over the surface of the window. After solvent evaporation, the single window was placed in a demountable cell and a reflectance spectrum was taken. Reflectance spectra were corrected and a base line drift was removed using the instrument software (OMNIC) (Dubis, *et al.*, 1999).

Differential Scanning Calorimetry

The melting temperature and the melting enthalpy (ΔH_m) were determined by differential scanning calorimetry (DSC). The melting points were defined as the peak of the endothermic curve. The DSC measurements were carried out with a Perkin-Elmer DSC7 differential scanning calorimeter under N_2 purge (flow rate = 1 ml/min.), at heating rate 10 °C/min. The temperature and heating flow calibration were performed with indium. The scanning range was from 25-350 °C.

UV-Visible Spectroscopy

DR-UV absorption spectra were recorded on a SHIMADZU UV-2550 UV-Visible Spectrophotometer. The spectra were corrected for the wavelength dependence on the instrumental response. The sample was in solid state. Next, it was compressed in specific mold (accessory of DR-UV) for UV-visible spectroscopy.

Gel Permeation Chromatography (GPC)

All polymers were characterized by GPC (WATERS 600E System Controller) in THF at room temperature at flow rate of 1 ml/min using Water Styragel™ HR 5E column (7.8x300 mm, Serial Number T41921A 03 and Part No. WAT044228 MILLIPORE, Effective molecular weight range = 2,000 – 4×10^6) and RI(WATER 410) detectors. Polystyrene standards for PS/THF system were used to calculate apparent values of molecular weights and molecular weight distributions (MWD). Samples were dissolved in THF, their concentrations were about 0.5 %(w/v).

In part of solubility, the molecular weight of polymer fractions that were dissolved in water was characterized by GPC (SHIMADZU) on condition at room temperature, pressure 1 MPa at flow rate 1 ml/min using water as eluent. The GPC composed of degasser (DGU-12A), system controller (SCL-10Avp), column oven (CTO-10Avp), liquid chromatograph (LC-10ADvp), refractive index detector (RID-10A), and fraction collector (FRC-10A). OHpak SB-803 HQ, OHpak SB-804 HQ, and OHpak SB-806 HQ were the columns that connect in this machine, their exclusion limit (PEG) were in the range of 5.5×10^4-1×10^5, 3×10^5-1×10^6, and 1×10^7-

2×10^7, respectively. Characteristic of columns were column size (8 mmx300 mm), column material (polyhydroxymethylmethacrylate gel), and in-column solvent (0.02% sodium azide). Glucose standards for Glucose/water system were used to calculate apparent values of molecular weights and molecular weight distributions (MWD), see also Figure B1 in Appendix B.

Total Organic Carbon Analyzer (TOC-V_{CSH})

The carbon quantity of polymers that were dissolved in water after 24 h was recorded on TOC (SHIMADZU and ASI-V SHIMADZU). Injection volume is 10 µl and the maximum calibration is 2000 mg/l. (Tomita *et.al.*, 2004)

Thermal Gravimetry - Dynamic Temperature Analysis (TG-DTA)

Thermal Gravimetry - Dynamic Temperature Analysis technique was used to determine thermal stability and the decomposition temperature of graft copolymers. Perkin-Elmer thermal gravimetry - dynamic temperature analyzer was used to characterize graft copolymers at heating rate 10°C/min under the nitrogen atmosphere. The mass change with increasing temperature was monitored and recorded. The decomposition temperature (T_d) was obtained from the derivative TG-DTA thermogram. The samples were in solid state.

Dynamic Mechanical Thermal Analyzer

A DMTA V (Rheometric Sciencentific) was used to measure the storage and loss moduli of the graft copolymers as a function of temperature using compression mode (apply load = 0.01 N). Specimen dimensions were approximately 10 mm diameter. All tests were performed at a frequency of 1 Hz, a strain of 0.1 and 30-130 °C.

Solubility

Sample was put in glass tube, then, solvent (water, chloroform, 0.1 %(w/v) salt water, methanol, propanol, or acetic acid (pH 4)) was gently dropped to samples until sample was totally dissolved. Volume of drops of solvent was determined by cylinder.

RESULTS AND DISCUSSION

Acylation

Due to the bulky acylating complex, It was appropriated to assume that acylation occurred only in the most accessible position of the aromatic ring, i.e. in the para position. The polypropionylation of an aromatic ring is improbable because the monopropionylated product deactivates the ring in further substitution.

The resulting ring-propionylated PS, so call "Polymer A" was characterized by FT-IR, GPC, ^{1}H and ^{13}C NMR spectroscopy. Yield of polymer A was 13.0435 g (pale yellow powder). Degree of substitution (D.S.), determined from ^{1}H NMR was 0.25 %mole. ^{1}H NMR ($CDCl_3$, ppm): 2.82 ($CO\text{-}CH_2\text{-}\underline{CH_3}$), 1.2 ($CO\text{-}\underline{CH_2}\text{-}CH_3$), 7.6 (aromatic protons metha to propionyl group) (see **Figure 1A**). ^{13}C NMR ($CDCl_3$, ppm): 200 ($\underline{CO}\text{-}CH_2\text{-}CH_3$), 145 ($C_1$ aromatic carbon in unsubstituted rings), 135 (C_4 aromatic carbon in substituted rings), 126-128 (the other aromatic carbons in substituted and unsubstitued rings), 26 ($CO\text{-}\underline{CH_2}\text{-}CH_3$), 9.2 ($CO\text{-}CH_2\text{-}\underline{CH_3}$) (see **Figure 1B**). The FT-IR spectrum exhibits a sharp absorption band at 1684 cm^{-1} attributed to carbonyl stretching, aliphatic hydrocarbon (2850-2950 cm^{-1}), para substituted aromatic hydrocarbon (3000-3080 cm^{-1} and 1800-2000 cm^{-1}) and mono substituted aromatic hydrocarbon (700 and 1600 cm^{-1}) (**Figure 2**). Molecular weight of ring-propionylated PS is about 81,042.53 (**Table 1**). All values are in good agreement with literature data for a polymer model, ring-acetylated polystyrene (Janata, *et al.*, 2001, **Figure C1**) and ring-acylated polystyrene from ChemDraw Ultra 8.0 Program for^{1}H and ^{13}C NMR (**Figures D1** and **D6**).

Figures A2-A4 shows GPC broaden curves of PS, PScut and polymer A, respectively. Furthermore, their molecular weights were 238,272.54, 77,810.64, and 81,042.53, respectively (**Table 1**). The molecular weight of PScut was decreased about 67.34% when PS chain was cut by dicumyl peroxide 0.5%(w/w), then PScut was modified by acylation (to be polymer A). Molecular weight of acetylated – PScut increases slightly about 4.153%.

Reduction

In the second step,the reduction of carbonyl groups in propionylated PS to hydroxyl groups using $LiAlH_4$ in THF was accomplished. The resulting PS with ring-bonded 1-hydroxypropylgroups (referred as "Polymer B") was characterized by FT-IR, GPC, ^1H and ^{13}C NMR spectroscopy. Yield of polymer B was 10.8925 g (pale yellow powder). Molecular weight is about 82,708.47(see **Table 1** and **Figure A5**). The FT-IR spectrum shows complete disappearance of the carbonyl band in favor of the broad band centered at 3415 cm^{-1} which is characteristic of hydroxyl groups, mono substituted hydrocarbon (300-3100, 1700-2000, 1600 and 1498 cm^{-1}), and aliphatic hydrocarbon (1372 and 1420 cm^{-1}) (**Figure 2**). In the ^1H NMR spectrum show in **Figure 3A**, the signals characteristic of three propionyl protons and aromatic protons ortho to the propionyl group vanished; a new signal appeared at 4.5 ppm, assigned the OCH proton in the 1-hydroxypropyl group. No signal of the carbonyl carbon was found in the ^{13}C NMR spectrum (see **Figure 3B**) of the polymer, while the signal of the OCH carbon in the 1-hydroxypropyl group appeared at 76 ppm, in agreement with the position of the corresponding signal in the ^1H and ^{13}C NMR of polystyrene ring-substituted with 1-hydroxyethyl group from Janata, *et al.* (2001) (**Figure C2**) and polystyrene ring-substituted with 1-hydroxypropylyl group from ChemDraw Ultra 8.0 Program (**Figure D2** and **D7**).

Thus, all the above spectra give clear evidence of complete conversion of acetylated PS into hydroxyl-functionalized PS. Moreover, due to a relatively high content of hydroxyl groups, the PS with 1-hydroxypropyl groups is soluble in methanol like other similar types of hydroxylated polystyrenes.

Figure A5 showed GPC broaden curve of polystyrene ring substituted with 1-hydroxypropyl group (polymer B) that changed from polymer A, the molecular weight (82,708.47, **Table 1**) increased slightly about 2.06% of polymer A.

Polystyrene Grafted with Poly(ε-caprolactone) or Polycaprolactam or Poly(DL-lactide)

Ring-opening polymerization of poly(ε-caprolactone) or polycaprolactam (or Nylon6) or poly(DL-lactide) initiated with secondary hydroxyl groups of the hydroxylated polymers and co-initiated/catalyzed with stannous octoate, served as a "grafting-from" reaction. The latter compound is commonly used as initiator/catalyst in ROP of lactones, lactams and lactides; we preferred it to aluminium-based initiators mainly due to its easier handling. Moreover, the undesirable transesterification reactions, otherwise typical of tin-based initiators, are less pronounced under mild reactions conditions and defined copolymer structures can be prepared. For this reason, we performed all grafting reactions at 90°C in toluene. To achieve homogeneous conditions from the very beginning of the grafting reactions, we added stannous octoate as a last component to a clear solution of mixed reactants pre-heated to 90°C. Successful grafting of poly(ε-caprolactone) or polycaprolactam or poly(DL-lactide) from this hydroxylated PS was confirmed by DR-UV, FTIR-HATR, GPC and NMR spectra.

Firstly, yield (PS: caprolactone) of PS-g-PCL were 2.1026g (1:1), 3.014g (1:2), 4.1108g (1:3) (pale yellow). Moreover, yield (PS:DL-lactide) of PS-g-PLA were 2.47g (1:1), 3.0453g (1:2), 4.5847g (1:3) (pale yellow). Lastly, yield (PS: caprolactam) of PS-g-Nylon6 were 1.4444g (1:1), 1.8385g (1:2), 2.4058g (1:3) (pale yellow). Weight of grafted copolymer increases with the more feeding monomer. These results showed weight of product was higher than initial weight of monomers and polymer B. Then, the products may be had the contamination of nitrobenzene because the color of copolymers were pale yellow as same as nitrobenzene color (this reason will describe in absorption properties of the grafting copolymer part), and the boiling point of nitrobenzene is about 210-211°C which it is difficult to eliminate from products because it was in degradation range of grafting polymer (this reason will describe in thermal properties part).

From **Figure 4**, weak absorption in the range of 1717-1738 cm^{-1} indicated the presence of some compounds containing carbonyl groups. HATR FT-IR is convenient and a rapid method of preliminary evaluation of surface plant material composition, especially for esters, ketones and aldehydes (Dubis, *et al.*, 1999). From IR results, the range of carbonyl group appeared about 1718 cm^{-1} (PS-g-PCL) and 1774 cm^{-1} (PS-g-PLA), and secondary amide or NH bend group appeared about 1668 cm^{-1} (PS-g-Nylon6).

^{1}H NMR spectra of the graft copolymers demonstrated nearly 100% substituted efficiency in ratio of PS : grafting polymer 1:2 and 1:3, signal of methine proton of the initiating Ø-$\underline{CH}(CH_2CH_3)$-OH groups at 4.5 ppm was decreasing as ratio of grafting polymer :PS were increased. In other words, all free hydroxy groups of the hydroxylated PS effectively initiated the ROP of ε-caprolactone or DL-lactide or caprolactam. Due to the grafted caprolactone or lactide or caprolactam unit(s), the latter groupings transformed to the Ø-$CH(CH_2CH_3)$-O- groupings and the signal of the methine proton shifted to 4.4-4.5 ppm. The signals characteristic of ethylene protons in grafted ε-caprolactone units appeared at 4.1, 2.4 and 3.60 ppm; the last value corresponds to the methylene protons in terminal CH_2OH group. ^{1}H NMR in ($CDCl_3$, ppm): 4.4-4.5 [Ø-$\underline{CH}(CH_2CH_3)$-O], 4.0-4.1 ($\underline{CH_2}$-O-CO-CH_2), 3.6-3.65 ($\underline{CH_2}$-OH), 2.2-2.4 (CH_2-O-CO-$\underline{CH_2}$). ^{13}C NMR ($CDCl_3$, ppm): 172-173 (CH_2-O-$\underline{CO}$-CH_2), 81-89 [Ø-$\underline{CH}(CH_2CH_3)$-O], 62-64 ($\underline{CH_2}$-O-CO-CH_2) (**Figures 5-7**). The signals of methine protons in grafted lactide units were detected at 5.20 and 4.40 ppm; the latter value corresponds to the methane proton in terminal $CH(CH_3)$-OH group. ^{1}H NMR ($CDCl_3$, ppm): 5.6-5.95 [Ø-$\underline{CH}(CH_2CH_3)$-O], 5.2-5.5 ($\underline{CH}(CH_3)$-O-CO), 4.4-4.7 ($\underline{CH}(CH_3)$-OH). ^{13}C NMR ($CDCl_3$, ppm): 169-172 ($CH(CH_3)$-O-$\underline{CO}$), 77-78 (Ø-$\underline{CH}(CH_2CH_3)$-O), 75-76 ($\underline{CH}(CH_3)$-O-CO) (**Figures 8-10**). The signals characteristic of amine protons in grafted caprolactam units appeared at 3.10, 8.00 and 2.1 ppm; the last value corresponds to the amino protons in terminal -NH_2 group. ^{1}H NMR ($CDCl_3$, ppm): 4.3-4.5 [Ø-$\underline{CH}(CH_2CH_3)$-O], 3.1-3.25 ($\underline{CH_2}$-NH-CO-CH_2), 2.1-2.3 (CH_2-$\underline{NH_2}$), 8.0 (CH_2-$\underline{NH}$-CO-CH_2). ^{13}C NMR ($CDCl_3$, ppm): 171-180 (CH_2-NH-$\underline{CO}$-CH_2), 81-83 [Ø-$\underline{CH}(CH_2CH_3)$-O], 41 ($\underline{CH_2}$-NH-CO-CH_2), 23-25.5 (CH_2-NH-CO-$\underline{CH_2}$) (**Figures 11-13**). The NMR results of PS-g-PLA, PS-g-PCL, and PS-g-Nylon6 were confirmed by NMR results in the previous work (**Figures C1-C3**) and NMR spectra from ChemDraw Ultra 8.0 Program (**Figures D3-D5** and D**8-D10**). The ^{1}H NMR results of nitrobenzene showed the group of peaks about 7.5, 7.6, and 8.3 ppm (**Figure E1**), then the product might have nitrobenzene as the contamination because ^{1}H NMR results showed small peak about 8.0 ppm. From **Figures E2-E7** , NMR results of the pure biocompatible polymers or oligomer which perhaps produced but were not grafted from PS were hard to identify because their peaks were shown nearly the same position as those of the grafted ones. The intensities of the mentioned signals and those of the signals of the aromatic protons were used to determine the average graft length and the copolymer composition. Grafting percentage can be calculated by weight and a number of protons from NMR that they are corresponding with ratio which was added. The calculating from peak NMR has more credible than that from weight, which might has impurity weight, then the latter showed the trend of grafting only. From **Table 2**, ε-caprolactone and DL-lactide can graft from PS much better than caprolactam.

In **Table 1**, molecular weights of the graft copolymers were higher than that of the hydroxylated PS. Furthermore, the increasing of the ratios of PS:grafting polymer enhances molecular weight of copolymer. When PS graft with PLA, it showed relatively high molecular weight for all ratios (253,270.73, 323,317.34, and 380,474.01 for ratio 1:1, 1:2, and 1:3, respectively see **Figures A9-A11**) in comparison to PS-g-PCL (107,753.40, 109,968.42, 116,890.44 for ratio 1:1, 1:2, and 1:3, respectively see **Figure A6-A8**) or PS-g-Nylon6 (95,369.39, 109,968.42, and 172,060.82 for ratio 1:1, 1:2, and 1:3, respectively see **Figure A12-A14**). The high molecular weight of PS-g-PLA was probably due to two functional ester groups on DL-lactide ring, whilst ε-caprolactone or caprolactam have only one ester functional group available for ring open polymerization. It is thus easier for DL-lactide to penetrate to PS-backbone and polymerize. It should be noted that molecular weight of the "grafted-from" copolymer could be higher than that determined by GPC as stated by Jeon, *et al.* (2004) that molecular weight of styrene-maleic anhydride-graft-polyamide6 was larger than the measured value by GPC because the hydrodynamic volume of a graft copolymer is smaller than polyamide6-block-polystyrene of linear block copolymer. So, it is possible that the molecular weights of all products are higher than measured value.

Janata *et al.* (2003) found that intramolecular transesterification (back-biting) caused degradation and formation of cyclic oligomers. Intermolecular transesterification modified the sequence of lactone/lactide units in the chain, and both intra- and intermolecular transesterification broaden molecular weight distribution in GPC results of a graft copolymer. In our case, however these reactions seem to be at least minimized because there was no GPC peaks or significant tail observed at high retention volume for any oligomers, except the broadening in molecular weight distribution when feeding monomer were increased. (**Figures A6-A14**).

The Grafting Percentage of Copolymer

The grafting of copolymers can be calculated by many methods such as by weight, by a number of protons from NMR and by weight loss from TGA (**Table 2** and **Figures 14-22**). Grafting percentages in the same sample have the specific quantity grafting value of each method that was difference. Grafting percentage by weight is the percentage of mass of grafting polymer by mass of back bone polymer. The slight weight difference may arise from the absorbed solvent that was stubborn (hard to remove). They can show trend of percentage of grafting increasing with the mass ratio of PS: grafting polymer.

Liu, *et al.* (2004) and Wu, *et al.* (2005) characterized the grafting percentage of poly(DL-lactide) graft onto chitosan as the back bone by the same calculation which are the ratio of grafting polymer weight to backbone polymer weight. Grafting percentages by weight were increased when feeding monomer increased in all types. From **Table 2**, PS-g-PCL in ratio 1:1, 1:2, and 1:3 showed 83.77, 158.90, and 240.79% (by weight), respectively. PS-g-PLA has 115.88, 175.60, and 299.79% (by weight) in ratio 1:1, 1:2, and 1:3, respectively. PS-g-Nylon6 in ratio 1:1, 1:2, and 1:3 showed 35.63, 77.23, and 131.68, respectively. For PS-g-PLA 1:1, the weight of graft copolymers were higher than weight of initial comonomer feeding. This error should be due to weighing error of the strong contamination of solvent from differential thermogravimetry (DTG) results (**Figures 14-22**). These show weight loss before the first peak of polymer degradation. Then mass ratio percentages by weight were calculated by equation in **Table 2**.

Grafting percentage by mass loss (or by TGA) is percentage of mass loss of grafting polymer (step1 in **Figures 14-22**) by mass loss of back bone polymer (step2 in

Figures 14-22). Percentage of mass loss in each step can be calculated by computer programs. The percentage mass loss of grafting polymer (in first step in graph) should be ratio with the percentage mass loss of back bone polymer as same as initial mass ratio. The percentage of grafting increasing with the comonomer feed ratio. Since the decompositions of these grafted coplymers were carried out in nitrogen gas there was black residue lower than 20 wt%. Silvalingam, *et al.* (2004) investigated the thermal degradation of various aliphatic polyesters such as poly(ε-caprolactone), and poly(DL-lactide), which was completely degrade (0% residue) at over 350 °C and 450 °C, respectively. The thermal decomposition of polyamide6 (or nylon6) followed by other volatile gases like CO_2 and NH_3 complete over 500°C (Pramoda, *et al.*, 2003). Then residue is only backbone polymer or PS. However, by using TGA-DTA the mass loss was more obvious and the calculating for grafting yield could be calculated directly from the mass loss of each transition without counting the initial loss before the first transition and the results for all products are in the reasonable range with some discrepancy to the weighing method above. From **Table 2**, PS-g-PCL in ratio 1:1, 1:2, and 1:3 showed 71.37, 95.23, and 136.29% (by weight), respectively. PS-g-PLA has 41.40, 88.94, and 202.78% (by weight) in ratio 1:1, 1:2, and 1:3, respectively. PS-g-Nylon6 in ratio 1:1, 1:2, and 1:3 showed 23.55, 31.16, and 116.4, respectively. Grafting composition from TGA calculated by equation in **Table 2**.

The mole ratio of poly(N-isopropyllacrylamide-b-DL-lactide) to poly(lactic acid) determined by NMR integration (Kohori, *et al.*, 1998). Arborescent polystyrene-graft-poly(2-vinylpyridine) copolymer determined composition using ^{1}H NMR spectroscopy (Kee, *et al.*, 2002). The grafting percentages were calculated by comparison between a number of protons of ortho position of benzene ring and a number of proton of grafting polymer. Grafting percentage (%mol) by NMR (^{1}H NMR) is the percentage of unique peak height of grafting polymer (ε-caprolactone, ~4.0-4.1 ppm.($-\underline{CH_2}$-O-CO-), DL-lactide, ~5.2-5.6 ppm.($C\underline{H}(CH_3)$-O-CO-), caprolactam, ~3.0-3.2 ppm ($-C\underline{H_2}-CH_2$-NH)) by standard peak of proton on ortho position of benzene ring (~6.4-6.8 ppm.) (Example of calculation in **Figure F1**). PS-g-PCL in ratio 1:1, 1:2 and 1:3 has 27.34, 60.00 and 97.22 %mol of PCL, respectively. PS-g-PLA in ratio 1:1, 1:2 and 1:3 has 28.76, 73.71 and 125.00 %mol of PLA, respectively. PS-g-Nylon6 in ratio 1:1, 1:2 and 1:3 has 4.53, 12.60 and 25.00 %mol of grafting polymer, respectively. This method is the most credible because it is measured in a molecule level. When the mass grafting polymer increase, the grafting percentage by NMR is increased too (Note that PS: Graft monomer are 1:1, 1:2 and 1:3 by weight equal to 50%, 33.3%, and 75% by weight of PS , respectively and 0.1362%, 0.0681% and 0.0454% by mole of PS, respectively in all copolymers because they have a near value of molecular weight).

The good grafting comonomers that gave high ‘graft from’ quantity are DL-lactide and ε-caprolactone. Caprolactam is rather poor grafting comonomer as it shows much low grafting composition, and the graft copolymer appear like highly viscous liquid; the more grafting, the more liquid-like which indicates plasticizing effect.

^{1}H NMR data can be used to calculate the average length of grafting polymer by comparison between total number of protons of methyl at end chain and total number of proton in grafting polymer chain (see **Table 3** and **Figure F1**). Only PS-g-PCL and PS-g-PLA were calculated but PS-g-Nylon6 was not calculated because peak of proton at end chain was broad peak and not so clear. PS-g-PCL in ratio 1:1, 1:2 and 1:3 has 2.8, 6.0 and 17.5 monomer of PCL per grafting polymer chain, respectively. PS-g-PLA, in ratio 1:1, 1:2 and 1:3, have 3.5, 6.0 and 8.0 monomers of PLA in grafting polymer chain, respectively. They are quite short chain grafting but with many grafted site per backbone chain PS-g-PCL in ratio 1:1, 1:2 and 1:3 have 78, 40 and 17 grafted site per backbone chain respectively while PS-g-PLAs have 427, 351 and 326 grafted site per chain in ratio 1:1, 1:2 and 1:3, respectively. These results showed that the more feeding a number of grafted sites per backbone chain decreased (**Table 3**). PS-g-PLAs have much more number of grafted sites than PS-g-PCL. The short size chain would be benefit for hydrolysis of ester linkage when dissolve in water. Moreover, Liu, *et al.* (2004) synthesized and characterized a brush-like copolymer of polylactide grafted onto chitosan. They found that when the content of lactide increased in the feeding ratio, the amount of short-branced chain rises in the copolymer. Chitosan has functional groups for polymerization higher than polymer B that only has degree of substitution about 0.25. From ^{1}H NMR spectrum, the chemical shift at about 4.5 ppm (Φ-CH(CH_2CH_3)-OH) decrease almost completely when feed monomer content is at higher ratio.

When chitosan was grafted with polylactide, its original integrity was also destroyed. The hydrogen bonds that existed in it were broken to a certain extent, which makes intermolecular interactions decrease. On the other hand, the ester bond is more flexible than that of a hydrocarbon. When used as the branched chain of chitosan, it can plasticize internally the rigid main chain of chitosan. Meanwhile, the branched ester linkage is more polarity than that of a hydrocarbon, so there is a strong repulsive force among molecule of the branched ester than that existing among hydrocarbons, which can be in favor of chitosan retaining its spatial configuration (Liu, *et al.*, 2004). Then morphology of samples was changed from original properties of PS that was high rigidity to softness when the comonomers were added at higher feeding monomer ratio.

Absorption Properties of the Grafting Copolymer

It is difficult to extract a great deal of information from a UV spectrum used by itself. It should be clear by now that a UV spectrum is most useful when at least a general idea of the structure is already known; in this way, the various empirical rules can be applied. Nevertheless, several generalizations can serve to guide our use of UV data. These generalizations are a good deal more meaningful when combined with infrared and NMR data-which can, for instance, definitely identify carbonyl group, ester group, aromatic ring, and other important chromophores. In the absence of infrared or NMR data, the following observations should be taken only as guidelines.

A single band of low to medium intensity (ε = 100 to 10,000) at wavelengths less than 220 nm usually indicates an n to σ^* transition. Amines, alcohols, and esters are possibilities, provided that the nonbonded electrons are not included in a conjugated system.

A single band of low intensity (e = 10 to 100) in the region 250 to 360 nm, with no major absorption at shorter wavelengths (200 to 250 nm), usually indicates an n to π^* transition. Since the absorption does not occur at long wavelength, a simple, or unconjugated, chromophore is indicated, generally one which contains an O, N, or S atom. Examples of this may include C=O, -NO2, $-CO_2R$, $-CO_2H$, or $-CONH_2$.

Two bands of medium intensity (ε = 1,000 to 10,000), both with λ_{max} above 200 nm, generally indicate the presence of an aromatic system. In polynuclear aromatic substances, a third band appears near 200 nm, a band which is simpler aromatics occurs below 200 nm, where it cannot be observed.

Simple ketones, acids, esters, amides, and other compounds containing both π systems and unshared electron pairs show two absorptions: an n to π^* transition at longer wavelengths (>300 nm, low intensity) and a π to π^* transition at shorter wavelengths (<250 nm, high intensity).

Compounds which are highly colored (have absorption in the visible region) are likely to contain a long-chain conjugated system or a polycyclic aromatic chromophore. However, some simple nitro compounds may also exhibit color.

UV-Visible absorption spectrum of each sample has different λ_{max} and structure of spectrum and it was corresponding with standard material, then it showed that structure of molecule is different.

UV-vis absorption measurements on quartz slides show a band of the n to π^* transition of the nitrobenzyl side group at 271 nm and visible absorption (Hesse, *et al.*, 1991) and **Figure G1** showed UV-vis absorption at 246.5, 304, 346.5 and 405 nm.

In **Figure 23**, the spectra DR-UV of each polymer showed its characteristic and specific absorbance. Then DR-UV method can indicate the difference of samples and its value compared with **Figure H1** identify color of products. The pure polystyene has two sharp UV-absorption peaks about 228 and 264 nm that make it white. Ring-acylated polystyrene showed three UV absorption peaks which are 252.4, 279.2, 330.1 and one visible absorption at 443.1 nm responsible for (pale yellow color of the product); and polystyrene ring substituted with 1-hydroxypropyl group showed broader spectra containing four peaks (243, 288.4, 332.2 and 405.8 nm) which are pale yellow product. When polystyrene was modified, it can absorb spectrum in wider range than pure polystyrene. The peaks at 252.4 and 243 refer to PS peak shifted while peaks at 330.1-332.2 nm represent acylated hydroxyl groups. The peaks at 279.2 and 288.4 nm probably represent nitrobenzyl side groups.

Spectra of poly(ε-caprolactone) and polystyrene (**Figure 24**) show their characteristic peaks at 224.8, 264 nm, respectively. The spectra of PS-g-PCL show higher intensity with increasing ε-caprolactone content The most broaden peaks from 190-860 nm were found for the ratio 1:1 and 1:2 but its ratio 1:3 are only absorbed in 190-600 nm. The shoulder peak at about 220 nm found for all three PS-g-PCL which reduced with increasing comonomer content and the peak at 260 nm became stronger to represent the carbonyl group in the comonomer. While in range 300-455 nm, nitrobenzene absorption was occurred to interfere the results which was minimized for the ratio 1:3. PS-g-PCL thus showed yellow product caused by nitrobenzyl group visible absorption at wavelength over 440 nm.

Spectrum of PS-g-PLA were compared with spectrum of polystyrene, poly(DL-lactide) and lactide monomer. It is clear that the monomer has sharper UV absorption peak than the polymer one (showing peak shift to 230.1 nm). The board absorption peak in ratio 1:1 to 1:2, found at 269.9 and 340.3 nm, respectively having a shoulder at 230 nm to represent the lactide group. For ratio 1:3, two peaks that were 342.6 and 455.7 nm from nitrobenzene were shown. In range 190-400 nm, ratio 1:2 is higher energy absorption than 1:3 and 1:1, respectively (**Figure 25**). PS-g-PLA showed yellow products due to nitrobenzene.

UV Absorption of PS-g-Nylon6 also revealed the present of nitrobenzene; e.g. in ratio 1:3 has three peaks (350.2, 455.1, and 673.1 nm), but the ratio 1:1 and 1:2 have only one peak (305.4 and 245.6 nm, respectively). The absorbance at 238.7 nm representing caprolactam was appeared as shoulder on the borad absorption peaks for all PS-g-Nylon6. In range 190-400 nm, the ratio 1:2 is higher absorbance than 1:1 and 1:3, respectively. In contrast, in range 400-800 nm, the ratio 1:3 is higher than 1:1 and 1:2, respectively (**Figure 26**). PS-g-Nylon6 showed yellow products, especially nylon13 showed bright yellow product.

Solubility

Chloroform is a good solvent of all copolymers that were synthesized. The copolymer grafted by poly(DL-lactide) shows the best dissolution in chloroform, poly(ε-caprolactone)-g-PS and polycaprolactam-g-PS are less soluble in chlorofrom, respectively (see **Table 4**). All copolymers were soluble in several solvents when grafting ratio increased. Solvents which made swelling of all copolymers were water, 0.1%(w/v) salt water, methanol, propanol and acetic acid (pH 4). Capek, *et al.* (2000) organized structures, consist of a compact core of hydrophobic PS chains surrounded by a corona of poly(ethylene oxide) water-soluble chains. This organization depends on the solvent polarity and its density decreases in the following order: water>DMF>THF. This finding indicates that there is not a true homogeneous concentrated solution of graft copolymer. The solubility parameter showed high to low in the following order: water (23.43) ~ 0.1%(w/v) salt water > methanol (14.49)> propanol (11.97)> acetic acid (10.45)> chloroform (9.21) (Shibata, *et al.*, 2002). Then all graft copolymers should have solubility nearly 9.21 of chloroform.

In water and 0.1%(w/v) salt water, some parts of all synthesized grafting copolymers were dissolved which could be detected by Total Organic Carbon Analyzer (TOC). Tomita, *et al.* (2004) found that poly(L-lactide) film was degraded in water and investigated by total organic carbon (TOC) concentration. In the medium, TOC content increased with time dissolved and the value was steady about ten days. For this experiment, the graft copolymers were dissolved in water and 0.1%(w/v) salt water for one day. In general, the grafted copolymer dissolved in water or salt solution better than its pure polymer about 3-30 times and 2-50 times, respectively. Among three comonomers, polycaprolactam, and poly(ε-caprolactone), have compatible solubility in water much better than polylactide. **Tables 5-6** showed that when grafting ratio increases, soluble amount of grafting polymers also enhances (although the value of dissolved content is small). Polystyrene grafted with caprolactam or ε-caprolactone or DL-lactide, copolymer show increasing carbon content in the dissolved part, respectively. Based on mass of carbon loss/mass sample,water can dissolve polycaprolactam (grafting polymer) better than 0.1% salt water while poly(DL-lactide) and poly(ε-caprolactone) differ from that. The water soluble parts of the copolymers were characterized by GPC and the molecular weights of polymers were showed in **Figures 27-29** and **Table** 7. The molecular weight of polymer (compared with standard curve in **Figure B1**) that was in water decreased when the percentage of grafting polymer increased. The ranges of molecular weight were 1300-1500 of poly(ε-caprolactone) as grafting polymer, 1120-1180 of poly(DL-lactide) as grafting polymer and 1500-1800 of polycaprolactam as grafting polymer. It is also noted that their pure polymer solubilities are in unit of mg/L which is typically considered as insoluble solid polymers.Then types of grafting polymer have influence on dissolution in water. Hydrolysis is catalyzed by either Brønstedt acids or bases and is schematically illustrated and exemplified by polylactic acid, PLA, in **Figure I1**. Chain scission results in the formation of carboxylic end-groups that, due to their acidic nature, will enhance the rate of further hydrolysis. This mechanism is denoted 'autocatalysis' and makes polyester matrices truly bulk eroding (Edlund, *et al.*, 2003). Recently Davis *et al.* (2003) have studied the thermal stability of injection moulded nylon6 nanocomposites by ^{13}C NMR. The virgin nylon6 and its nanocomposites were injection moulded at 300 °C. Nylon6 does not degrade at processing temperature, whereas there is significant decrease in molecular weight in nanocomposites in the same conditions. It was observed that the degradation might depend upon the percentage of water in the nanocomposites, which might cause hydrolytic cleavage in **Figure I2**. The linear short chain nylon6 may be blend in PS-g-Nylon6, then TOC analysis found high carbon content of the low MW nylon6 that easily dissolved in water because nylon6 hardly to degrade in room temperature by pure water. PCL and PLA are easily degraded by water at room temperature their degradations occur randomly; i.e. difficult to indicate the positions were cut the shorter side chains, in the graft copolymer with monomer ratio 1:1 and 1:2 are protected by longer chain PS backbone so their dissolved solids were less than that of monomer ratio 1:3. Then its side chain polymers was protected from PS amorphous (high MW).

The percentage of grafting (see **Table 2**) can calculate by the mass loss of biodegradable polymers to the mass loss of polystyrene. These results that PCL can polymerize and graft to PS are more easily than Nylon6. PS-g-PCL can be dissolved in water better than PLA but at higher monomer feed ratio its solubility reduces due to increase in crystallinity as well as 1:1 PS-g-PLA. Solubility at high PLA content is better due to the disappearance of crystalline.

Thermal Properties of the Grafting Copolymer

Glass transition temperature is characteristic of each polymer. It can be detected by DSC and for this work temperature scan was from 85 °C to 116 °C. T_g of PS showed about ~85.4 °C. T_g of PS shift to ~97.9 °C when PS is modified by ring-acylated (polymer A). After polymer A changed to polymer B; i.e. from carbonyl group (C=O) to hydroxyl group (-C-OH), T_g was raised to ~115.8 °C (**Figure 30**). This indicates stronger intermolecular force induced by polar group attraction. When grafting copolymers were characterized to observe T_g, the spectra did not clearly show glass transition temperature.

The melting enthalpies and peak temperatures are also shown in **Table 4**. The DSCs curves are illustrated in **Figures 31-33**. The melting temperatures of pure PLA, PCL and Nylon6 are 175.1, 53-60, and 223 °C, respectively (Chen *et al.*, 2003, Huang *et al.*, 2004, Jiang *et al.*, 2005). The degradation temperature of PLA, PCL and Nylon6 are 295 °C, 402°C and 470 °C, respectively (Sivalingam *et al.*, 2003 and Pramoda *et al.*, 2003). In case of PLA, T_g of PLA is near to room temperature (55 °C, Chen, *et al.*, 2003). Melting peak of caprolactone11 is the smallest among the three ratios; i.e. the melting peak temperature increases with PCL content in the copolymer. Corresponding with Cretua, *et al.* (2004) who investigated the thermal properties of poly(2-hydroxyethyl methacrylate)-g-poly(ε-caprolactone) copolymers, containing 34% or 50% of PCL, its melting temperature was 46.16°C and 47.52 °C, respectively. For PLA, the melting temperature is peaked at 175.6 °C. When PLA is grafted to PS at ratio 1:1, its peak area reduced more than half and its T_m peak reduced to 153.82 °C. Chen, *et al.* (2003) studied physical properties such as the crystalline melting point, glass transition point (T_g) of poly-L-lactic acid (PLLA) and poly-DL-lactic acid (PDLLA) or polycaprolactone characterized by thermogravimetric analysis, differential scanning calorimetry (DSC), etc. From DSC results T_g's of PLLA and PDLLA are 57.4 °C and 51.6 °C. The glass transition temperature of PLLA mixed with PDLLA without adding surfactant can be viewed as two regions, while the melting point did not change significantly. T_m's of PDLLA did not appear because PDLLA is amorphous polymer. T_m's of PCL about 53.1 °C and ΔH_m's PCL was decreased when the ratio of PCL to PLLA decrease. Huang, *et al.* (2004) found that the thermal properties of the polymers in the form of powder were investigated by DSC. All the three polymers were semicrystalline with only one melting peak, in agreement with the amorphous nature of racemic PLA segments. The melting temperature (T_m) of the copolymer was so closed to those of PCL, while the melting enthalpy (ΔH_m) of the copolymer was much lower, indicating that the presence of PLA blocks decreased the crystallinity of the copolymer with respect to the PCL homopolymer. A series of poly(ε-caprolactone)/poly(L-lactic acid) was synthesized and characterized. The length of central PCL segment was kept constant (MW=2000), while the molecular weight of the $(PLA)_n$ blocks spanned from 550 to 6000 Da. When MW of $(PLA)_n$ blocks was higher than 1100, they showed crystallinity and MW lower than 1100, PLA blocks were too short to crystallize (Cohn, *et al.*, 2005). As PLA content increased in PS, the melting peak of PLA is absence, revealing the loss of crystalline in the copolymer. The multiple peaks show at higher temperature are related to degradation of PLA, starting at about 200 °C for 1:1, at about 210 °C for 1:2 and at about 250 °C for 1:3 PS:PLA ratio (more PCL percentage as a grafting polymer chain, more heat resistance) corresponded to results from DTG. Crystallinity and amorphous in polymer depends upon cooling rate, tacticity, backbone and side group structures. Crystallisation is facilitated by regular or order backbone structure, favorable interchain interaction, and lower molecular weight. In results, higher ratio of PS-g-PLA did not present melting peak due to type of lactide monomer; i.e. when DL-lactide was polymerized, it is atactic polymer resulting in amorphous nature and polymer chain is not long enough to pack to crystalline phase, shown in **Table 3**, the shorter grafting polymer of PS-g-PLA in the ratio 1:1 (MW is lower than 1100). Despite the low MW PLA side chain for 1:1 PS-g-PLA, its crystalline was shown the crystalline phase. PS-g-PCL showed melting temperature in all ratio because PCL as the side chain has tacticity and polarity between chains. The melting ranges of PS-g-PCL in all ratios are 44.95 °C to 50.84 °C corresponding with Chen, *et al.* (2003) discussed above. Nojima, *et al.* (1997 and 2004) studied morphology of melt-quenched polystyrene-block-poly(ε-caprolactone) and polyethylene-block-poly(ε-caprolactone), respectively. The melting temperature of PCL blocks was ca. 55 °C.

Li, *et al.* (1998) showed the nylon domains, which serve as physical crosslinks, play a predominant role the information of a stable network structure for the graft copolymer(polyethylene/nylon6) that were obtained during the melt-blending process (nylon6 about 5-20 wt%). DSC experiment did not show crystallization and melting behavior of nylon6. DSC curves of PS-g-Nylon6 in all ratios did appear melting temperatures but showed degradation temperatures as same temperature as differential thermalgravimetry (DTG) curves. DSC results in **Figure 33** showed melting temperature two peaks in all samples, 186.64 °C and 221.36 °C for Nylon6 pure and the degradation temperature showed 105.23 °C and 270.32 °C for Nylon13, 194.41 °C and 324.56 °C for Nylon12, and 271.72 °C for Nylon11 (comparing range of degradation from the DTG results in **Figures 20-22**).

The thermal degradation profiles show in **Figures 14-22** consist of two transitions corresponded to each component in the graft copolymer. The weight loss (TG) and DTG results of all the samples are shown in **Table 8**.

Based on DTG, the first peak is the degradation temperature of grafted polymer, and the latter peak is the degradation temperature of polystyrene (**Figure J1**). The degradation temperature of polystyrene is about 406 °C, hence the grafted polymers influence the shifting to lower degradation temperature of polystyrene in **Table 8**.

The DTG curves of PS-g-PCL samples (**Figures 14-16**) showed an intense first endothermic reaction about 35-370 °C with mass loss 49.0%, 56.0%, and 64.8% (PS: PCL = 1:1, 1:2 and 1:3, respectively) when it was subtracted percentage of contamination, mass loss were 36.4%, 41.9%, and 47.7%, respectively and second at 388.5-465.2 °C with mass loss 40.2%, 31.8%, and 25.6% (PS: PCL = 1:1, 1:2 and 1:3, respectively) when it was subtracted percentage of contamination, mass loss were 21.7%, 42.6%, and 62.2%, respectively The first DTG peak is considered to be the result of thermal degradation of poly(ε-caprolactone). Sivalingam, *et al.* (2004) investigated the thermal degradation of binary physical mixtures and copolymer of poly(ε-caprolactone), poly(DL-lactide), poly(glycolide). The PCL (M_n =80,000) results showed onset temperature about 275 °C, maximum decomposition peak temperature 402 °C, and complete degradation temperature (0%char yield) over 475 °C. PS-g-PCL in ratio 1:1, produced the second DTG peak (365-452 °C) as high as the first one (284-365 °C). Moreover, the degradation peaks of PS-g-PCL in ratio1:2 and 1:3 (the second peak ranged 388-450 °C and 370-450 °C, respectively) is lower than their first peaks (284-388 °C and 299-370 °C, respectively). Residue percentage of PS-g-PCL in ratio 1:1, 1:2, and 1:3 showed 10.8%, 12.2%, and 9.4%, respectively. Residue is the part of PS or backbone polymer.

DTG curves of PS-g-PLA samples (**Figures 17-19**), e.g. lactide11, showed the first peak at 35-300 °C with mass loss of 34.3% and a second at 300-490°C with a mass loss between 44.7%. Moreover, the first peak is lower than the second peak for lactide11. The degradation reaction of the first DTG peak in lactide12 and lactide13 (218-310 °C and 205-310 °C, respectively) were constantly higher than the second one (383-495 °C and 386-491 °C, respectively), with a mass loss 52.1% and 75.0% in first peak, 21.1% and 14.0% in second peak, respectively. The first peak, when it was subtracted percentage of contamination, mass loss were 17.9%, 22.9%, and 51.8%, respectively Sivalingam, *et al.* (2004) The PLA results (M_v = 1790-2850) showed onset temperature about 150 °C, maximum peak decomposition temperature 295 °C, and complete degradation temperature (0%char yield) over 350 °C. Then PLA as side chains were degrade completely in this experiment and residue percentage should be backbone polymer or PS (21.0%, 16.8%, and 10.3% in ratio 1:1, 1:2, and 1:3 of PS-g-PLA, respectively).

The DTG curves of PS-g-Nylon6 samples (**Figures 20-22**) showed an intense first degradation reaction about 35-290 °C with mass loss 24.0%, 26.5%, and 55.5% (PS: Nylon6 = 1:1, 1:2 and 1:3, respectively) and second at 300-450 °C with mass loss 56.5.1%, 60.2%, and 35.5% (PS: Nylon6 = 1:1, 1:2 and 1:3, respectively). The first degradation peak is considered to be the result of thermal degradation of polycaprolactam. The second degradation peak is related to the degradation of polystyrene structure. ε-caprolactam11, caprolactam12, and caprolactam13 produced the first endothermic reaction at 100-250 °C, 100-291 °C, and 90-252 °C, respectively which are lower than the second ones (302-448 °C, 300-491 °C, and

310-450 °C, respectively). Pramoda, *et al.* (2003) showed the onset temperature for the degradation is 12 °C higher for Nylon6-2.5 wt% clay nanocomposite compared to that of neat nylon6 and clay weight loss between 200 and 500 °C. Nylon6 pure remained 0% char yield at 500 °C. Then PS-g-Nylon6 can start degradation in room temperature and nylon6 degrade completely in this experiment (35-590 °C). Residue percentage in PS-g-Nylon6 should be backbone polymer or PS. PS-g-Nylon6 in ratio 1:1, 1:2, and 1:3 showed residue percentage 19.5%, 13.3%, and 9.0%, respectively.

All DTG curves appeared the shoulder peak before the first peak that is additive or low molecular weight polymer degradation. Franco, *et al.* (2004) studied degradation of polycaprolactone and starch blend, and composites with sisal fiber. DTG curved showed the broad peak about 100-230 °C, due to the loss of low weight compounds such as natural additives.

DMA curves of PS-g-PLA (see **Figures 34-36**) in ratio 1:1 and 1:2 showed T_g about 109.86, 106.47 °C, respectively, but its ratio 1:3 did not show T_g. PS-g-PLA in ratio 1:1 showed storage modulus (G') is higher than loss modulus (G") in 30-70 °C, then it is more solid-like at room temperature in accordance to the presence of crystallinity. PS-g-PLA in ratio 1:2, without crystallinity, showed storage modulus is lower than loss modulus in 30-130 °C (experiment range), it is stiff in room temperature but softer than in ratio 1:1 because T_g is higher than room temperature. PS-g-PLA in ratio 1:3 is more rubbery like with higher modulus than the other twos. Both G' and G'' are comparable until 88 °C, tanδ and loss modulus becomes gradually higher than storage modulus indicating the softening before flowing of material.

CONCLUSION

The molecular weight of the grafting-from copolymers increased with monomer feed ratio. Among the three copolymers, PS-g-PCL showed the highest MW. PS-g-PCL and 1:1 (monomer feed weight ratio) PS-g-PLA contained some crystallinity while PS-g-Nylon6 was amorphous (like soft solid or highly viscous liquid) for all monomer feed ratios. Grafting number and average grafting length determined by NMR, weighting, and TGA-DTG increased with monomer feed ratio and, as result, enhanced amorphous structure and plasticizing effect. PS-g-PCL showed the lowest T_g (soft solid) and the lowest T_d among the three copolymers and its T_g and T_d tended to increase with increasing ε-caprolactone amount. PS-g-PLA exhibited relatively high T_g and thus presented as rigid solid with moderate T_d. Moreover, PS-g-PLA exhibited increase in modulus with lactide content but its storage and loss moduli were comparable within a wide range of temperature. PS-g-PCL and PS-g-Nylon6 became softer with increasing caprolactone and caprolactam content in accordance to better solubility in water and 0.1 wt% aqueous salt solution. On the other hand, PS-g-PLA showed better dissolution in aqueous salt solution than in water. The three copolymers were completely dissolved in chloroform (PS-g-PCL was the best) and swollen in methanol, propanol, and acetic acid (pH4).

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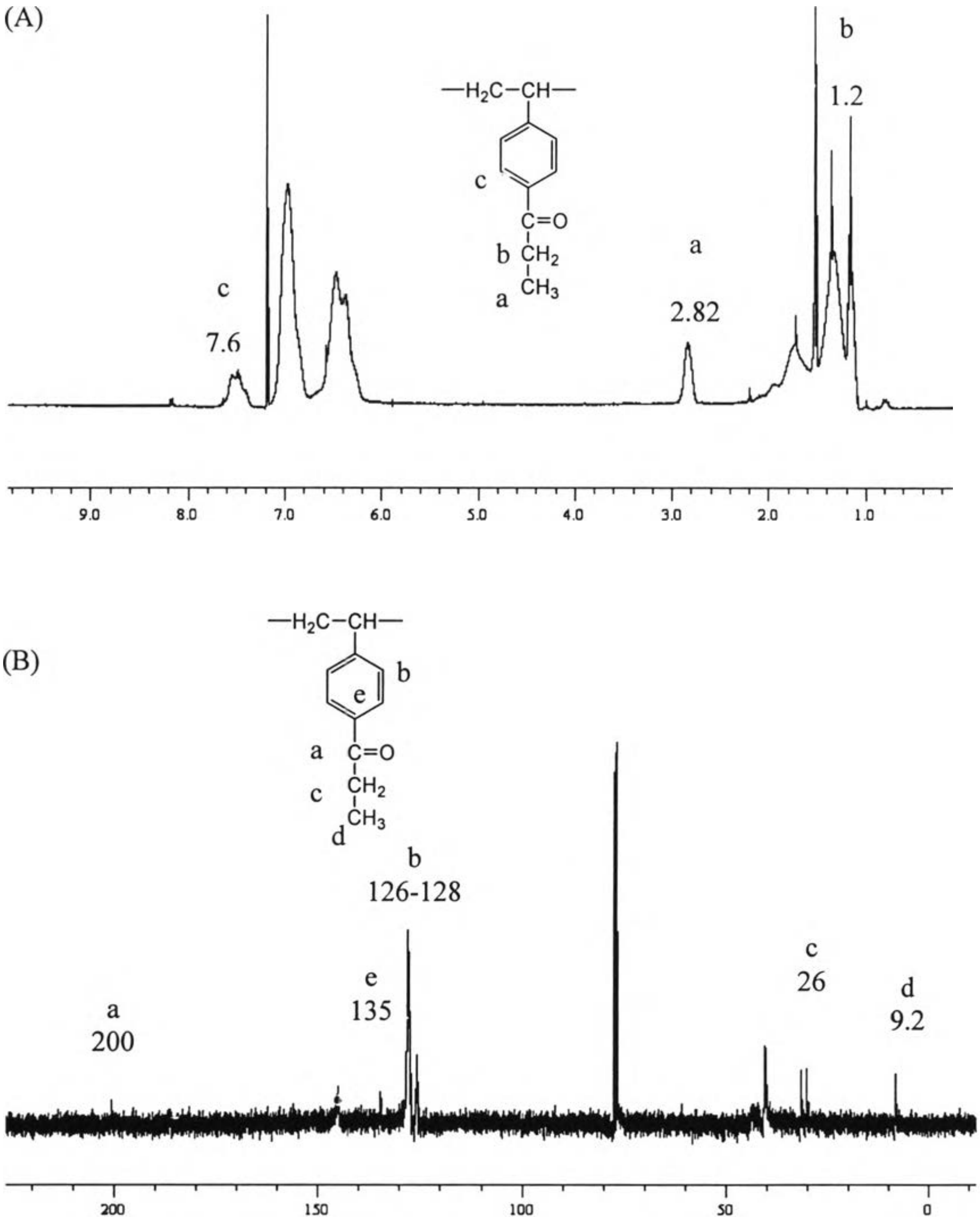
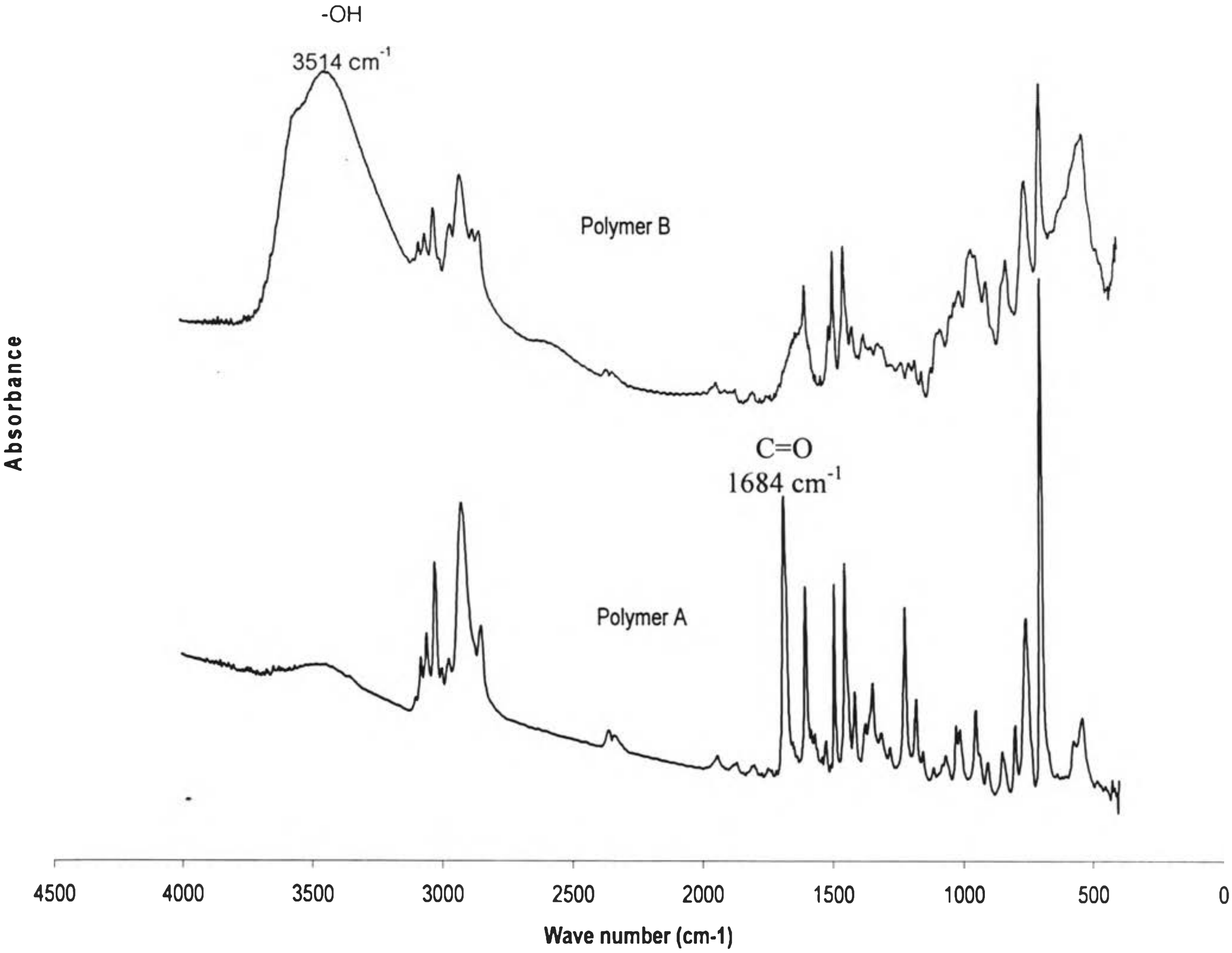


Figure 4.1 (A) ^{1}H and (B) ^{13}C NMR spectra of ring-acylated polystyrene.



e 4.2 The FTIR spectra of ring-acylated polystyrene (polymerA) and polystyrene ring substituted with 1-xypropyl group (polymer B).

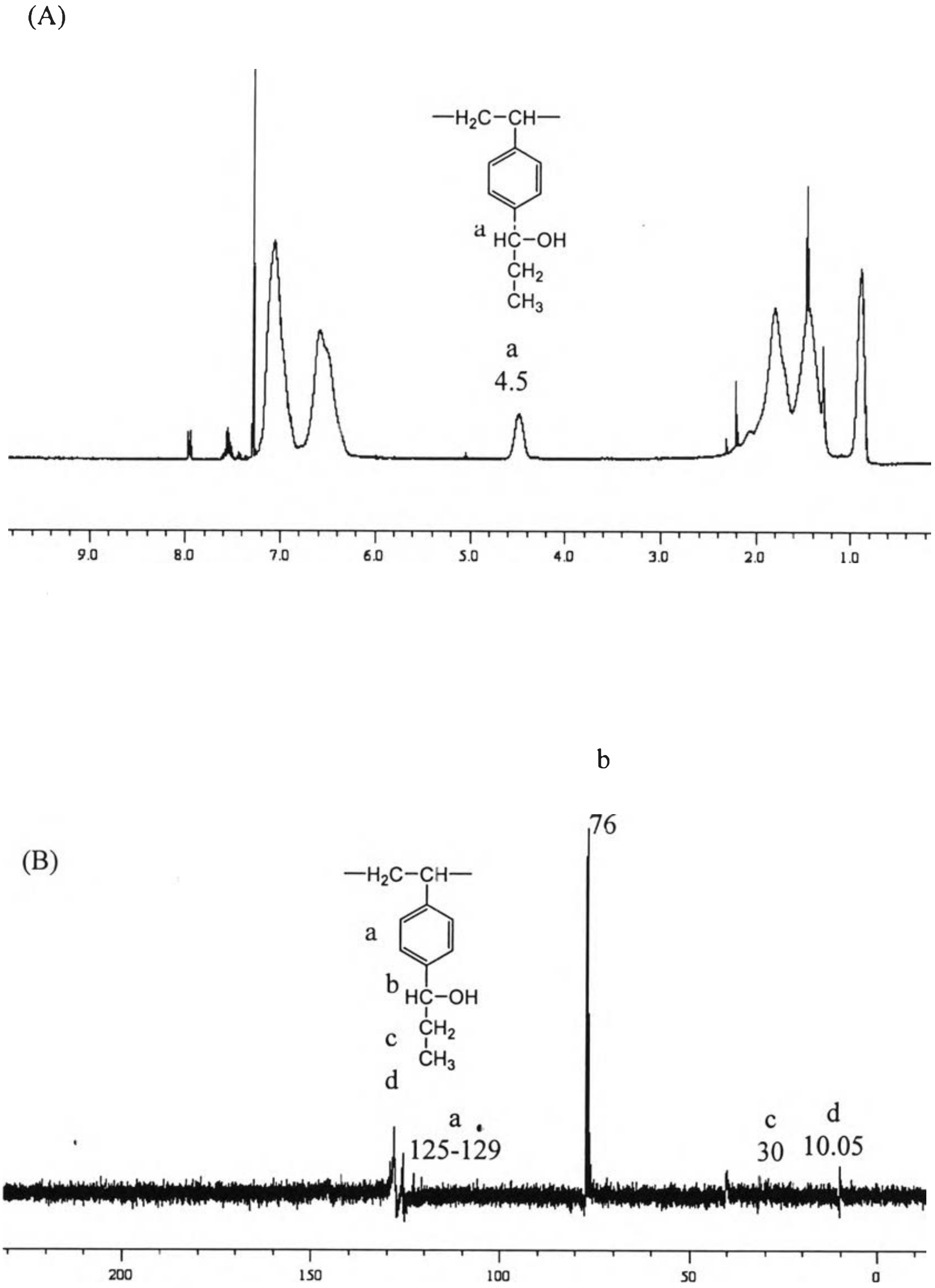


Figure 4.3 (A) ^{1}H and (B) ^{13}C NMR spectra of polystyrene ring substituted with 1-hydroxypropyl group.

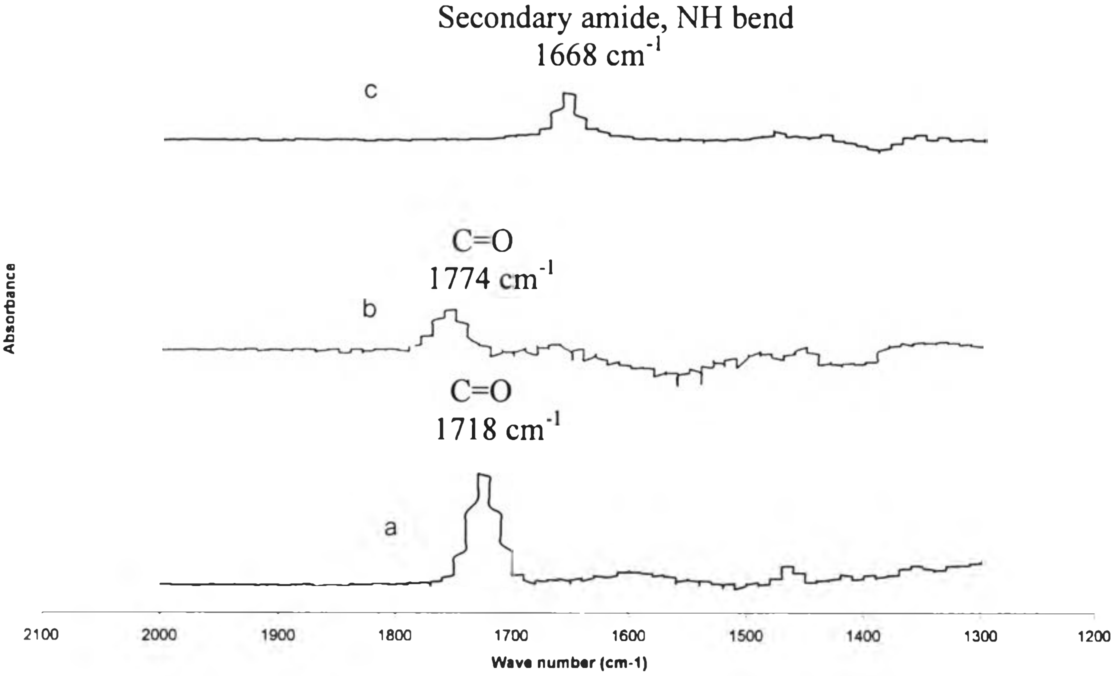


Figure 4.4 The FTIR/HATR spectra for polystyrene grafted with (a) ε-caprolactone, (b) DL-lactide, (c) caprolactam or nylon6.

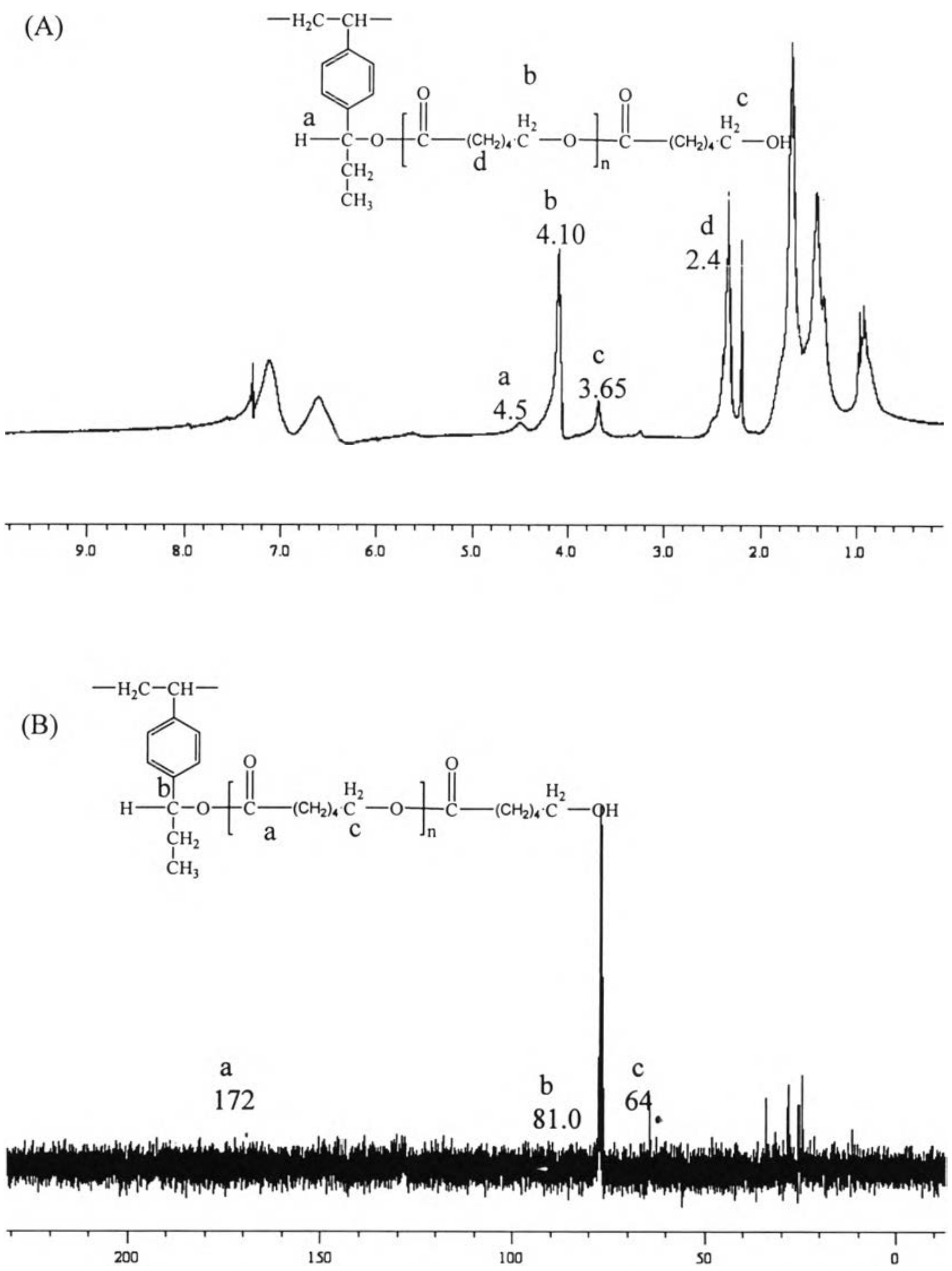


Figure 4.5 (A) ^{1}H and (B) ^{13}C NMR spectra of polystyrene-graft-poly(ε-caprolactone) (ratio 1 :1).

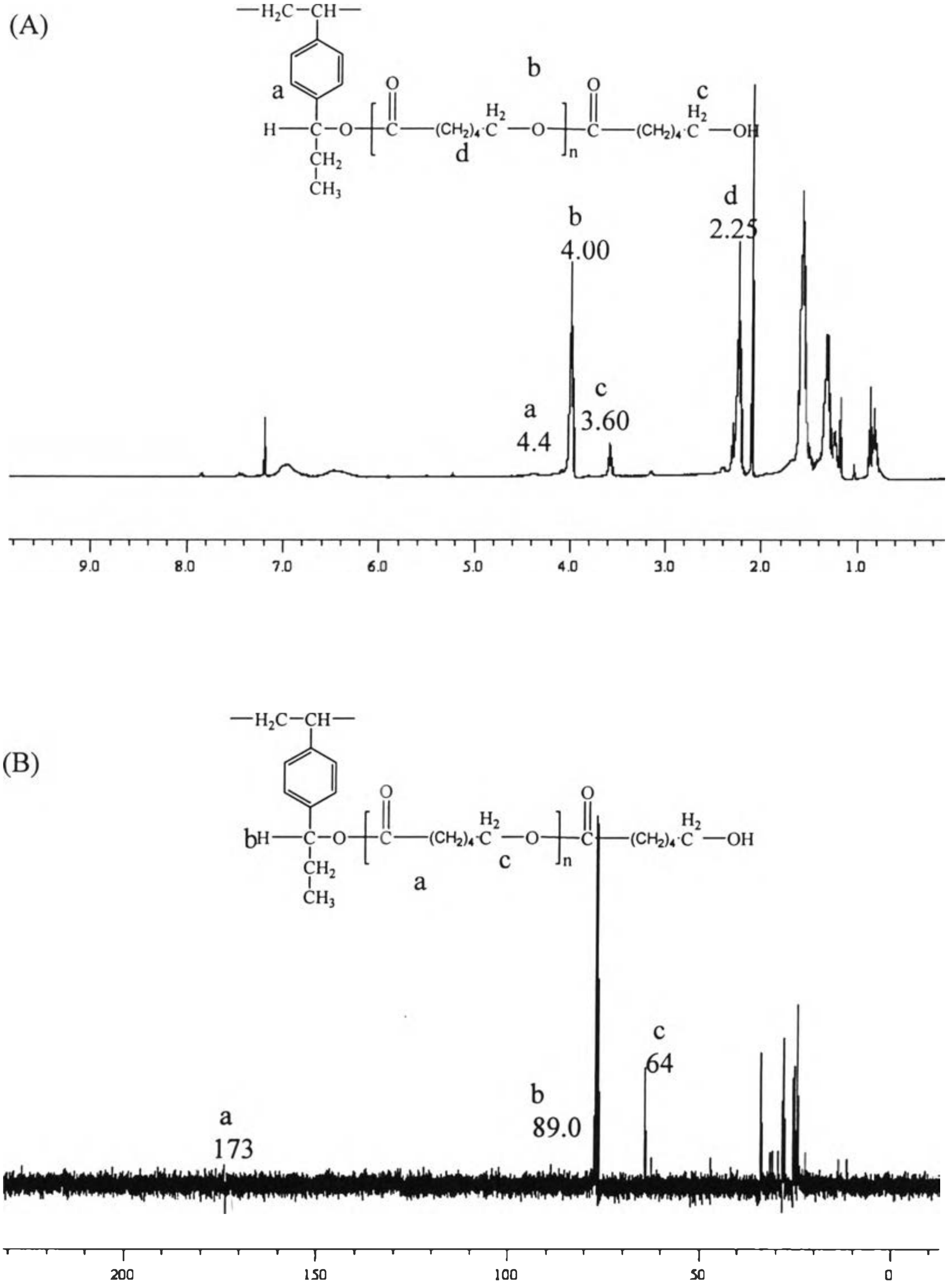


Figure 4.6 (A) ^{1}H and (B) ^{13}C NMR spectra of polystyrene-graft-poly(ε-caprolactone) (ratio 1 :2).

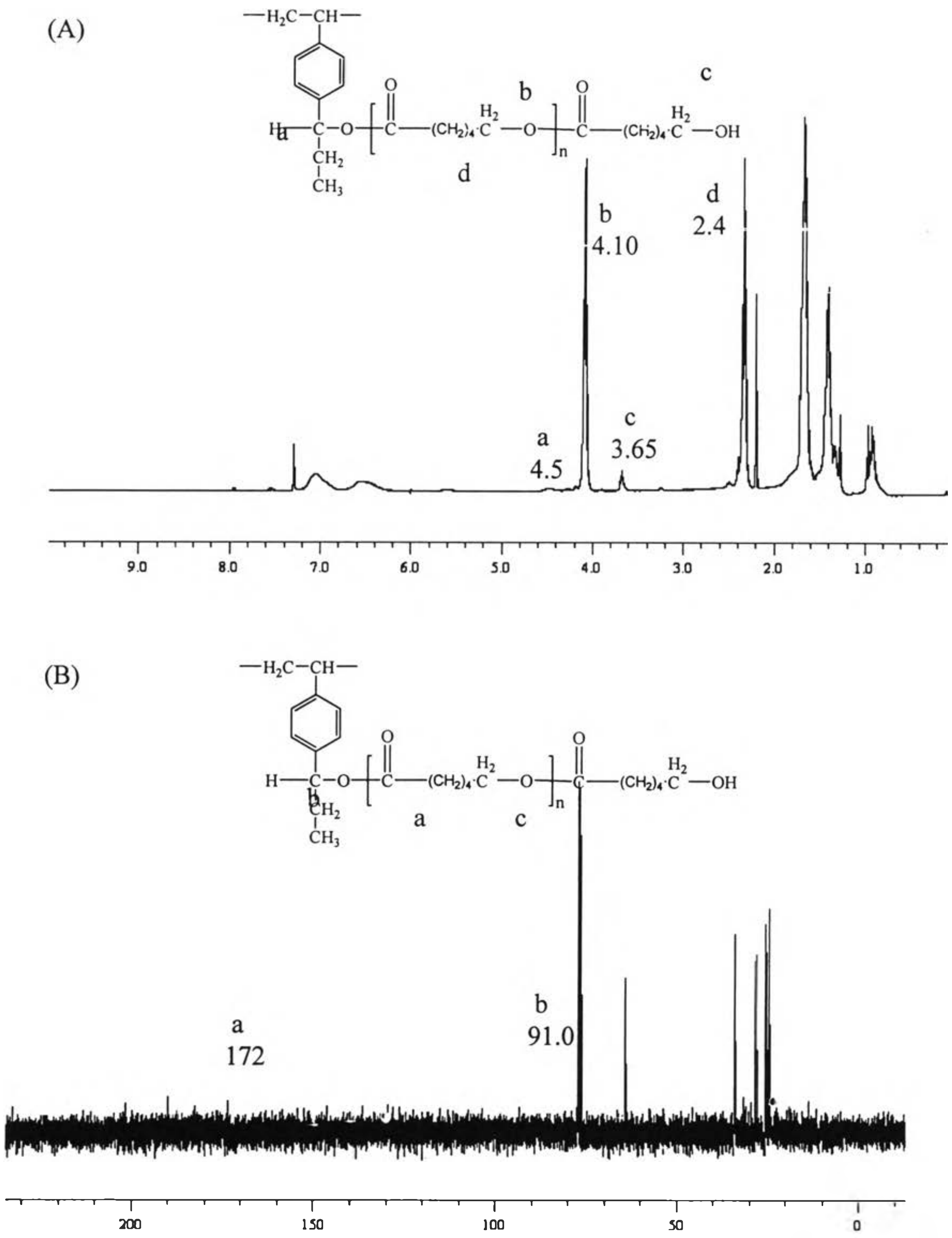


Figure 4.7 (A) ^{1}H and (B) ^{13}C NMR spectra of polystyrene-graft-poly(ε-caprolactone) (ratio 1 :3).

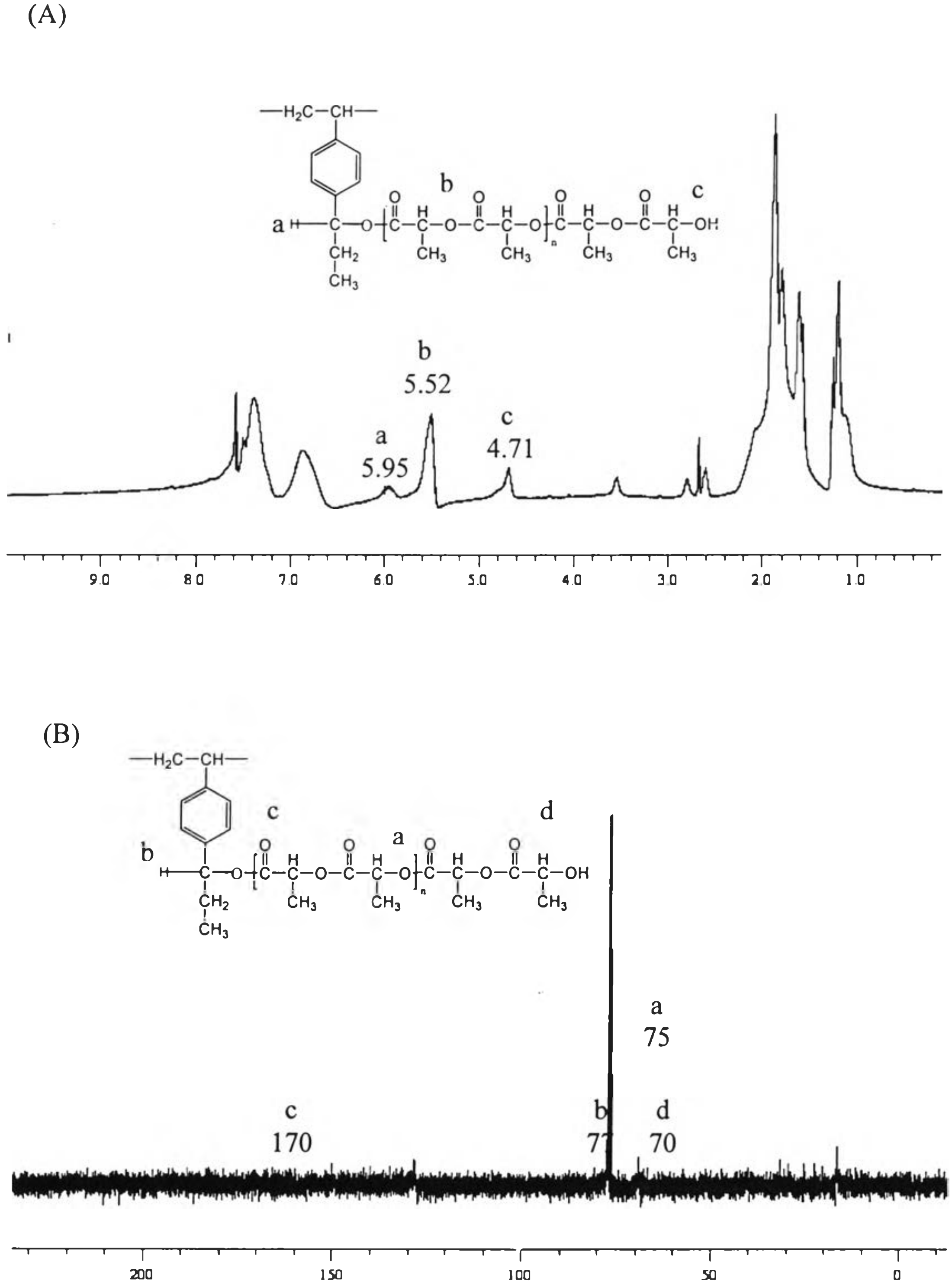


Figure 4.8 (A) ^{1}H and (B) ^{13}C NMR spectra of polystyrene-graft-poly(DL-lactide) (ratio 1 :1).

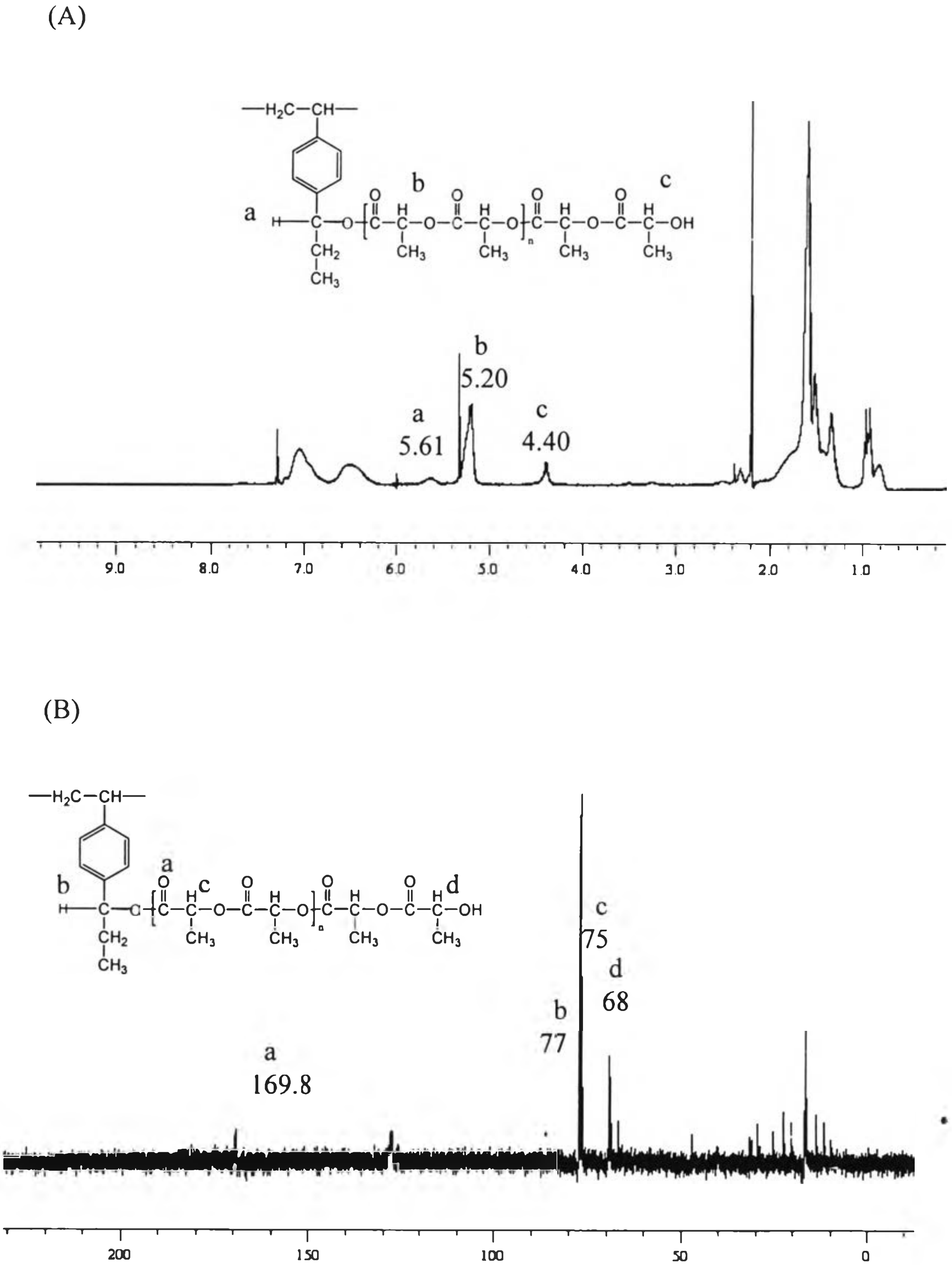


Figure 4.9 (A) ^1H and (B) ^{13}C NMR spectra of polystyrene-graft-poly(DL-lactide) (ratio 1 :2).

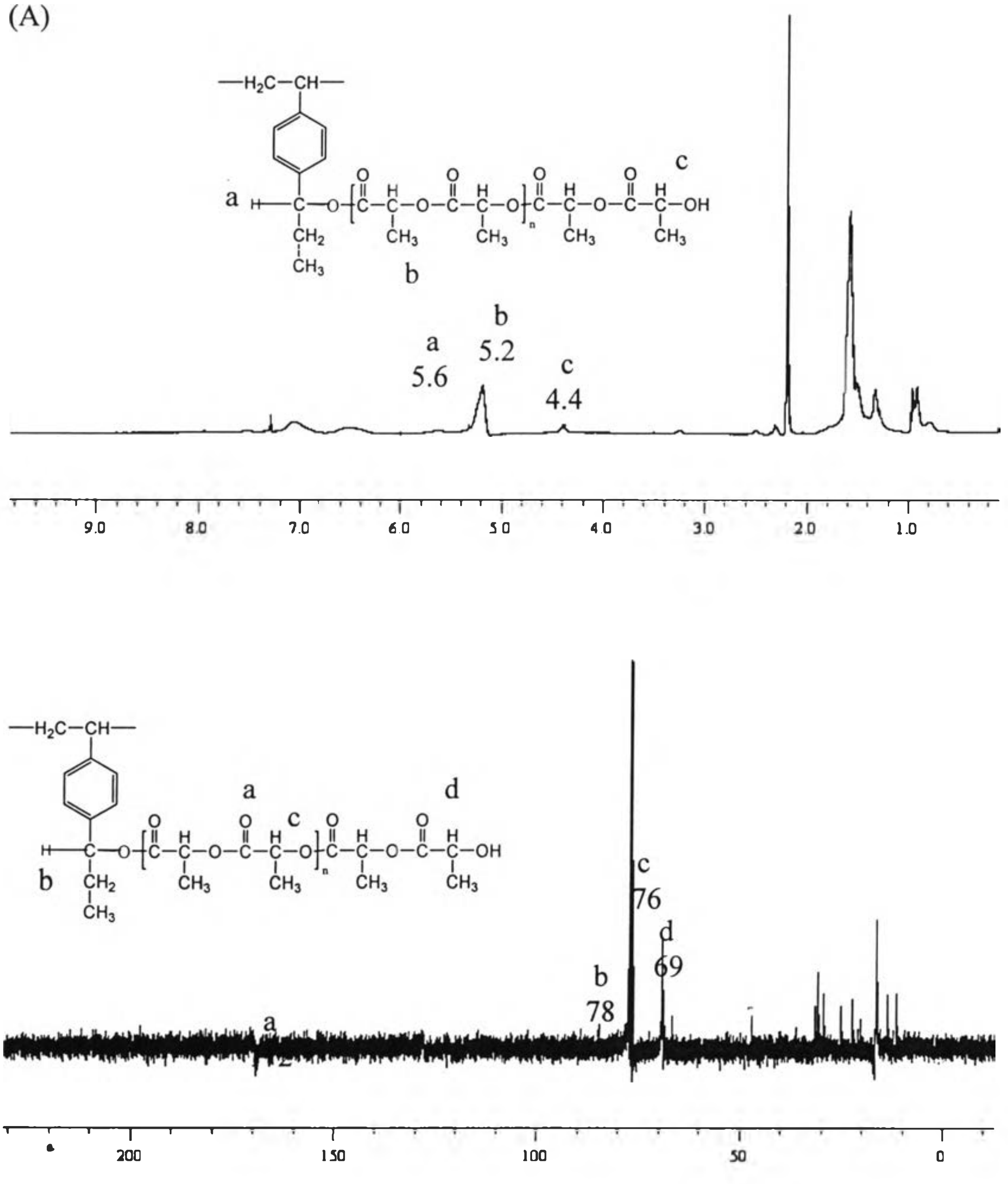


Figure 4.10 (A) ^{1}H and (B) ^{13}C NMR spectra of polystyrene-graft-poly(DL-lactide) (ratio 1 :3).

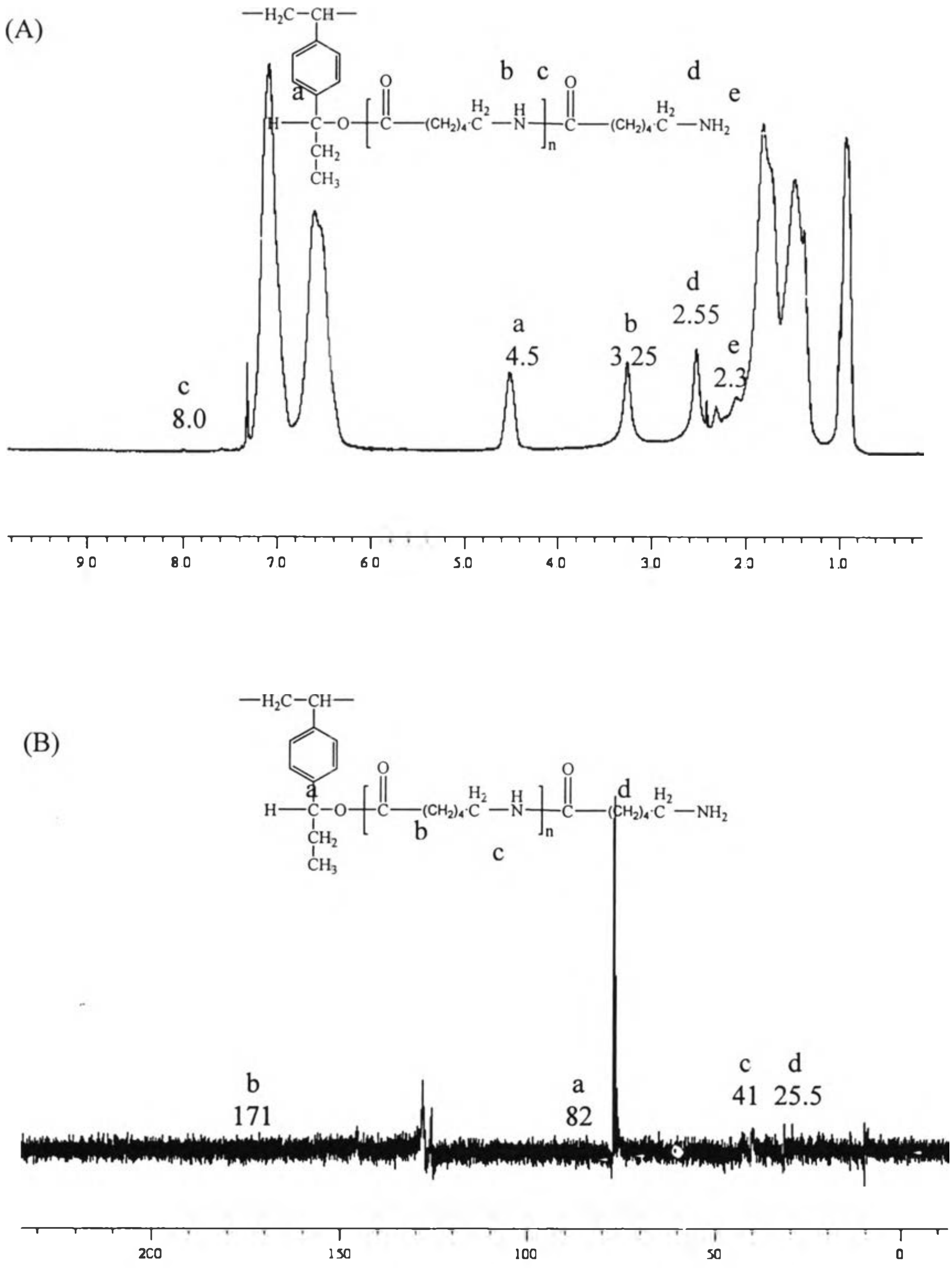


Figure 4.11 (A) ^1H and (B) ^{13}C NMR spectra of polystyrene-graft-polycaprolactam (ratio 1 :1).

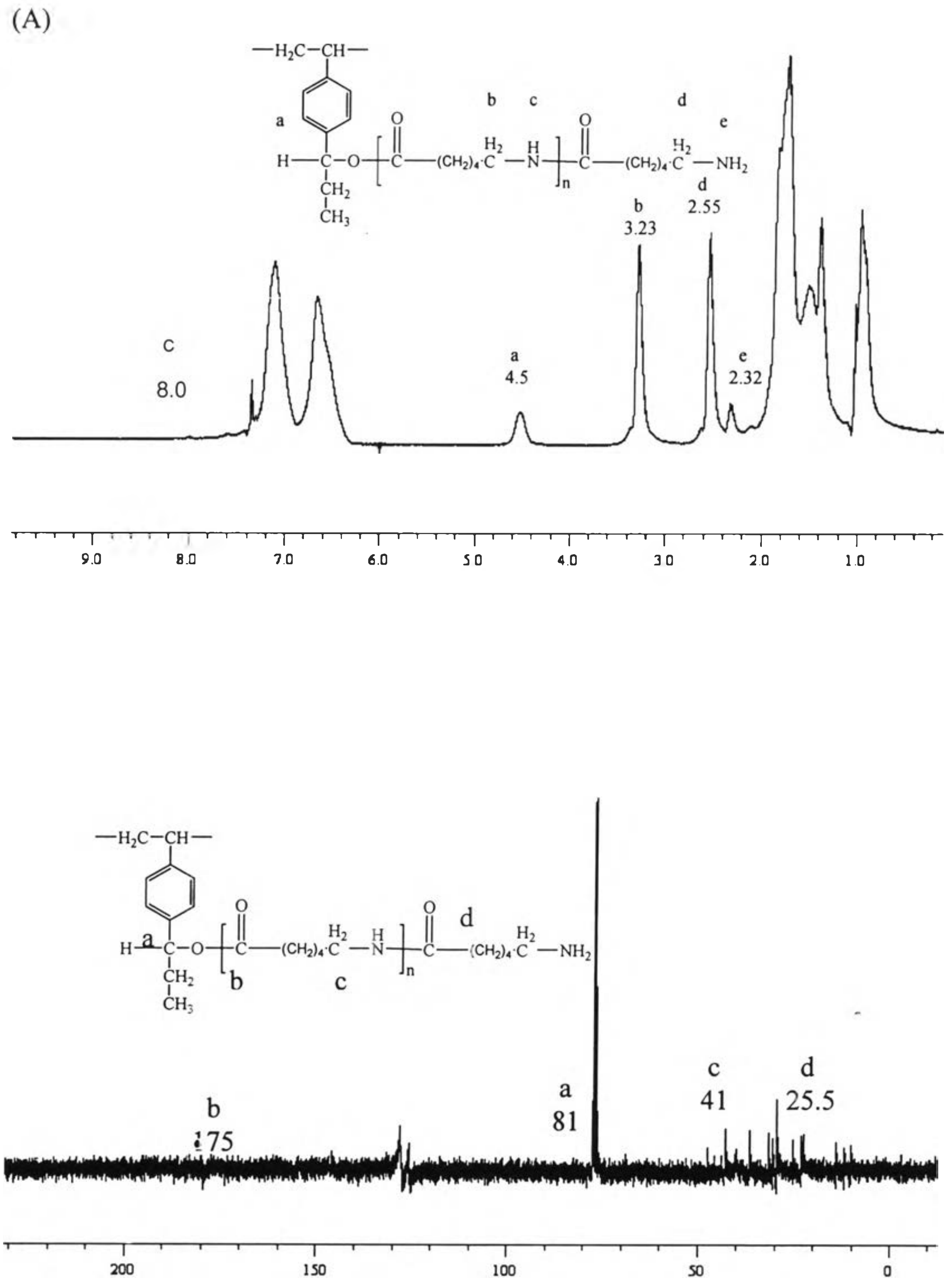


Figure 4.12 (A) ^1H and (B) ^{13}C NMR spectra of polystyrene-graft-polycaprolactam (ratio1 :2).

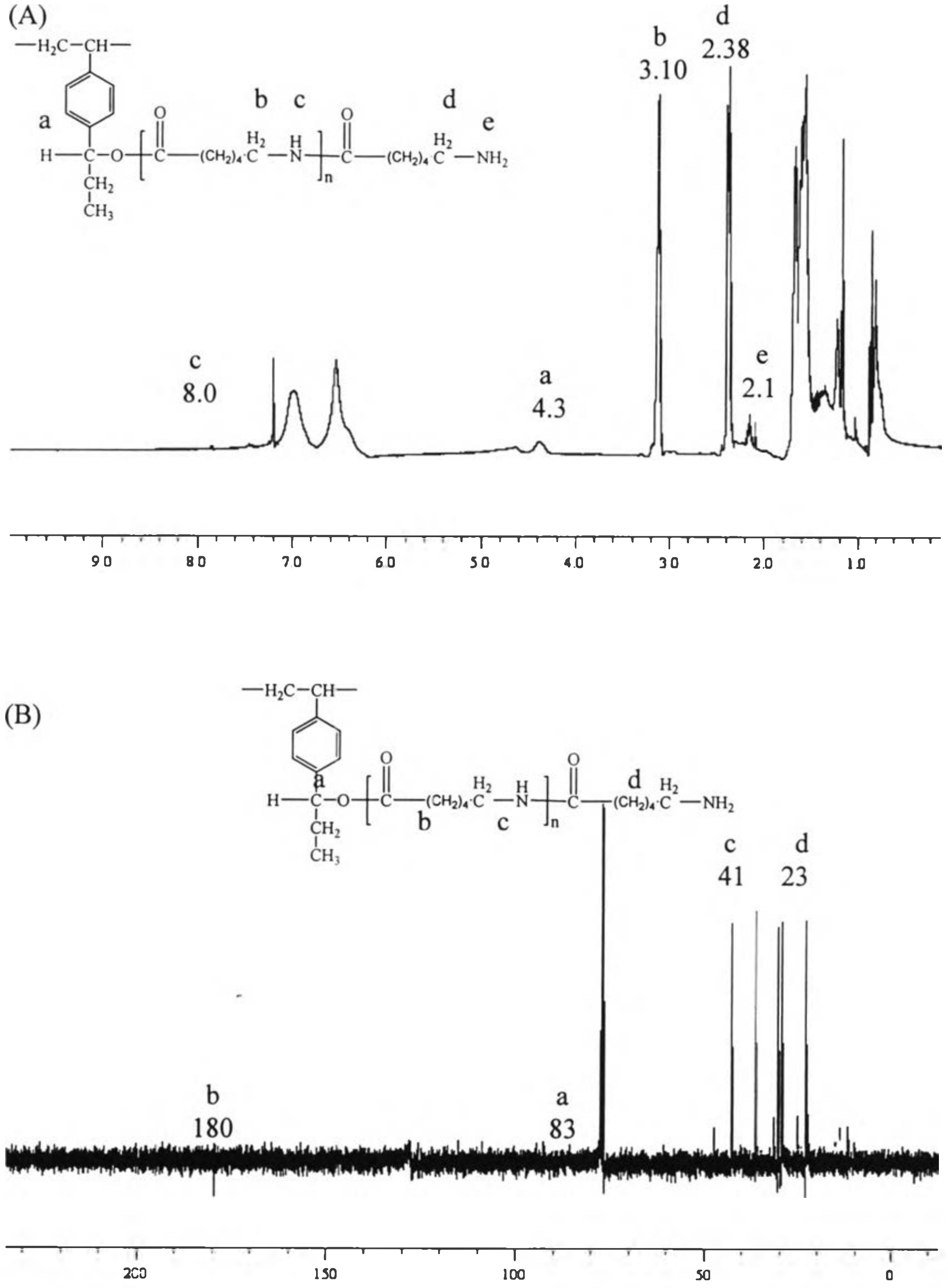


Figure 4.13 (A) ^1H and (B) ^{13}C NMR spectra of polystyrene-graft-polycaprolactam (ratio 1 :3).

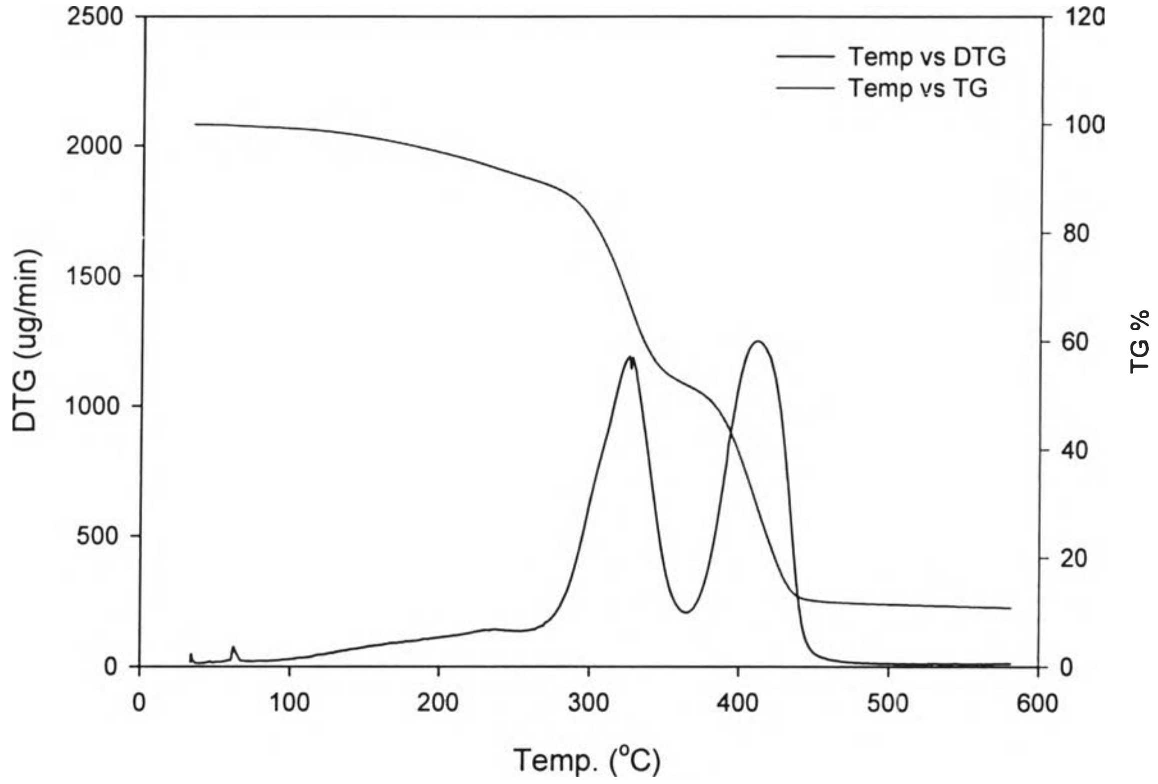


Figure 4.14 TG-DTA spectra of polystyrene-graft-poly(ε-caprolactone) in ratio 1:1.

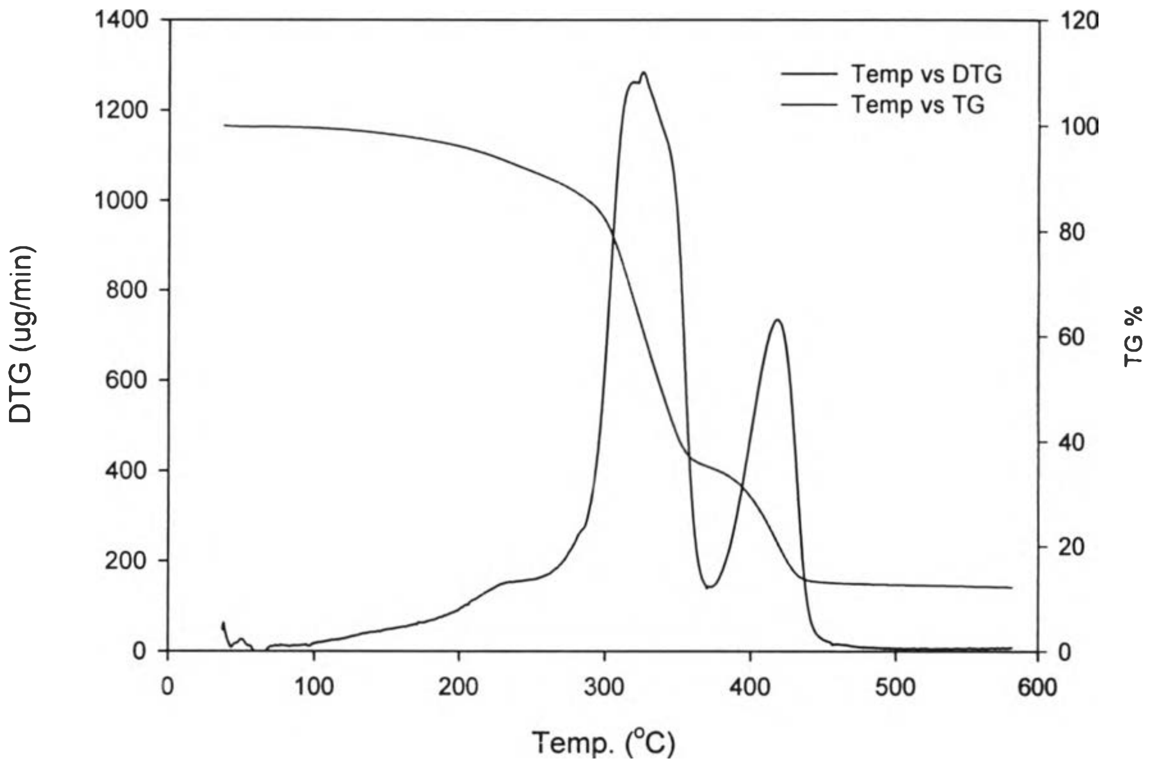


Figure 4.15 TG-DTA spectra of polystyrene-graft-poly(ε-caprolactone) in ratio 1:2

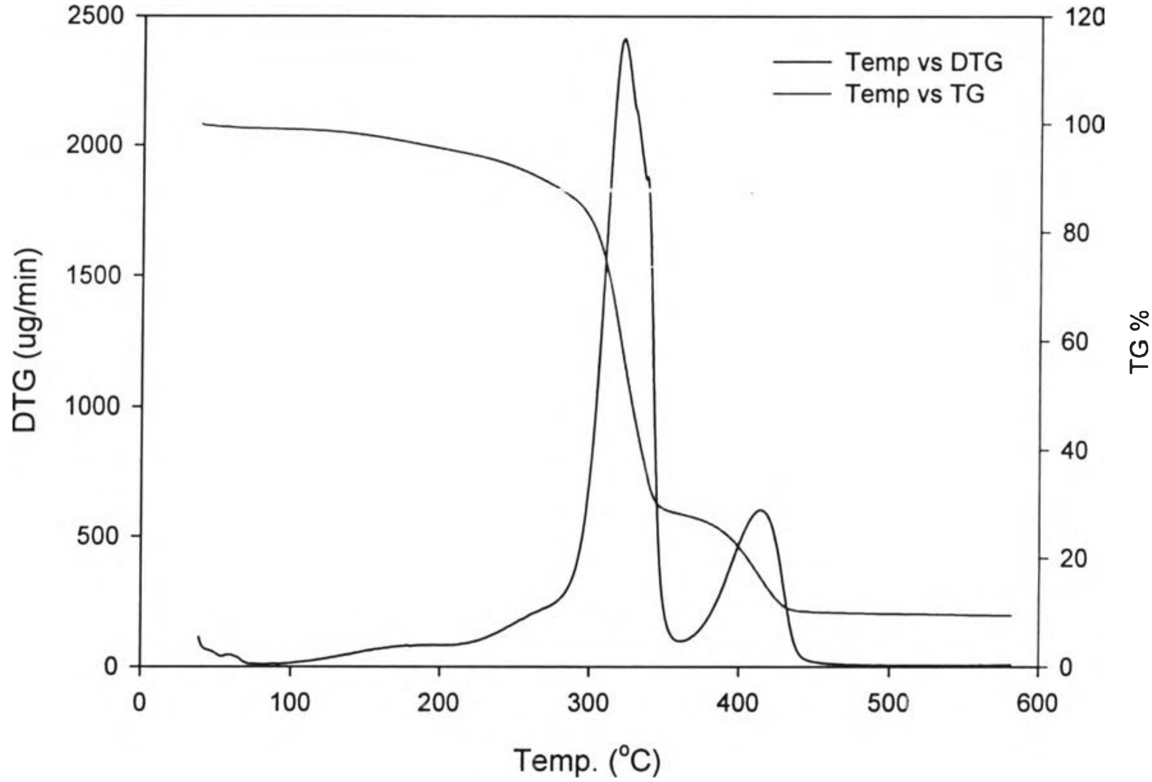


Figure 4.16 TG-DTA spectra of polystyrene-graft-poly(ε-caprolactone) in ratio 1:3.

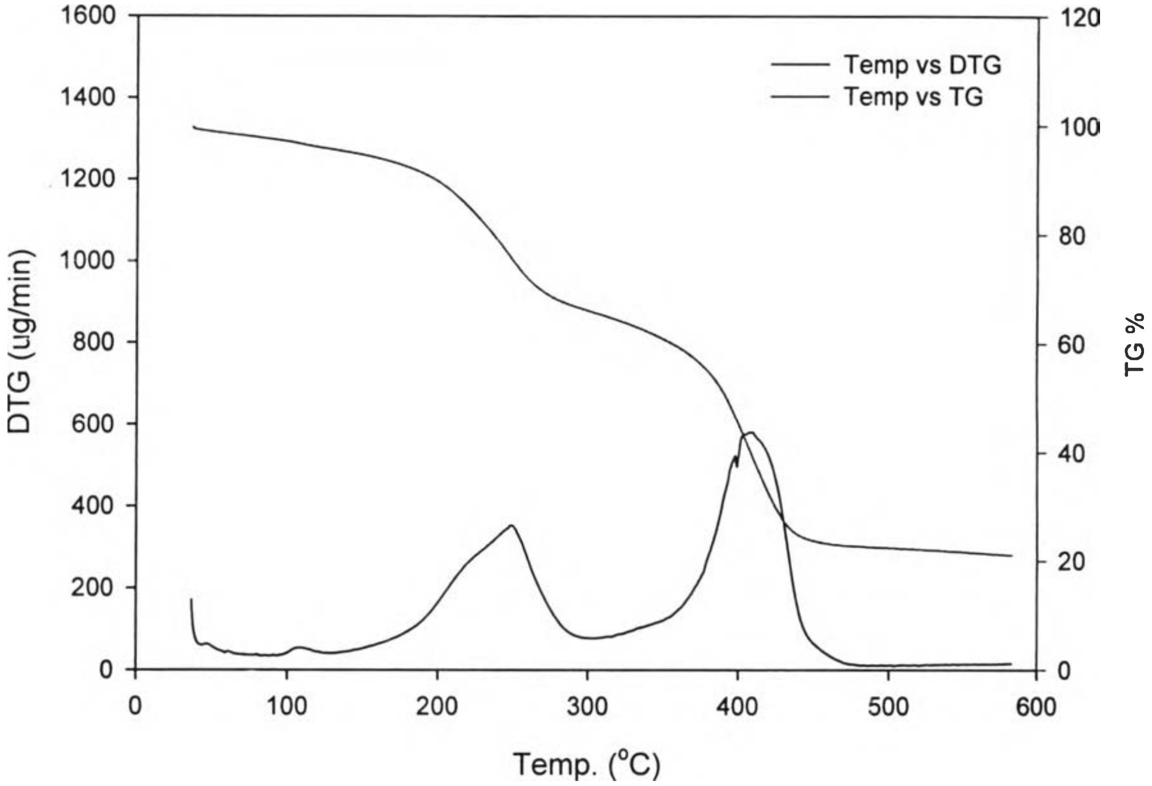


Figure 4.17 TG-DTA spectra of polystyrene-graft-poly(DL-lactide) in ratio 1:1.

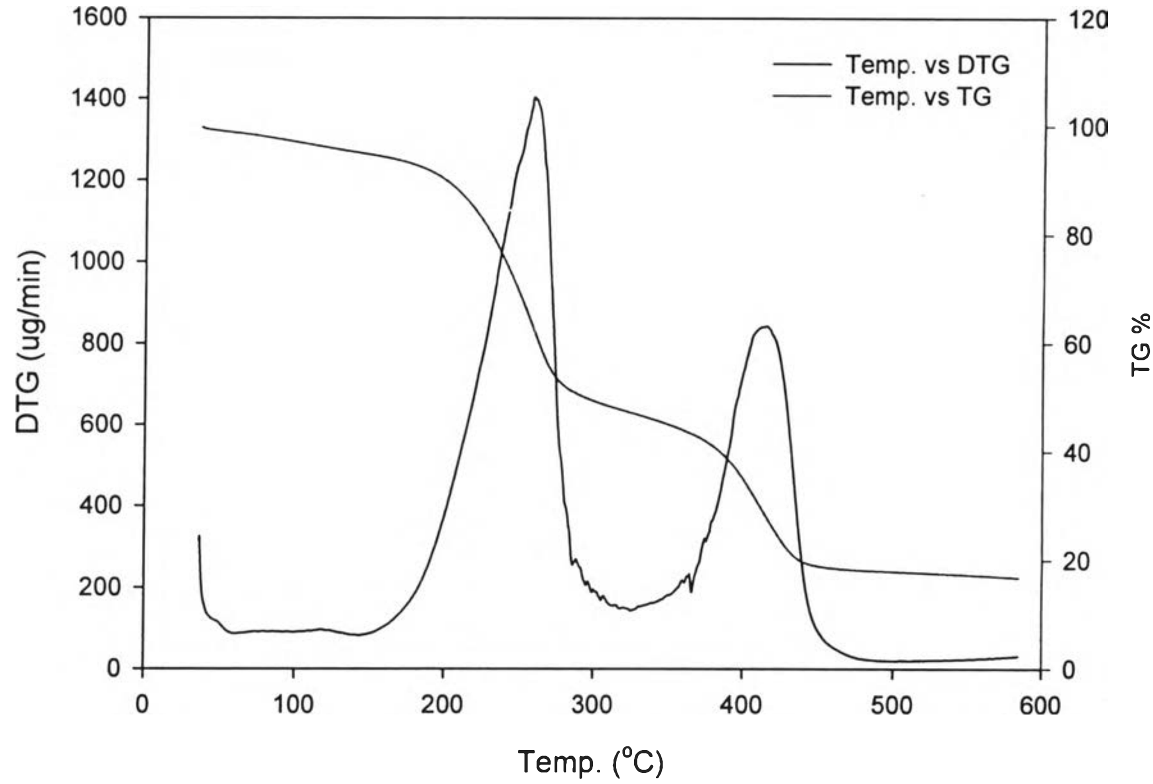


Figure 4.18 TG-DTA spectra of polystyrene-graft-poly(DL-lactide) in ratio 1:2.

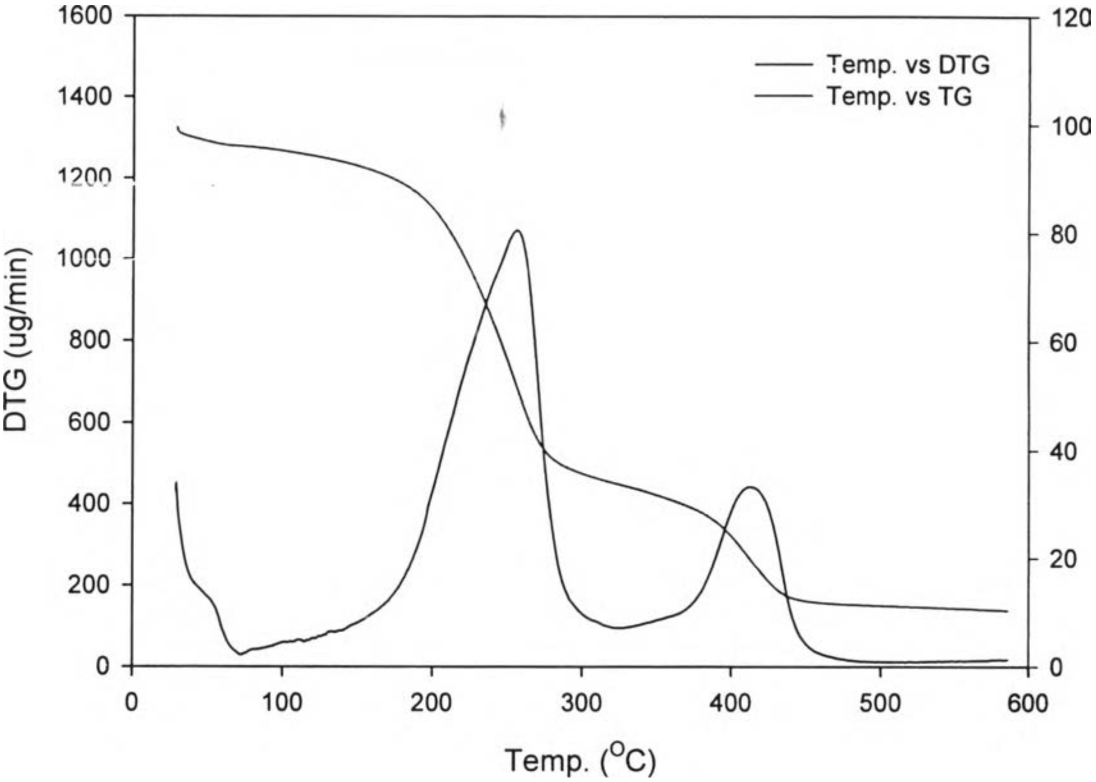


Figure 4.19 TG-DTA spectra of polystyrene-graft-poly(DL-lactide) in ratio 1:3.

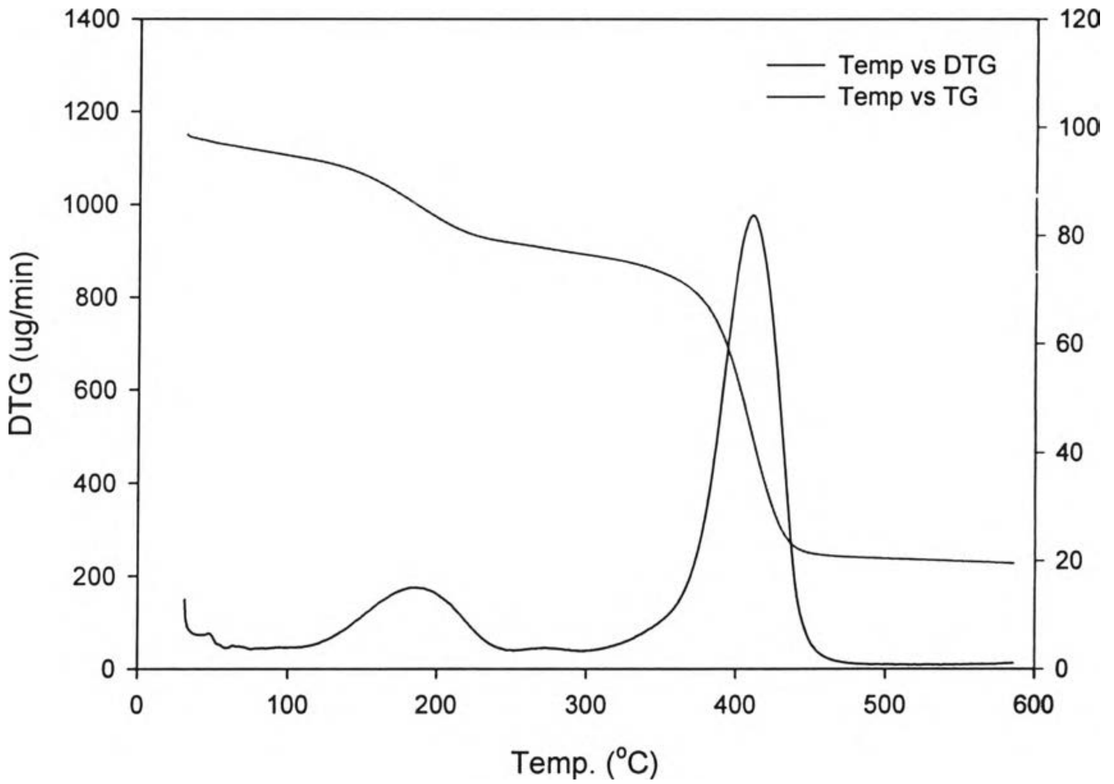


Figure 4.20 TG-DTA spectra of polystyrene-graft-polycaprolactam in ratio 1:1.

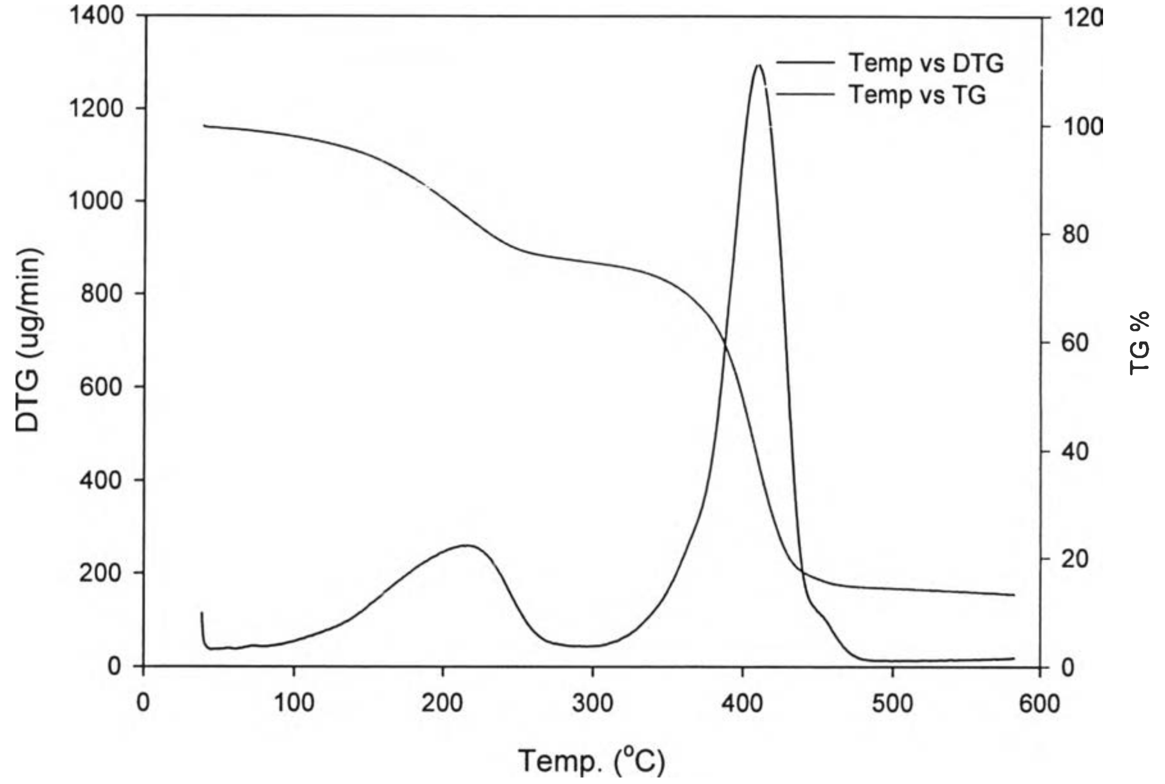


Figure 4.21 TG-DTA spectra of polystyrene-graft-polycaprolactam in ratio 1:2.

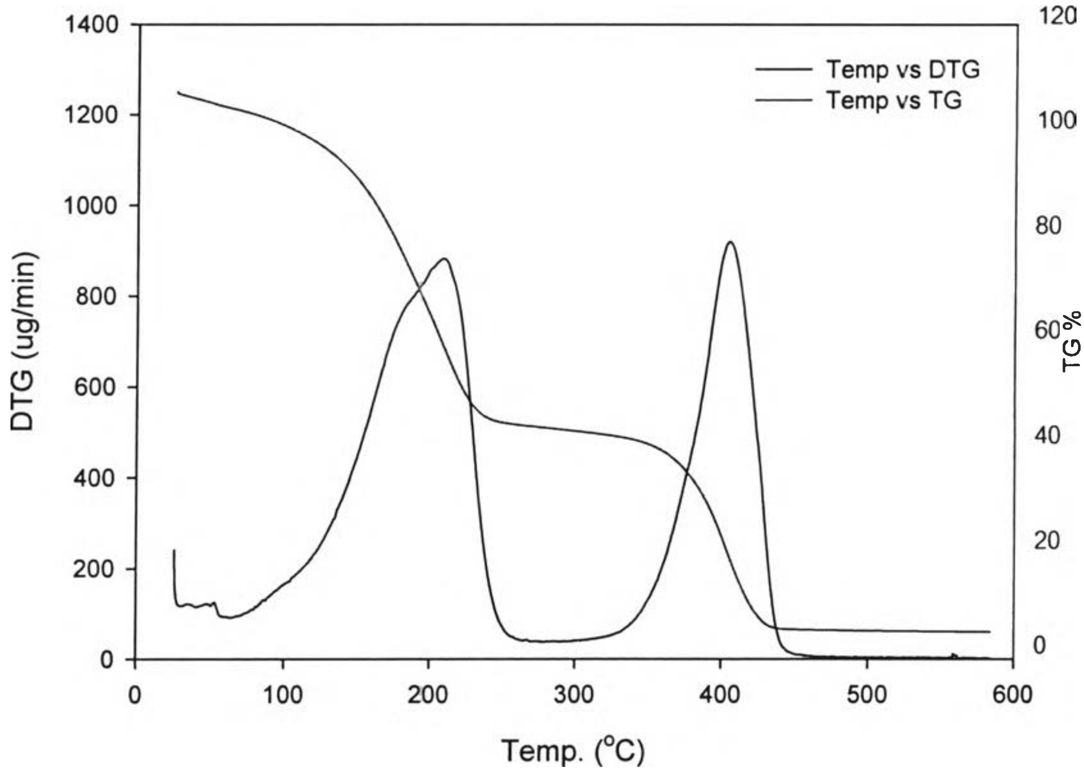


Figure 4.22 TG-DTA spectra of polystyrene-graft-polycaprolactam in ratio 1:3.

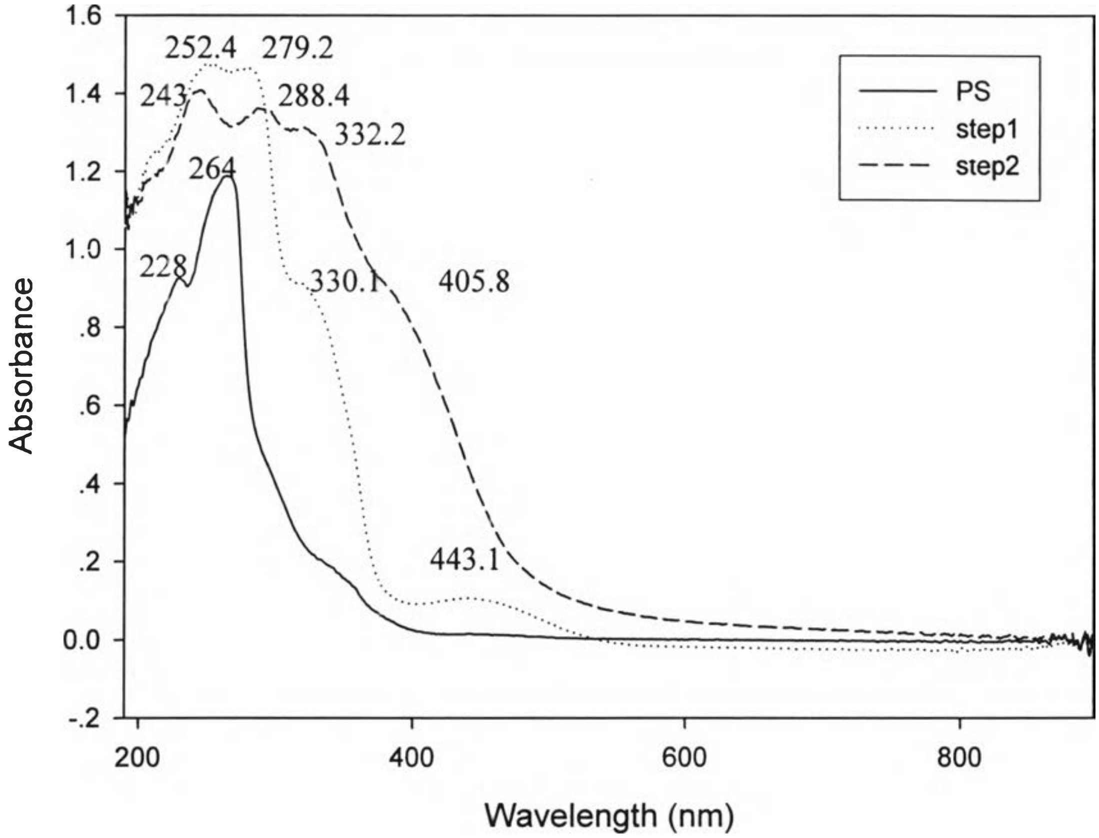


Figure 4.23 Absorption spectra of PS, polymer A and B.

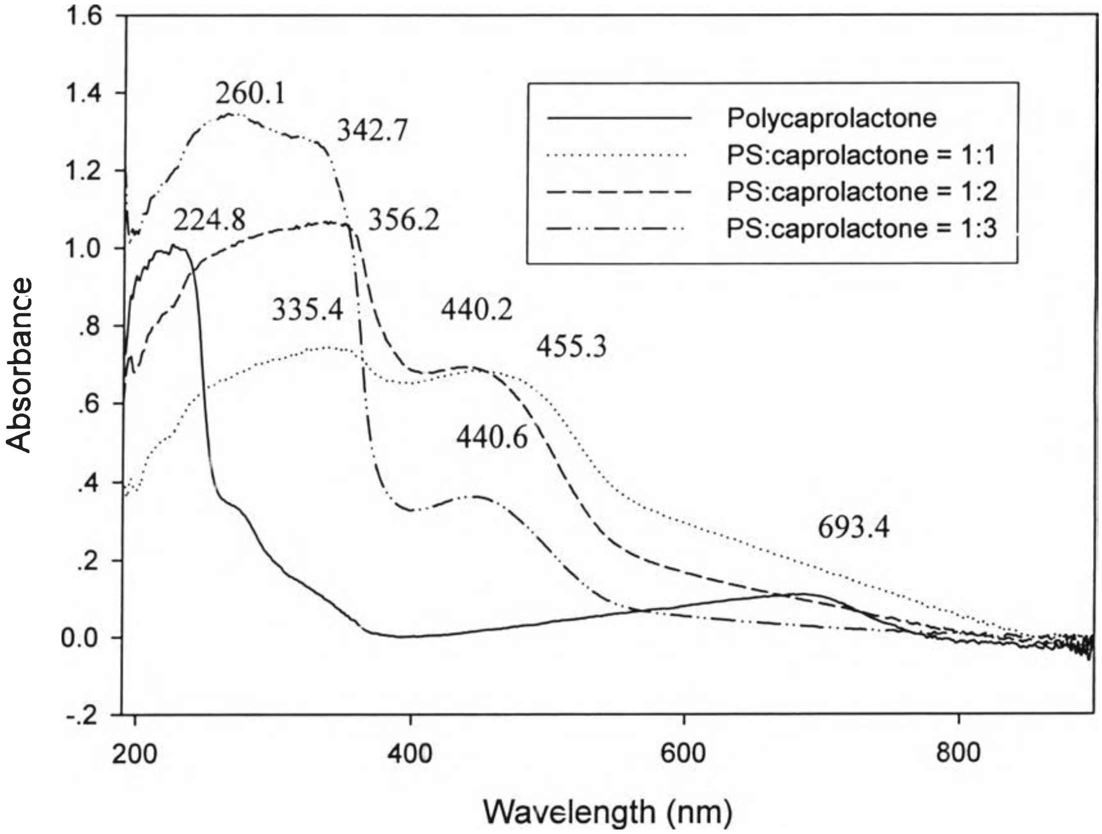


Figure 4.24 Absorption spectra of PS-g- PCL.

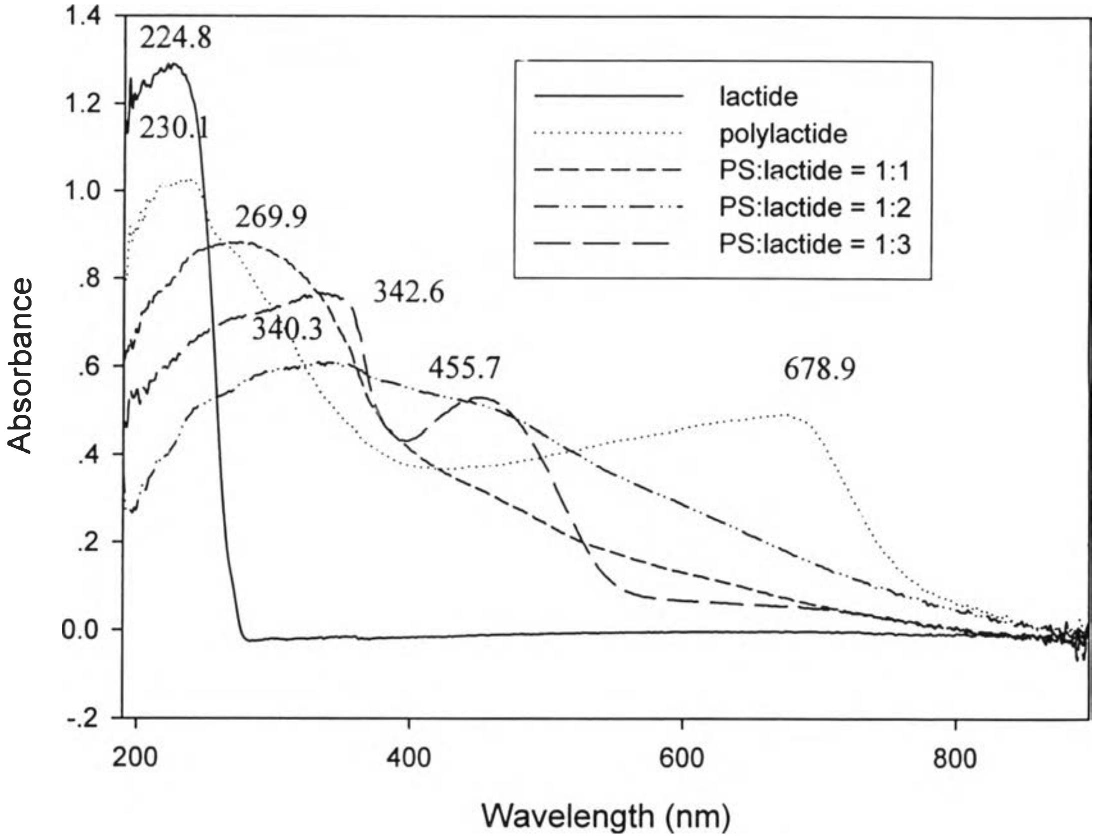


Figure 4.25 Absorption spectra of PS-g-PLA.

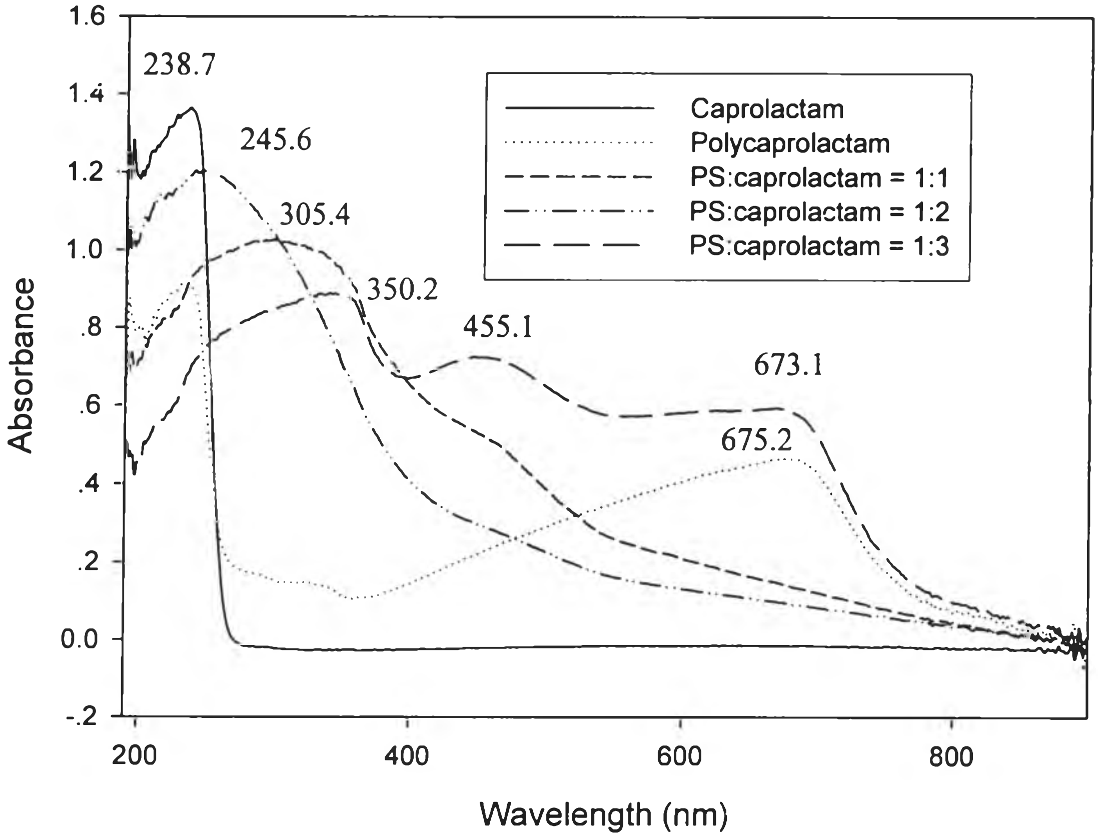


Figure 4.26 Absorption spectra of PS-g-Nylon6.

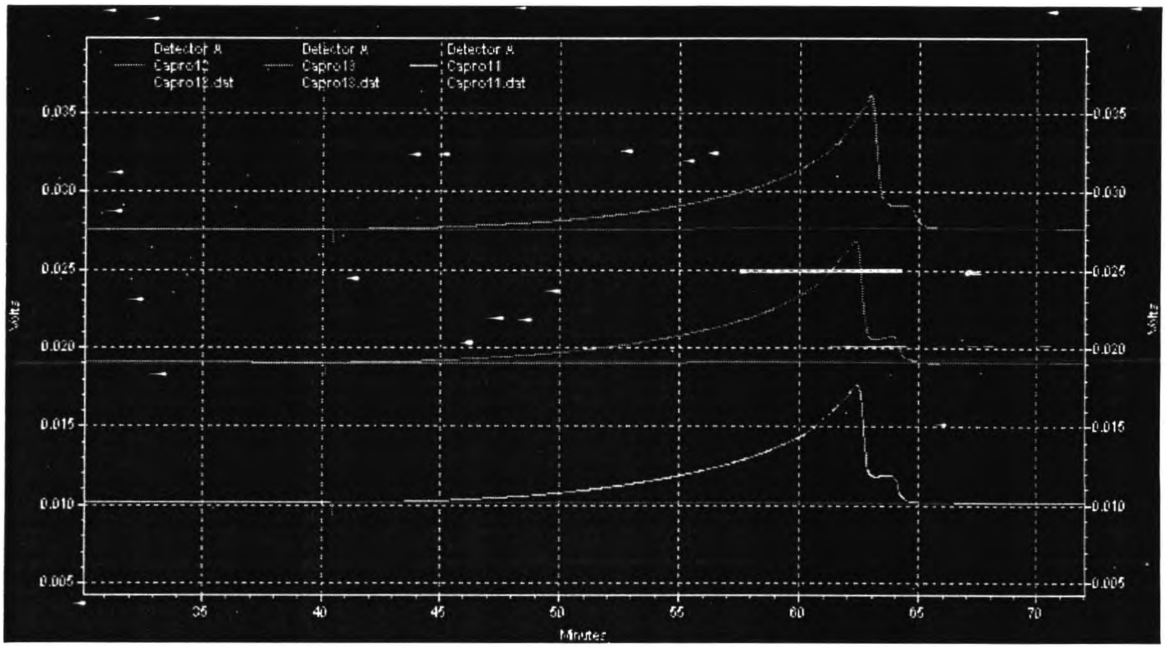


Figure 4.27 GPC curve of polymer in water that PS-g-PCL was dissolved over night.

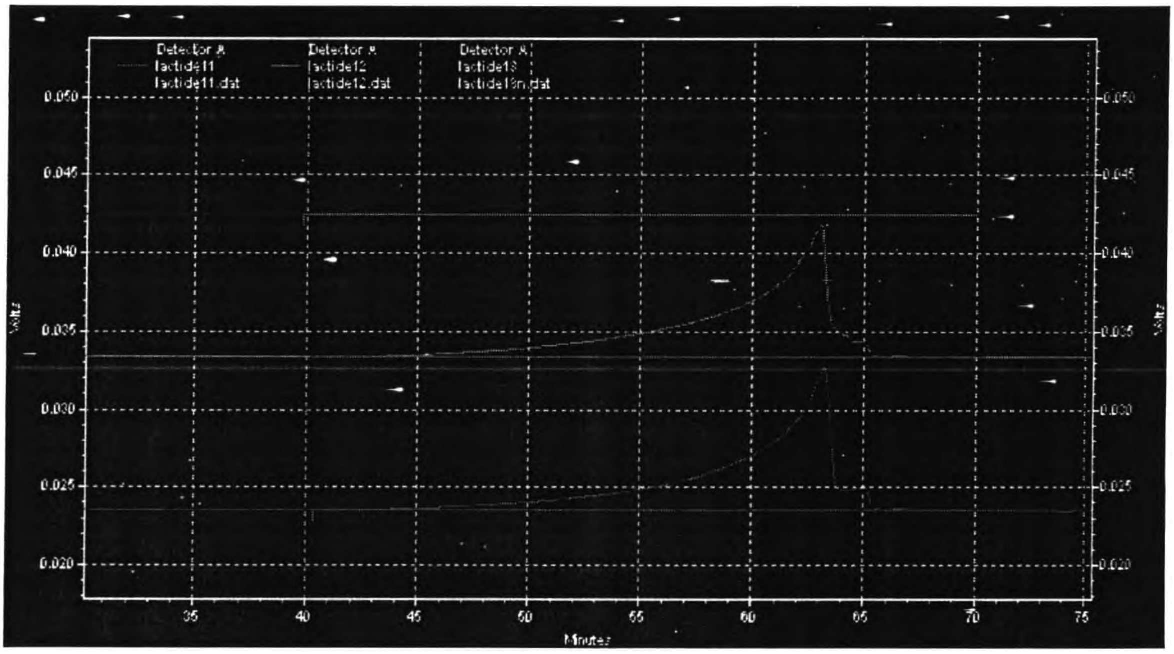


Figure 4.28 GPC curve of polymer in water that PS-g-PLA was dissolved over night.

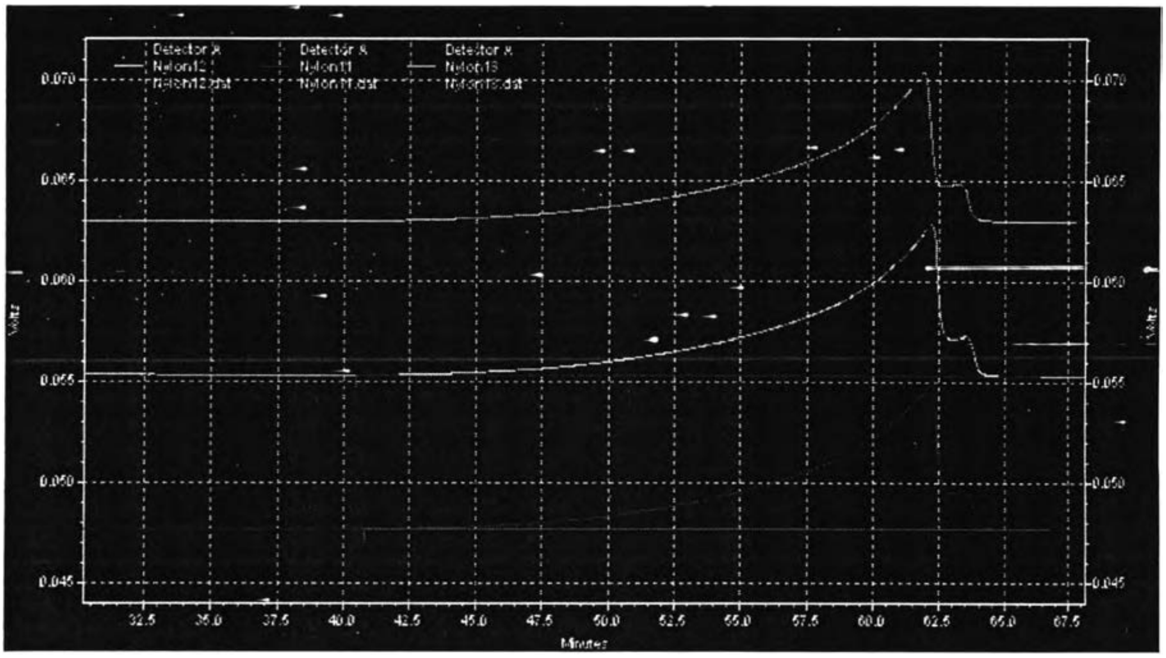


Figure 4.29 GPC curve of polymer in water that PS-g-Nylon6 was dissolved over night.

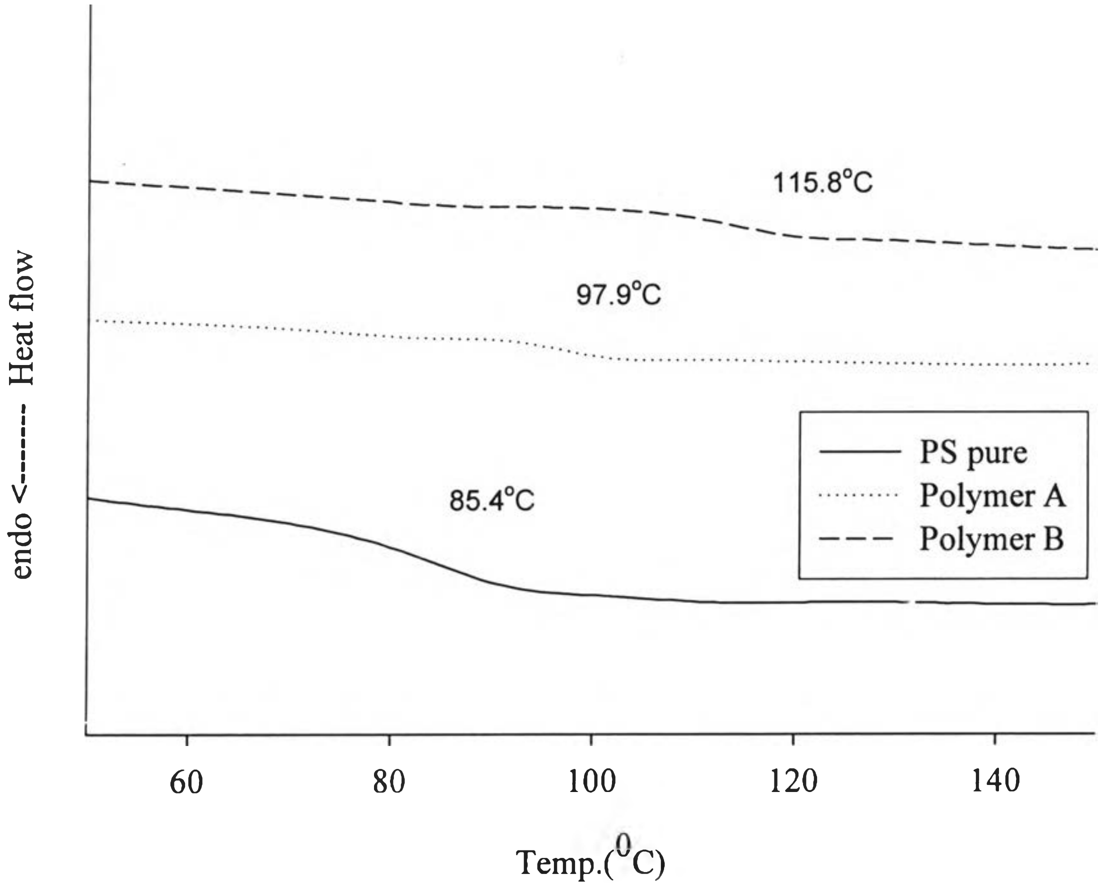


Figure 4.30 The temperature of glass transition curves: PS, polymer A, polymer B.

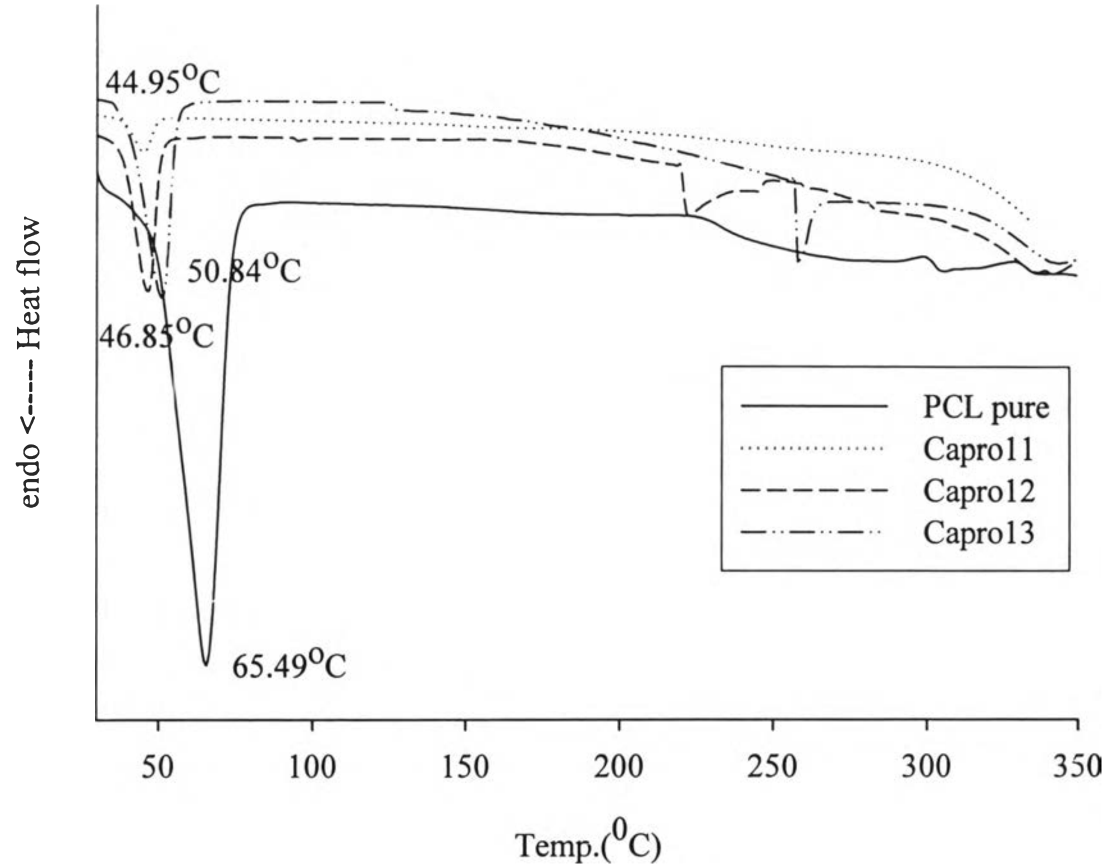


Figure 4.31 The DSC curves of PS-g-PCL in ratio 1:1, 1:2, and 1:3.

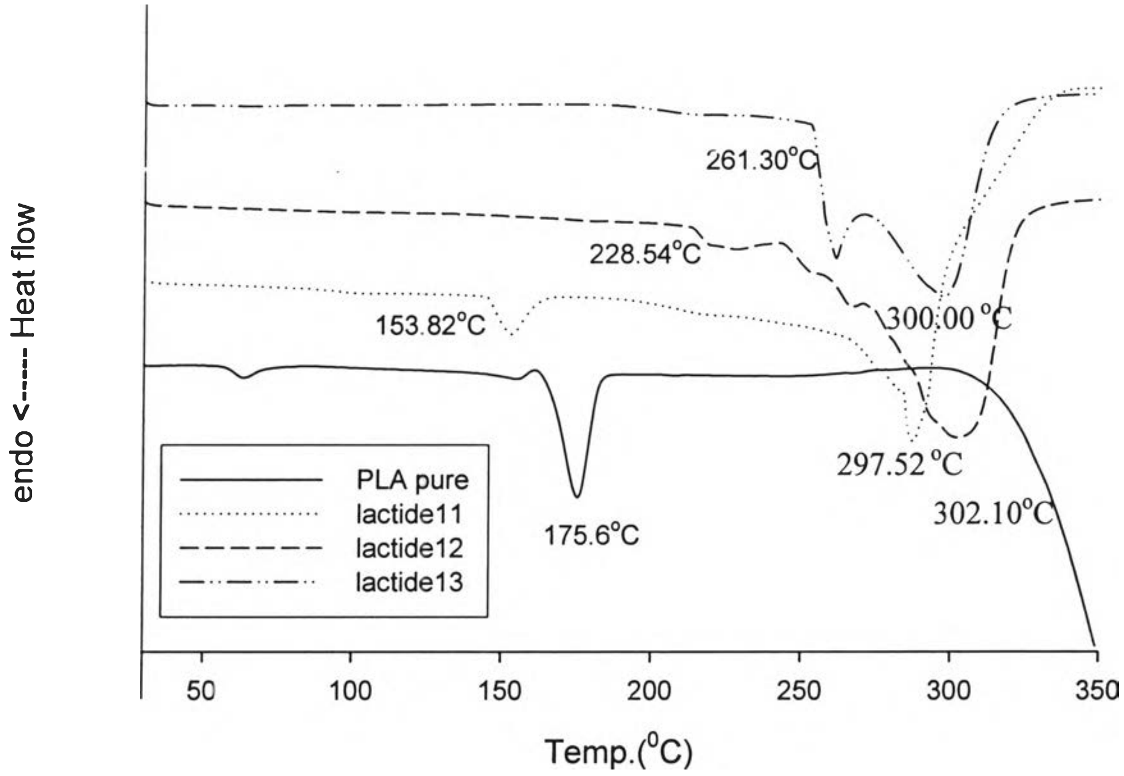


Figure 4.32 The DSC curves of PS-g-PLA in ratio 1:1, 1:2, and 1:3.

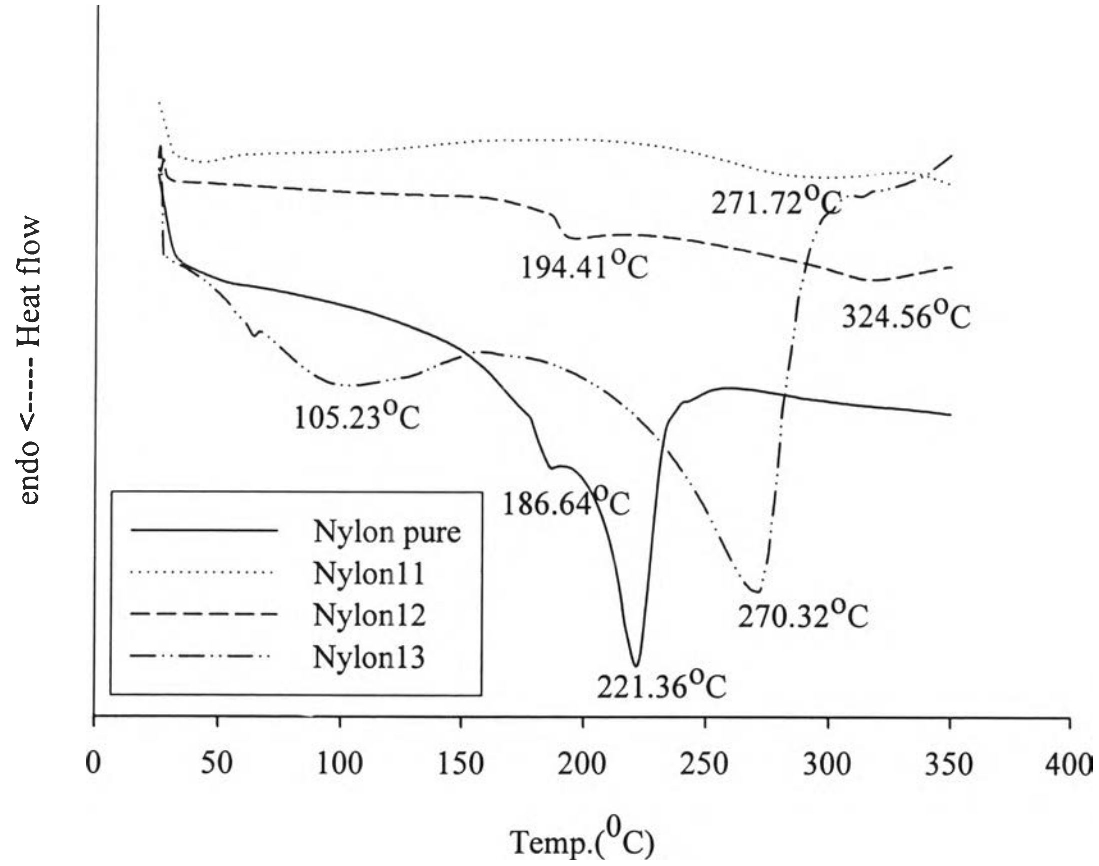


Figure 4.33 The DSC curves of PS-g-PLA in ratio 1:1, 1:2, and 1:3.

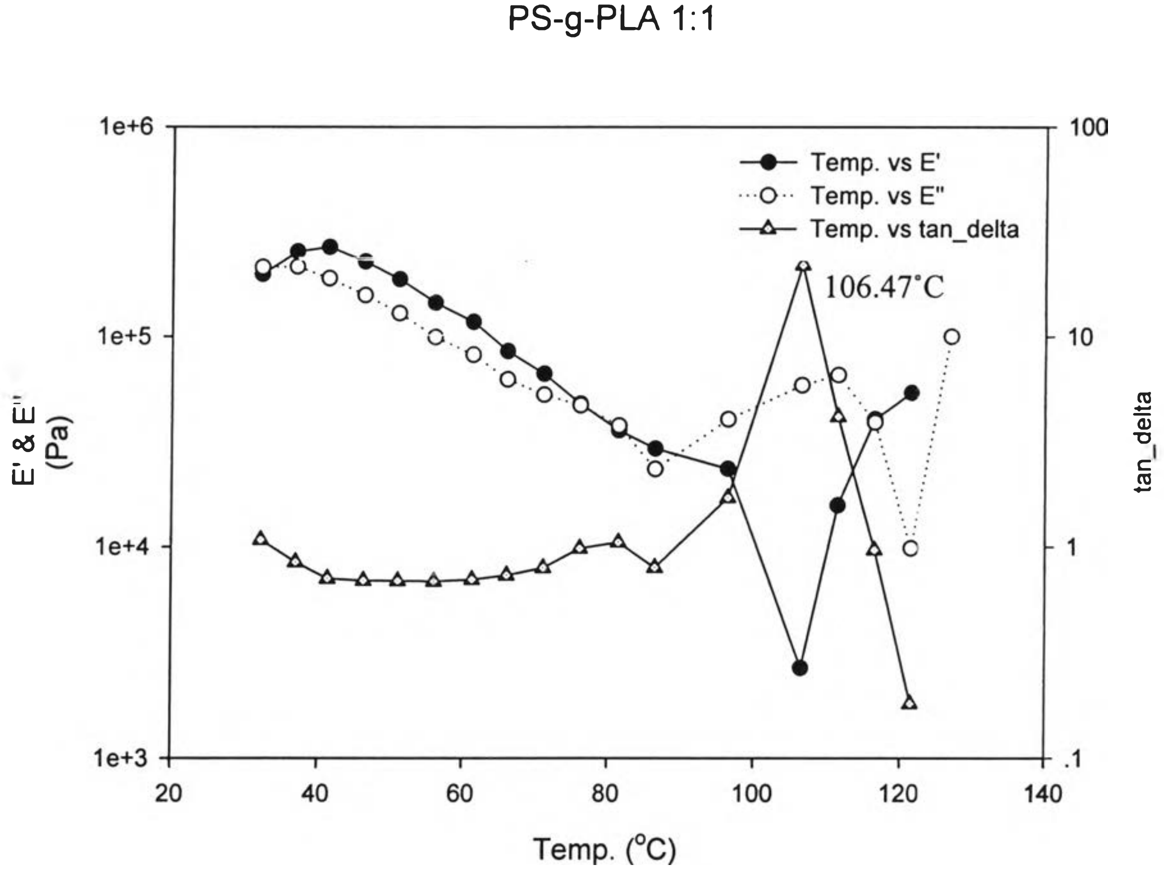


Figure 4.34 DMA curves of PS-g-PLA in ratio 1:1 by compression mode (30-130 °C).

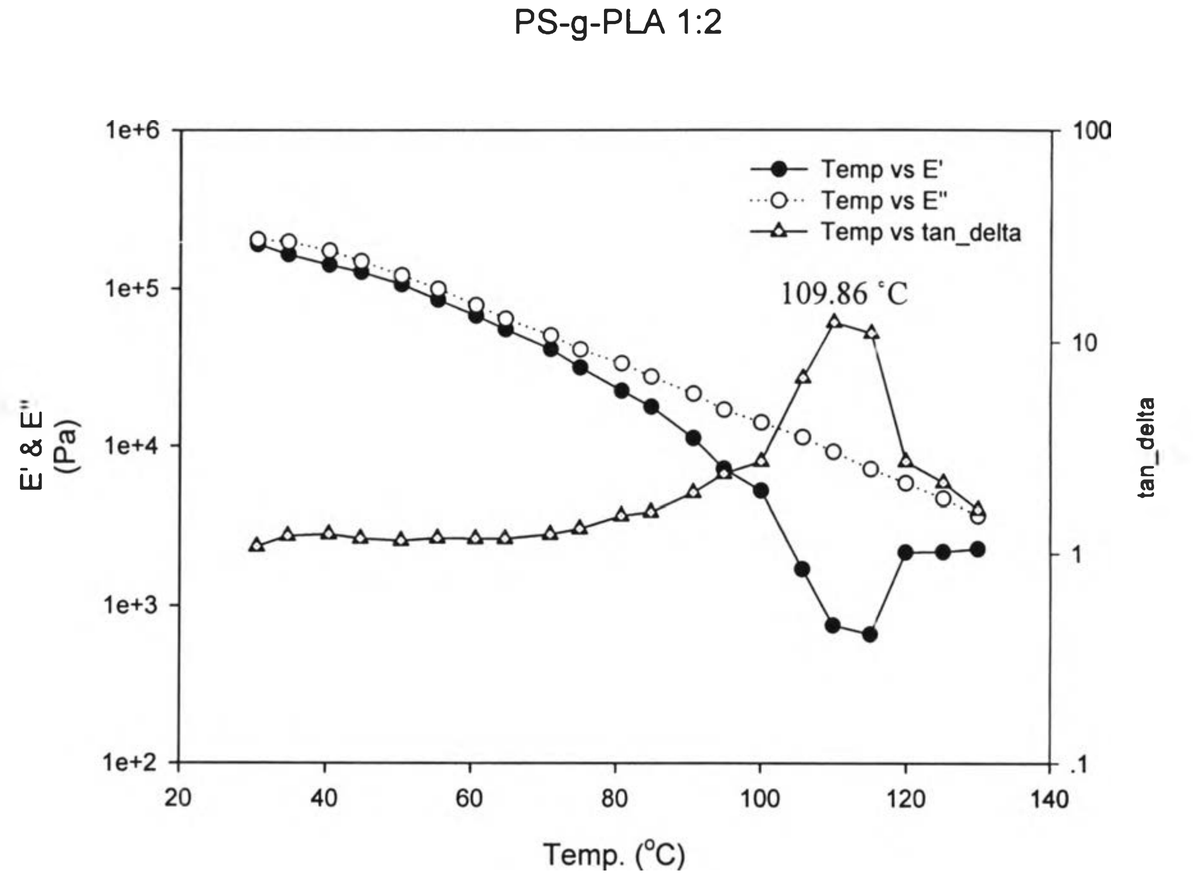


Figure 4.35 DMA curves of PS-g-PLA in ratio 1:2 by compression mode (30-130 °C).

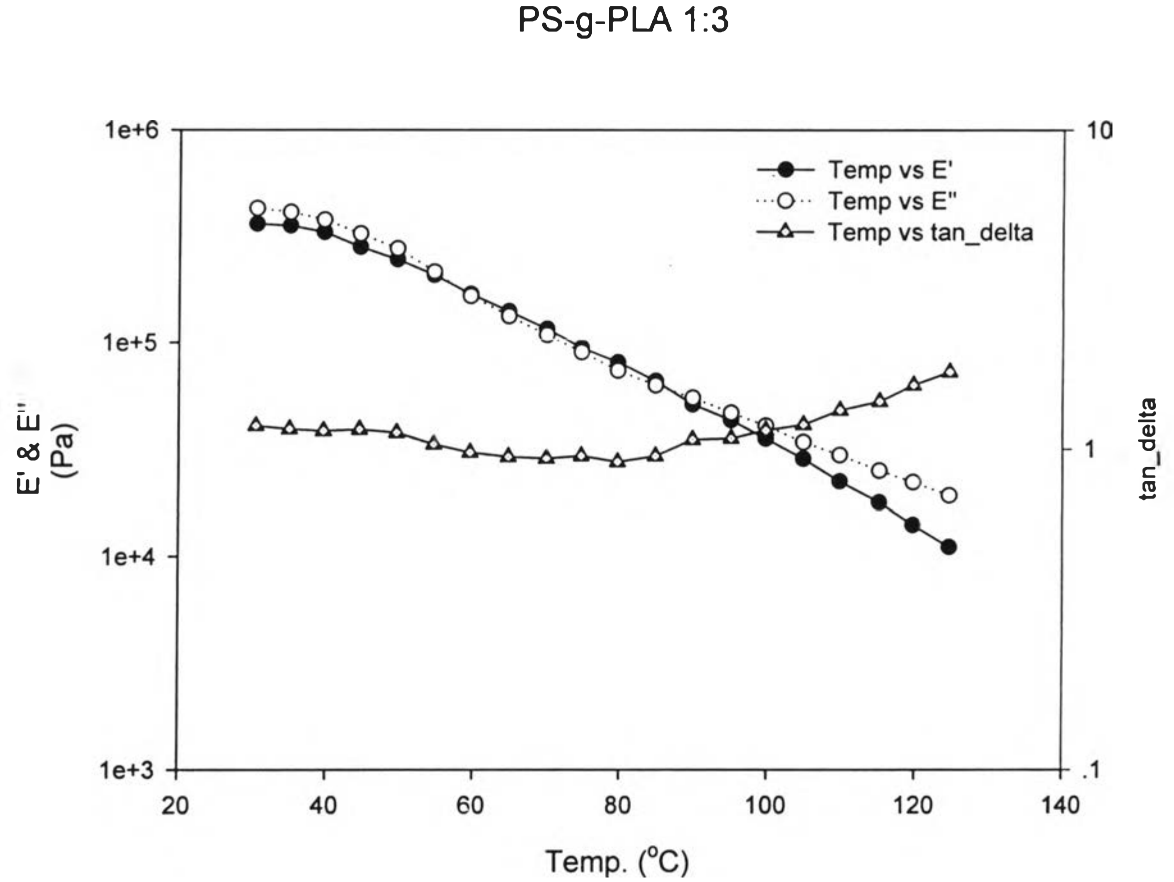


Figure 4.36 DMA curves of PS-g-PLA in ratio 1:3 by compression mode (30-130 °C).

Table 4.1 Molecular weights of polymers were characterized by GPC (rate 1ml/min)

Sample	Retention time	log MW	MW
PS	7.98	5.37707	238,272.54
PS cut	8.53	4.89104	77,810.64
Step1	8.51	4.90871	81,042.53
Step2	8.5	4.91755	82,708.47
Caprolactone11	8.37	5.03243	107,753.40
Caprolactone12	8.36	5.04127	109,968.42
Caprolactone13	8.33	5.06778	116,890.44
Lactide11	7.95	5.40359	253,270.73
Lactide12	7.83	5.50963	323,317.34
Lactide13	7.75	5.58033	380,474.01
Caprolactam11	8.43	4.97941	95,369.39
Caprolactam12	8.36	5.04127	109,968.42
Caprolactam13	8.14	5.23568	172,060.82

log MW = 12.429 - (0.8837 x Retention time)

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le 4.2 Grafting ratio calculated from TGA-DTA data in comparison to grafting ratio determined by weight and number of proton n ^{1}H NMR

ample	Mass ratio (PS : compatible polymer)	Theoretical %mass ratio of comonomer	Yield of grafted Copolymer (g)	Initial wt. of hydroxylated-PS (g)	Grafting percentage by weight [a] (%)	Grafting percentage by Mass loss [b] (%)	Grafting percentage by NMR [c] (%mol)
-g-PCL	1:1	100	2.1026	1	83.77	71.37	27.34
	1:2	200	3.0140	2	158.90	95.23	60.00
	1:3	300	4.1108	3	240.79	136.29	97.22
-g-PLA	1:1	100	2.4700	1	115.88*	33.03	28.76
	1:2	200	3.0453	2	175.60	88.94	73.71
	1:3	300	4.5847	3	299.79	202.78	125.00
PS-g- ylon6	1:1	100	1.4444	1	35.63	23.55	4.53
	1:2	200	1.8385	2	77.23	31.16	12.60
	1:3	300	2.4058	3	131.68	116.40	25.00

Table 4.3 Length and a number of grafting chain polymers calculated by ^{1}H NMR spectrum

Types of copolymer	Ratio (PS:Biocompatible polymer)	Number of monomer in a grafting polymer chain[a]	Number of chain[b]
PS-g-PCL	1:1	2.8	78
	1:2	6.0	40
	1:3	17.5	17
PS-g-PLA	1:1	3.5	427
	1:2	6	351
	1:3	8	326

Note : MW of ε-caprolactone = 114.144

MW of DL-lactde = 116.072

MW of caprolactam = 114.152

[a] From ^{1}H NMR

$$\text{Number of monomer in a grafting polymer chain} = \frac{\text{Height of specific peak of proton in grafting polymer chain}}{\text{Height of specific peak of proton at end grafting polymer chain}}$$

[b]

$$\text{Number of chain} = \frac{\text{MW.of graft copolymer} - \text{MW. of polymer B}}{\text{MW.of monomer x number of monomer in a chain}}$$

Table 4.4 T_m, T_d, ΔH_m of T_m, ΔH_d of T_d from DSC results and solubility in chloroform

Types	Ratio (w/w)	Solubility[a] (g/L)	ΔH_m of T_m (cal/g)	T_m (°C)	ΔH_d of T_d (cal/g)	T_d (°C)
PS-g-PLA	1:1	5.13	21.19	153.82	22.68	290.20
	1:2	6.43			28.73	228.54
	1:3	11.83			36.35	261.3
PS-g-PCL	1:1	2.85	6.37	44.95		
	1:2	3.8	44.98	46.85		
	1:3	5.2	57.71	50.84		
PS-g-Nylon6	1:1	0.82			19.7	271.72
	1:2	0.77			21.43	194.41
	1:3	13.48			229.76	105.23

[a] in Chloroform

Table 4.5 Total organic carbon content of the graft copolymers dissolved in water over night

Type	weight before (mg)	Conc. (g/L)	TOC (mg/L)	Carbon loss/Sample[a] (mg/g)	weight after[b] (mg)	weight after real (mg)	weight loss[c] (mg)
Water			9.032				
Lactide11	43.20	2.880	32.660	11.340	42.710	42.50	0.4899
Lactide12	46.10	3.073	35.740	11.629	45.564	44.90	0.536
Lactide13	35.00	2.333	60.460	25.911	34.093	34.20	0.907
Capro11	19.10	1.273	32.280	25.351	18.616	18.60	0.484
Capro12	21.00	1.400	51.500	36.786	20.228	19.90	0.773
Capro13	7.50	0.500	24.040	48.080	7.139	7.10	0.361
Nylon11	19.20	1.280	51.260	40.047	18.431	18.20	0.769
Nylon12	8.30	0.553	30.030	54.271	7.850	7.70	0.450
Nylon13	8.80	0.587	148.700	253.466	6.570	6.50	2.231
PLA-pure	52.00	3.467	4.347	1.254	51.935	52.00	0.065
PCL-pure	38.00	2.533	12.020	4.745	37.820	37.90	0.180
Nylon-pure	27.00	1.800	5.537	3.076	26.917	27.00	0.083

[a] Carbon loss/Sample = TOC/Conc.

[b] Weight after = Weight before-((TOC*15)/1000)

[c] Weight loss = Weight before-Weight after

Table 4.6 Total organic carbon content of the graft copolymers dissolved in 0.1wt% salt water over night

Type	weight before (mg)	Conc. (g/L)	TOC (mg/L)	Carbon loss/Sample[a] (mg/g)	weight after[b] (mg)	weigth after real (mg)	weight loss[c] (mg)
salt water			18.780				
Lactide11	18.67	1.245	31.810	25.557	18.193	18.10	0.48
Lactide12	14.24	0.949	25.650	27.019	13.855	13.50	0.38
Lactide13	13.95	0.930	27.160	29.204	13.543	13.20	0.41
Capro11	9.70	0.647	16.930	26.180	9.446	9.20	0.25
Capro12	9.92	0.661	28.610	43.261	9.491	9.00	0.43
Capro13	12.40	0.827	50.450	61.028	11.643	11.50	0.76
Nylon11	16.11	1.074	26.190	24.385	15.717	15.70	0.39
Nylon12	14.16	0.944	50.670	53.676	13.400	13.40	0.76
Nylon13	16.67	1.111	263.400	237.013	12.719	12.60	3.95
PLA-pure	56.00	3.733	6.307	1.689	55.905	56.00	0.09
PCL-pure	32.50	2.167	7.643	3.528	32.385	32.50	0.11
Nylon-pure	28.40	1.893	5.752	3.038	28.314	28.40	0.09

[a] Carbon loss/Sample = TOC/Conc.

[b] Weight after = Weight before-((TOC*15)/1000)

[c] Weight loss = Weight before-Weight after

Table 4.7 The retention time and molecular weight of dissolved polymer in water at room temperature (over night) with Gel Permeation Chromatograph (rate 0.5 ml/min)

Sample	Retention time	log MW	MW
Capro11	62.043	3.176797	1,502.44
Capro12	62.1939	3.157135	1,435.935
Capro13	62.5744	3.107556	1,281.019
Lactide11	62.9807	3.054615	1,134.005
Lactide12	63.008	3.051058	1,124.754
Lactide13	62.8471	3.072023	1,180.383
Nylon11	61.407	3.259668	1,818.31
Nylon12	61.798	3.208721	1,617.039
Nylon13	61.9361	3.190726	1,551.409

log MW = 11.261 - (0.1303 x Retention time)

Table 4.1 Molecular weights of polymers were characterized by GPC (rate 1ml/min)

Sample	Retention time	log MW	MW
PS	7.98	5.37707	238,272.54
PS cut	8.53	4.89104	77,810.64
Step1	8.51	4.90871	81,042.53
Step2	8.5	4.91755	82,708.47
Caprolactone11	8.37	5.03243	107,753.40
Caprolactone12	8.36	5.04127	109,968.42
Caprolactone13	8.33	5.06778	116,890.44
Lactide11	7.95	5.40359	253,270.73
Lactide12	7.83	5.50963	323,317.34
Lactide13	7.75	5.58033	380,474.01
Caprolactam11	8.43	4.97941	95,369.39
Caprolactam12	8.36	5.04127	109,968.42
Caprolactam13	8.14	5.23568	172,060.82

log MW = 12.429 - (0.8837 x Retention time)