CHAPTER 2

SYNTHESIS AND CHARACTERZATION OF THE RANDOM AND BLOCK TERPOLYMERS

2.1 Introduction

In recent year co- and terpolymer of L-lactide, ε-caprolactone and glycolide have attracted considerable interest due to their abilities to biodegrade. Therefore they have potential uses for biomedical applications. Gilding and Reed [23] have shown that homopolymer and copolymers of glycolic and lactic acids can be made by ionic polymerization of the cyclic diesters glycolide and lactide with tin-containing catalysts. It was found that the reactivity ratio of glycolide was higher than L-lactide that lead to blocks of glycolide separated by only one or two lactide units. Nevertheless, glycolide/L-lactide copolymers are amorphous for the compositions in the range of 25 to 70 mol% glycolide. Grijpma and Pennings [24] also reported that the large difference in reactivity of L-lactide and ε-caprolactone in ring-opening polymerization with $Sn(Oct)_2$, lead to the formation of copolymers with blocky structures. However, the polymerization temperature has a large effect on molecular weight and average monomer sequence lengths in L-lactide and ε-caprolactone copolymers. The blockiness of the copolymers is decreased at higher temperature due to transesterification reactions and a smaller difference in reactivity of the monomers.

Cai et al. [25-26] have produced segmented triblock terpolymers poly[(L-lactide-co-glycolide)-b-ε-caprolactone-b-(L-lactide-co-glycolide)],(b-PGLC), with different compositions using polycaprolactone diols as an initiator of polymerization of glycolide and L-lactide in the presence of $Sn(Oct)_2$. Random terpolymers poly(L-lactide-co-ε-caprolactone-co-glycolide), (r-PGLC), were also synthesized by using $Sn(Oct)_2$ as acatalyst. They found that r-PGLC presented amorphous structures while b-PGLC showed PCL crystalline and PLG amorphous domains. This makes the b-

PGLC quite different from r-PGLC in physical appearance, crystallinity and thermal behaviors. Baimark [27-28] synthesized and characterized an ABA segmented triblock co- and terpolymer, poly[(L-lactide-co-glycolide)-b-(L-lactide-co-ε-caprolactone)-b-(L-lactide-co-glycolide)],(PLG-PLC-PLG), and poly[(L-lactide)-b-(L-lactide-co-ε-caprolactone)-b-(L-lactide)],(PLL-PLC-PLL), with various compositions. In the synthesis procedures of these terpolymers, PLC (prepolymer) was first prepared as the middle (B) block using $Sn(Oct)_2$ and diethylene glycol (DEG) as initiator and coinitiator respectively. The $Sn(Oct)_2$ concentration was more influential on the rate of polymerization as well as on the polydispersity and monomer sequencing, while the molecular weight of the prepolymer was controlled by the DEG concentration. The prepolymer was then used as macro-initiator in the second-step reaction to add end blocks.

In this work, random and block terpolymers with a total composition of 70: 25: 5 mol% of L-lactide, ε-caprolactone and glycolide were synthesized and characterized, as described in this chapter.

2.2 Chemical and instruments

2.2.1 Chemicals

The chemicals used in this research project were as listed in Table 2.1

Table 2.1 Chemicals used in this research project

Chemical	Usage	Grade	Supplier
L(+)-lactic acid	Monomer Precursor	88%	Carlo Erba
Glycolic acid	Monomer Precursor	99%	Carlo Erba
ε-Caprolactone	Monomer	99%	Fluka
p-tolulene sulfonic acid	Catalyst	AR Grade	H&W
Antimony trioxide	Catalyst	Lab reagent	BDH
Stannous octoate*	Initiator	95%	Sigma
Diethylene glycol	Co-initiator	AR Grade	Fluka AG

Table 2.1 Chemicals used in this research project (continue)

Chemical	Usage	Grade	Supplier
Ethyl acetate	Solvent	Commercial	Merck
Chloroform	Solvent	Commercial	Merck
Calcium hydride	Drying agent	95%	Alfa Division
Molecular sieves 4 Å	Drying agent	Lab reagent	Merck

*** systematic** name = tin(II)-bis-2-ethylhexanoate, $Sn(Oct)_2$

2.2.2 Instruments

The main items of equipment used in this research project were as listed in Table 2.2

Table 2.2 Instruments used in this research project

Instruments	Company	Model
FT-IR Spectrometer	Nicolet	510
250 MHz ^{1}H-NMR Spectrometer	Bruker Advance	DPX250
100 MHz ^{13}C-NMR Spectrometer	Bruker Advance	AMX400
Differential Scanning Calorimeter	Perkin Elmer	DSC2*
		DSC7
Thermogravimetric Analyzer	Perkin Elmer	TGA7
Gel Permeation Chromatograph	Waters	717 plus Autosampler
Automatic Viscosity Measuring System	Schott-Geräte	AVS300
Controlled Atmosphere Glove Box	Labconco	50004
Vacuum Oven	Eyela	VOS-301SD

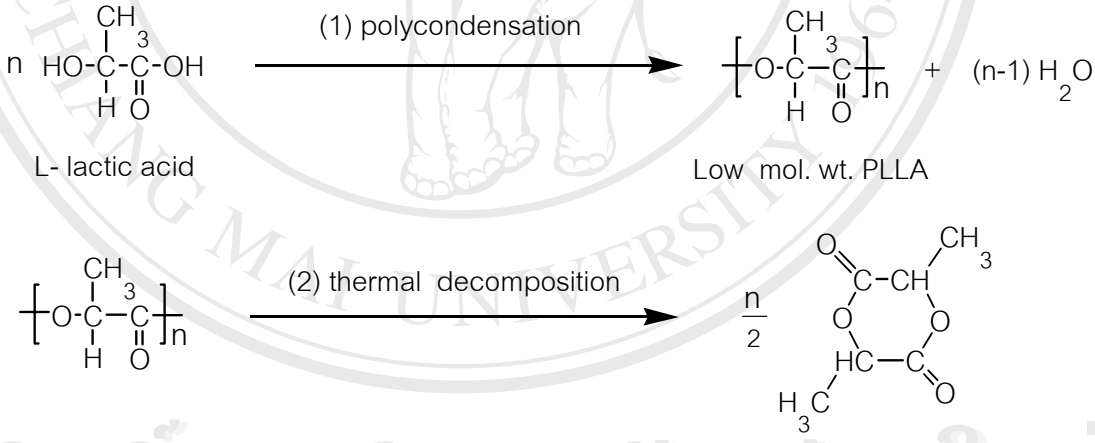
* used for sub-ambient measurements

2.3 Monomer preparation and purification

L-lactide and glycolide were synthesized from L-lactic acid and glycolic acid as described in the following sections 2.3.1 and 2.3.2. However, the mechanism for preparing L-lactide and glycolide as reported by Srisa-Ard [32] had not been explained in this thesis. ε-caprolactone was purchased for use and purified by drying with CaH_2 followed by vacuum distillation.

2.3.1 Synthesis of L-lactide and purification

The synthesis of L-lactide is possible by the polycondensation of L-lactic acid with acid catalysation. The resulting polymer has low molecular weight poly(L-lactic acid), (PLLA). The polymer was then decomposed to yield L-lactide, as shown below.



In the experiment, L-lactic acid of 200 g was put into a 250 ml round-bottomed flask, and then 1 % by weight p-toluene sulphonic acid was added as catalyst. The flask was then heated at 160°C under a nitrogen atmosphere in a conventional short-path distillation apparatus see Fig. 2.1 (a). Heating was continued for about 4 hours, then vacuum was applied to the system for 3 hours until the water of

polycondensation ceased to distill from the reaction flask. The polymer obtained was low molecular weight Poly (L-lactic acid).

The apparatus was then adapted for high vacuum take-off, as shown in Fig. 2.1 (b), and Antimony trioxide (Sb_2O_3) 1% by weight was added. The reaction flask was immersed in an oil bath at heating temperature in the range of 220 – 240°C under reduced pressure of about 4-5 mmHg for 4 hours. The crude L-lactide which had collected in the air condenser was obtained as pale yellow crystalline solid. It was later purified 3 times by re-crystallization from distilled ethyl acetate. The purified L-lactide was obtained as a white, needle-like. It was dried in a vacuum oven at 55°C for 72 hours before use.

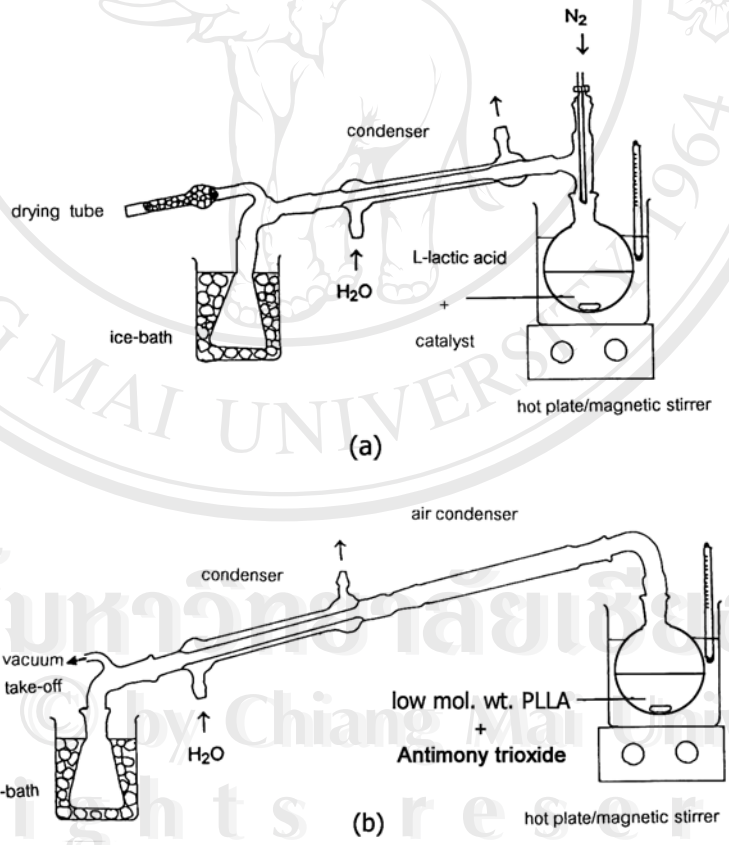


Fig. 2.1 Apparatus used in the two-stage preparation of L-lactide :

(a) L-lactide acid polycondensation to low molecular weight PLLA

(b) Thermal decomposition of low molecular weight PLLA to L-lactide

Purity analysis was carried out by Differential Scanning Calorimetry (DSC) (see in appendix B). The scan rate of 2°C/mins and small sample size in the range of 1-3 mg were used. The high purity of monomers are important for producing high molecular weight of the polymer. The purified L-lactide had a sharp melting peak from about 95-97°C, as shown in Fig. 2.2 which was similar to that found by Leenslag, J. W and Penning, A. J. [29]. From the Van't Hoff plot which was shown in Fig. 2.3, a purity of 99.88% was obtained for L-lactide.

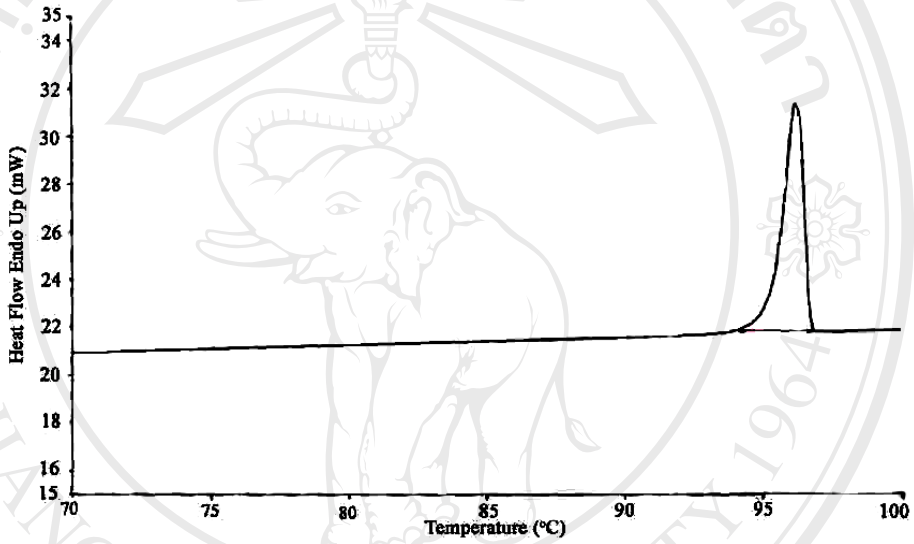


Fig. 2.2 DSC curve of purified L-lactide

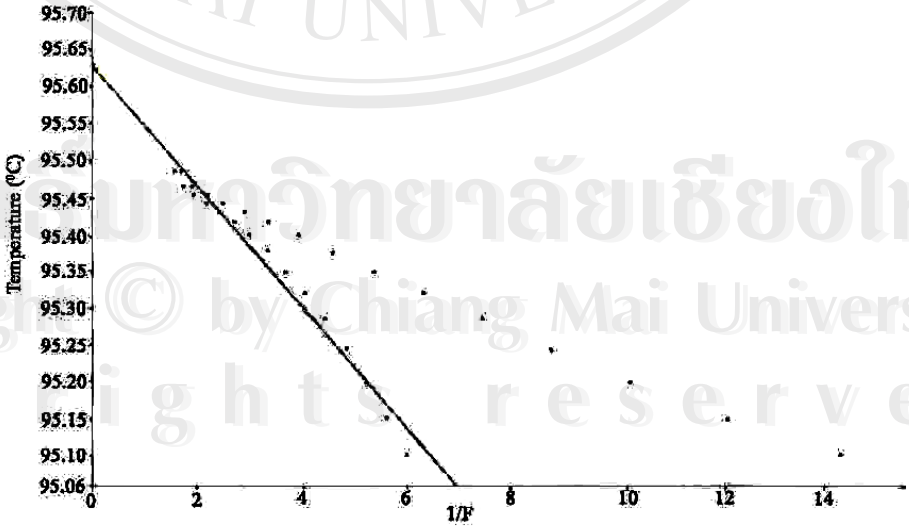
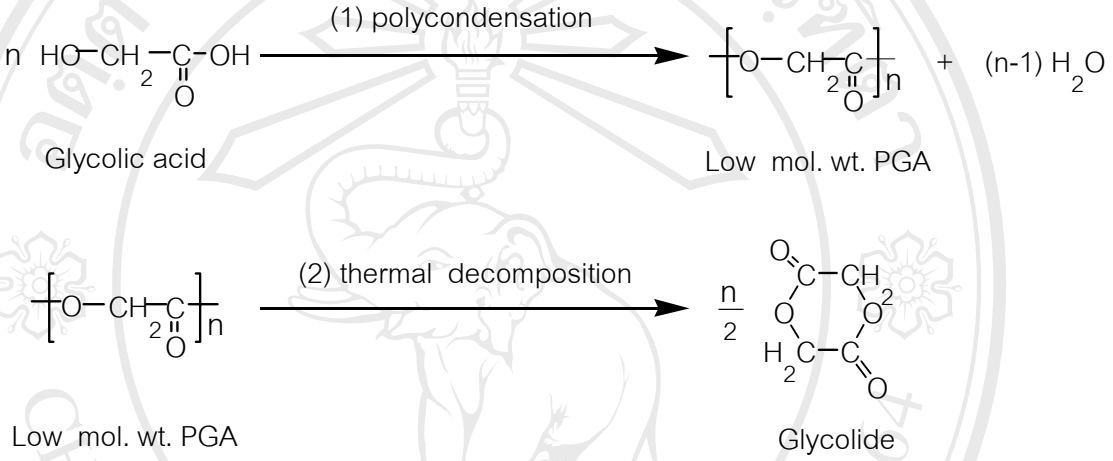


Fig. 2.3 Van't Hoff plot of the purity analysis data for the purified L-lactide.
(F = mole fraction of sample which has melted)

2.3.2 Synthesis of glycolide and purification

Glycolide was prepared in a similar manner to L-lactide and the mechanisms for this preparing are also similar to L-lactide. The synthesis of glycolide was shown below.



The apparatus was set as in Fig. 2.1 (a) approximately 130 g of glycolic acid and 1% by weight of Sb_2O_3 were added into the reaction flask. The reaction temperature was kept at 180°C for 4 hours under a nitrogen atmosphere. After that, vacuum was applied to the system for 1 hour until the water ceased to distill from the reaction flask. The product at this stage was low molecular weight poly(glycolic acid),(PGA).

The apparatus was then adapted for vacuum take-off (as in Fig. 2.1 (b)) and the heating temperature was increased up to 220–240°C under reduce pressure 4-5 mm Hg for 4 hours. Glycolide was collected initially as white crystals and later as a pale yellow crystal.

The crude glycolide was purified 3 times by re-crystallization from distilled ethyl acetate. The purified glycolide was obtained as a white, leaf-like , crystalline solid with a melting peak from about 81 – 84°C by DSC at scan rate of 2°C/min (see in Fig. 2.4). It was found to be in the range of 80 - 85°C by Gilding, D. K. et. al and Bero, M. et. al.[23, 30]. From the Fig. 2.5, a purity of 99.83% was obtained for the purified glycolide.

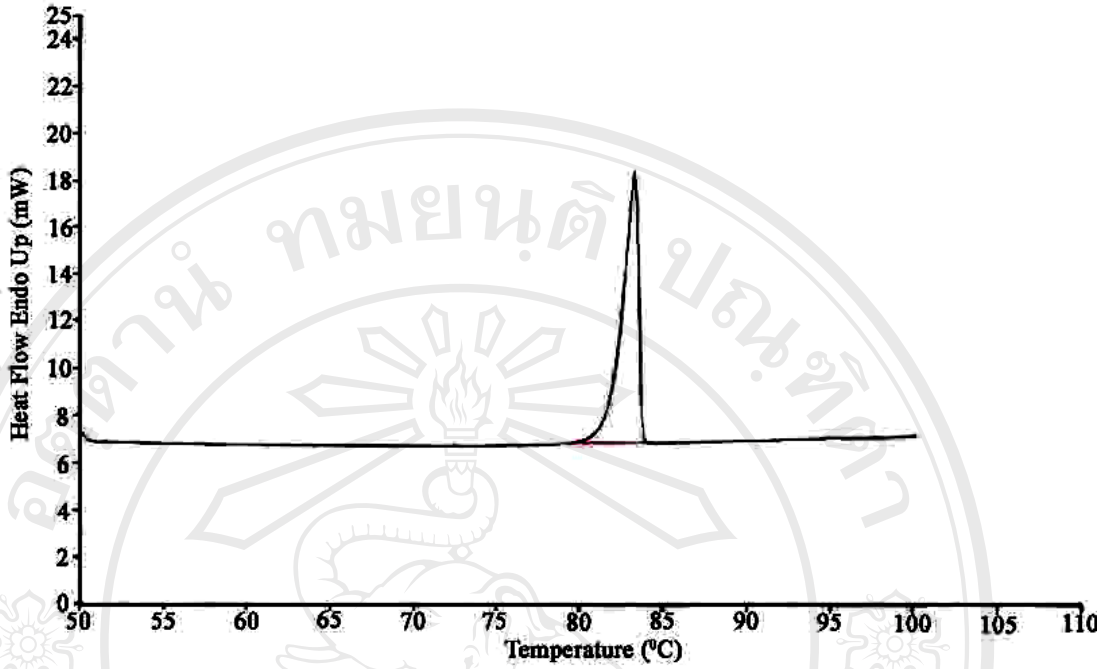


Fig. 2.4 DSC curve of purified glycolide.

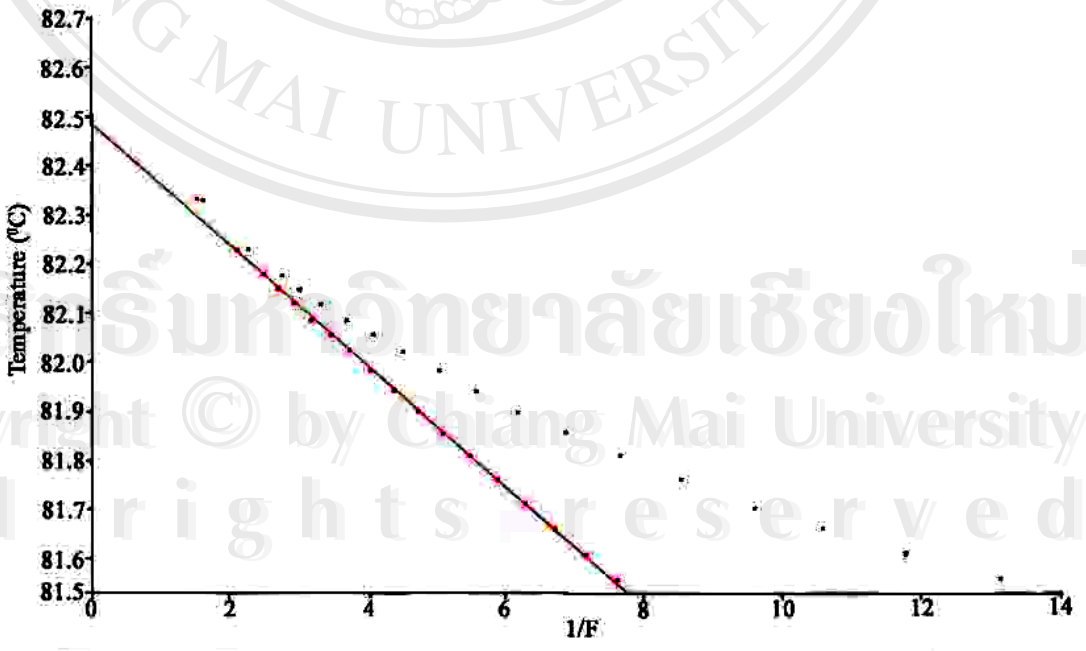


Fig. 2.5 Van't Hoff plot of the purity analysis data for the purified glycolide.
(F = mole fraction of sample which has melted)

2.3.3 Purification of ε-caprolactone by fractional vacuum distillation

Commercial ε-caprolactone (Fluka, assay > 99%) was purified by drying with CaH_2 (approximately 1 g/5 ml) over one night followed by vacuum distillation prior to use (see Fig. 2.6). During subsequent vacuum distillation, the constant boiling fraction at 80°C/2 mmHg was collected. Pure ε-caprolactone was obtained as a colourless liquid at room temperature. It was stored over molecular sieves (4 Å) in a refrigerator in a tightly sealed container until required for use in polymerization.

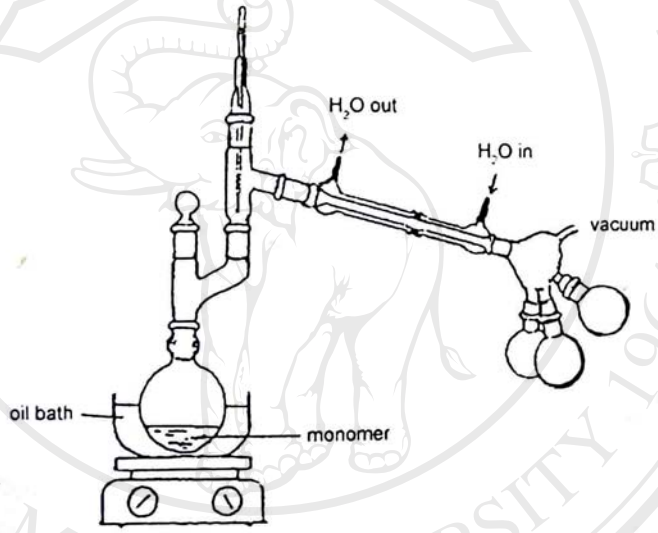


Fig. 2.6 Vacuum distillation apparatus used for the purification of ε-caprolactone.

2.3.4 Purification of diethylene glycol by fractional vacuum distillation

Commercial diethylene glycol (DEG) (assay > 98%) was purified by vacuum distillation prior to use (see Fig. 2.6). During subsequent vacuum distillation, the constant boiling fraction at 120 - 125°C/10 mmHg was collected. Purified DEG was obtained as a clear colourless liquid at room temperature. It was stored over molecular sieves (4 Å) in a refrigerator in a tightly sealed container until required for use in polymerization.

2.4 Terpolymer synthesis

2.4.1 Random terpolymer synthesis

The ring-openning random terpolymerization of L-lactide, ε-caprolactone and glycolide was performed in bulk with a composition ratio of 70: 25: 5 mol% respectively and using $Sn(Oct)_2$ as the initiator. The reaction mechanism for this polymerization was shown by Baimark [112]. Each batch of preparation was for 100 g of the random terpolymer. All glassware, including magnetic stirring bars, were dried at 150°C overnight and cooled in a dry glove box before use. Firstly, ε-caprolactone and glycolide were added into 100 ml round-bottomed flask which were equipped with magnetic stirring bar and were then stirred as a solution under dry nitrogen in a controlled atmosphere glove box at room temperature. L-lactide and $Sn(Oct)_2$ 0.01 mol% (0.8 M in toluene) as initiator were added into flask. The flask was closed with glass stopper. After that removing the flask from glove box, it was immersed in an oil bath kept constant at 140°C for 18 hours.

The product was obtained as fawn-coloured. It was purified by cutting into small pieces and heating in vacuum oven at 100°C for 24 hours to remove any unreacted monomers before characterization. Random terpolymer product was stored in vacuum desiccator until required for use.

2.4.2 Block terpolymer synthesis

Segmented triblock terpolymer (A-B-A) synthesized were composed of side blocks (A) of a random copolymer of L-lactide and glycolide, P(LL-ran-G), with a composition ratio of 50:5 mol%, and a centre block (B) of a random copolymer of L-lactide and ε-caprolactone,P(LL-ran-CL), with a composition ratio of 20:25 mol%. The overall composition ratio was therefore the same as for the random terpolymer. The preparation described below was for 50 g of the block terpolymer.

The polymerization procedure requires two separate steps with sequential monomer addition. In the first step, a centre block (B) was synthesized as a

prepolymer using $Sn(Oct)_2$ and DEG as a initiator and coinitiator respectively. The centre block contains two OH and groups were then used as the macro-initiator for adding two side blocks (A). The reaction mechanism for this polymerization was also similar to random terpolymerization, as shown in Baimark [112]. Details of the synthesis are as followed.

First stage, random copolymer of P(LL-ran-CL) was prepared as a prepolymer (B). All glassware, including magnetic stirring bars, were dried at 150°C overnight and cooled in a dry glove box before use. A mixture of L-lactide, ε-caprolactone and DEG 0.327 mol% (based on the total number of moles of the 2 comonomers) was put into a 50 ml round-bottomed flask with a magnetic stirring bar under dry nitrogen in a controlled atmosphere glove box at room temperature. Then 0.01 mol% (0.8 M in toluene) of $Sn(Oct)_2$,which based on the overall composition ratio of 3 monomers was added as an initiator. The flask was sealed with a glass stopper and evacuated. It was immersed in a silicone oil bath kept constant at 140°C for 10 hours. Prepolymer was pale-yellow colored rubbery material. It was purified by cutting into small pieces and heating in a vacuum oven at 55°C for 24 hours to remove any residual monomer, moisture and/or low molecular weight oligomer.

Second stage, L-lactide and glycolide were weighted into a 50 ml round-bottomed flask with a magnetic stirring bar and closed with a glass stopper. The flask was immersed in an oil bath kept at 160°C until all of reagents in the reaction flask was melted to homogeneous solution. The heating temperature was decreased to 140°C for 24 hours. The product was purified by cutting into small pieces and heating in a vacuum oven at 100°C for 24 hours to remove any unreacted monomer and then stored in vacuum desiccators until required for use.

2.5 Instrumental methods for polymer characterization

In this research project, the polymer products obtained were characterised by the following combination of instrumental methods:

(i) Gel permeation chromatography (GPC)
- for molecular weight determination (averages and distribution)

(ii) Dilute-solution viscometry
- for molecular weight determination (intrinsic viscosity)

(iii) Infrared spectroscopy (IR)
- for qualitative structural characterization

(iv) Nuclear magnetic resonance spectrometry (^{1}H-NMR and ^{13}C-NMR)
- for quantitative compositional and microstructural characterization

(v) Differential scanning calorimetry (DSC)
- for temperature translations and crystallinity studies

(vi) Thermogravimetry (TG)
- for thermal stability

2.5.1 Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) is an extremely powerful method for determining the complete molar mass distribution of a polymer. GPC is a type of size-exclusion chromatography (SEC). It is a technique that employs porous non-ionic gel beads to separate polymers in solution. Beads containing pores of various sizes (in the range of 50 – 10^6 Å and distributions are packed into a column in SEC. Such beads are commonly made of glass or cross-linked polystyrene. A dilute polymer solution is injected into a solvent stream which then flows through a column packed. Fractionation of the polymer sample results as different-sized molecules are eluted at different times. The smallest polymer molecules in the solution are able to pass through most of the pores in the beads and so require more time to elute as their retention time volume is larger. The largest polymer molecules cannot penetrate the pores within the cross-linked gel beads and so they will elute first and their retention volume is smaller (Fig. 2.7). A SEC result is a plot of detector response as a function of the retention volume (V_R). In order to obtain a molecular weight distribution, the column must be calibrated by using fraction of a known molecular weight so as to relate molecular weight to the eluted volume. Commercially available PS samples

with narrow molecular weight distributions are often used as calibration standards [10, 31].

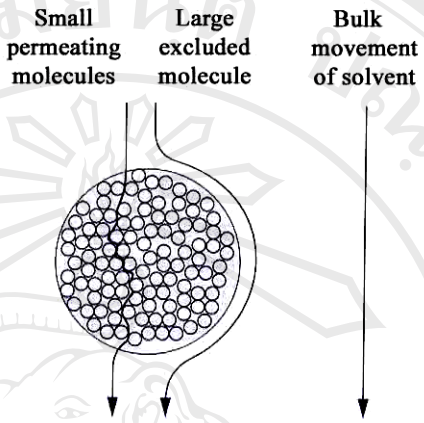


Fig. 2.7 Illustration of the separation of polymer molecules of different sizes in size-exclusion chromatography [31].

In this research project, the GPC instrument used was a Waters Model 717 plus Autosampler Gel Permeation Chromatograph operating under the following conditions

Solvent	:	THF
Flow rate	:	1.0 ml/min
Temperature	:	40°C
Injection volume	:	100µl
Type of column	:	styragel® HR 5E and HR 4E THF
Calibration method	:	Polystyrene standard calibration

2.5.2 Dilute-solution viscometry

For the determination of molecular weights of polymers by dilute solution viscosity method, it is one of the most well-known. Dilute solution viscosities are usually measured in glass capillary viscometers of which there are three typical

viscometers as shown in Fig. 2.8. The measurement of viscosities are usually determined the flow-times of a certain volume of solution through a capillary of fixed length. The various viscosity terms that have been defined are listed in Table 2.3 below.

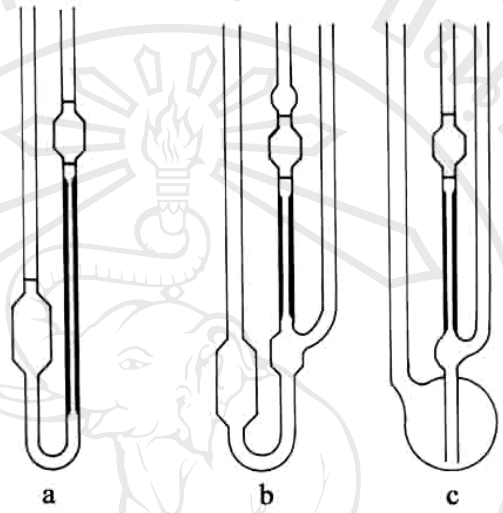


Fig. 2.8 Diagrams of (a) an Ostwald U-tube viscometer, (b) a Ubbelohde suspended-level viscometer, and (c) a modified Ubbelohde viscometer with a large reservoir bulb for dilutions [10].

Table 2.3 Definitions of dilute-solution viscosity terms.

Common name	IUPAC name	Definition
Relative viscosity	Viscosity ratio	$\eta_{rel} = \eta/\eta_0 = t/t_0$
Specific viscosity	-	$\eta_{sp} = \eta_{rel} - 1 = (\eta - \eta_0)/\eta_0 = (t - t_0)/t_0$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp}/c = (\eta_{rel} - 1)/c$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = \ln \eta_{rel}/c$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = (\eta_{sp}/c)_{C=O} = (\eta_{inh})_{C=O}$

Relative viscosity (η_{rel}) is the ratio of the viscosity of the solution (η) to the viscosity of the pure solvent (η_0), which is proportional, to a good approximation for dilute solutions, to the ratio of the corresponding flow-times (t, t_0). **Specific viscosity** (η_{sp}) is the fractional increase in viscosity as compared with the original viscosity of the pure solvent alone. Both η_{rel} and η_{sp} are dimensionless quantities. As concentration increases, so does viscosity. Hence, to eliminate concentration effects, the specific viscosity is divided by concentration. This is the so-called **reduced viscosity** (η_{red}) which is then extrapolated to zero concentration to give the intrinsic viscosity ($[\eta]$). Not uncommonly, viscosities are determined at a single concentration and the **inherent viscosity** (η_{inh}) is used as an approximate indication of molecular weight. Inherent viscosity extrapolates to the same $[\eta]$. Concentration, c, in the above expressions is in units of grams per 100 ml of solvent. Thus, the reduced, inherent, and intrinsic viscosities all have units of deciliters per gram [32, 33].

An average molecular weight of a particular polymer can be obtained from its intrinsic viscosity $[\eta]$, using Mark-Houwink-Sakurada equation, given as follows:

$$[\eta] = K\overline{M_V}^{a}$$

Where $\overline{M_V}$ is the viscosity-average molecular weight of the polymer

K and a are constants for a given polymer in a given solvent at a given temperature. They are usually obtained from the 'Polymer Handbook'. However, K and a for the terpolymers that are prepared in this research are not available in the 'Polymer Handbook'. Thus, their molecular weights can not be calculated but their $[\eta]$ values still provide useful indications as to the level of their molecular weight.

In this research project, viscosities were measured in chloroform solution at 30°C with a Schott-Geräte Ubbelohde-type viscometer (Type No. 532 00, Capillary No. 0) in conjunction with the Schott- Geräte AVS 300 Automatic Viscosity Measuring System.

2.5.3 Infrared spectroscopy (IR)

Infrared spectroscopy finds widespread application to qualitative and quantitative analyses. This method provides information about molecular vibrations and rotations and about molecular structure. Infrared spectroscopy is a particular type of absorption spectroscopy. It can be used to measure molecular vibrational frequencies. These vibrational spectra can be used directly, simply as molecular "fingerprints" to characterize and identify the molecule, or they can be used as "coded" pieces of information about the molecular structure. The infrared spectroscopy involves absorption of electromagnetic radiation in the infrared region of the spectrum, normally 4000 to 200 cm^{-1}. "This is because the molecules undergo transitions between vibrational states of different energies causing both the absorption and emission of radiation." The frequency,ν, and wavelength, λ, of the radiation are related to the difference in energy between the states, ΔE , by the following equation.

$$\nu = \Delta E / h = c / \lambda$$

where h is Planck's constant and c is the velocity of light. Organic molecules tend to have values of ΔE that correspond to the frequencies and wavelengths of infrared radiation. It is possible to relate the infrared spectrum exactly to particular vibrational modes only for simple molecules containing a few atoms. For the infrared spectra of polymers which contain a large number of atoms, could be extremely complicated, but since polymer molecules are made up of sequences of many identical units the spectra are often unexpectedly simple. This is because the vibrations of groups of atoms take place at a frequency which is often independent of the length of the polymer chain and also similar to the frequencies at which the same groups vibrate in short molecules. The wavelengths and frequencies of the characteristic absorption bands of different groups of molecules commonly found in synthetic polymers are given in Fig. 2.9 [16, 34-35].

In this type of application infrared can be used more powerfully in conjunction with nuclear magnetic resonance (NMR).

In this research, FT-IR was used mainly for the structural characterization of random and block terpolymer. A Nicolet FT-IR 510 Fourier-Transform Infrared spectrometer was used for the recording of all FT-IR spectra. The terpolymer samples were prepared as thin films cast from solution in chloroform onto NaCl discs.

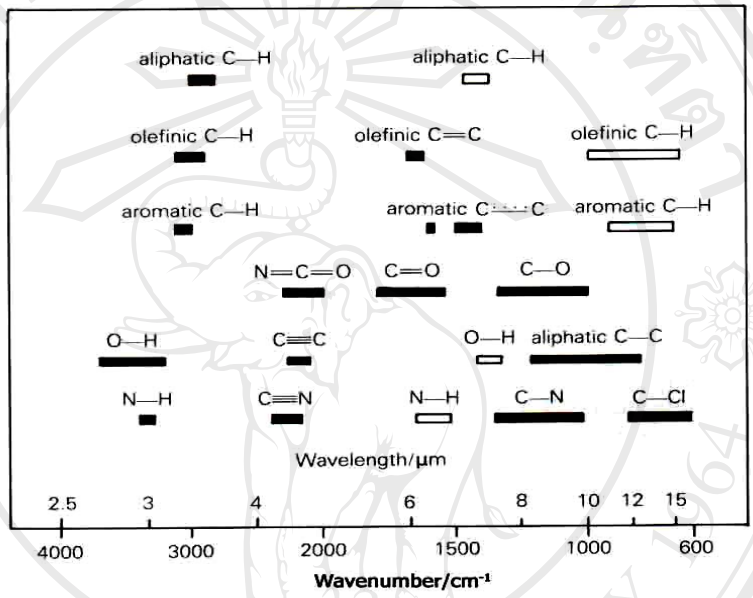


Fig. 2.9 The position of different infrared absorption bands used in the analysis of polymers [10].

2.5.4 Nuclear magnetic resonance spectrometry (NMR)

NMR is now a powerful technique available for the characterization of the detailed microstructure of macromolecules. Under normal circumstances the nuclear spin moments are randomly oriented but these moments may become oriented when placed in a strong magnetic field. Radio-frequency radiation may be absorbed by nuclei with nonzero spins such as ^{1}H, and ^{13}C in which the spin number $I = \frac{1}{2}$. The interaction of an external magnetic field (H) and the spin of hydrogen nuclei will cause these nuclei to 'flip' their spin orientations from $I = -\frac{1}{2}$ to $I = +\frac{1}{2}$. Thus, absorption of energy is detected and translated into a spectrum characteristic of this

hyperfine structure. The nuclei of different types of atoms resonate at widely different frequencies, but the most important aspect of NMR is that nuclei of the same type of atom in a molecule will resonate at slightly different frequencies depending upon the chemical environments of the atoms. This gives rise to the phenomenon of *chemical shift*. Because there is no fundamental zero of chemical shift, the shifts are given relative to those in a standard reference chemical. Tetramethyl silane, (TMS), is taken as the standard reference substance for protons and the magnitudes of the shifts are given in terms of the parts per million relative change in field strength (either δ or τ) [16, 36]. The chemical shifts of ^{1}H, and ^{13}C nuclei in groups commonly found in polymers are given in Figs. 2.10 and 2.11.

In this research project, NMR spectroscopy was used for terpolymer compositional analysis by ^{1}H-NMR and microstructure analysis by ^{13}C-NMR. The ^{1}H-NMR spectra was recorded in $CDCl_3$ as solvent using 250 MHz Bruker Advance DPX250 and ^{13}C-NMR spectra was also recorded in $CDCl_3$ as solvent using 100 MHz a Bruker Advance AMX400 spectrometer.

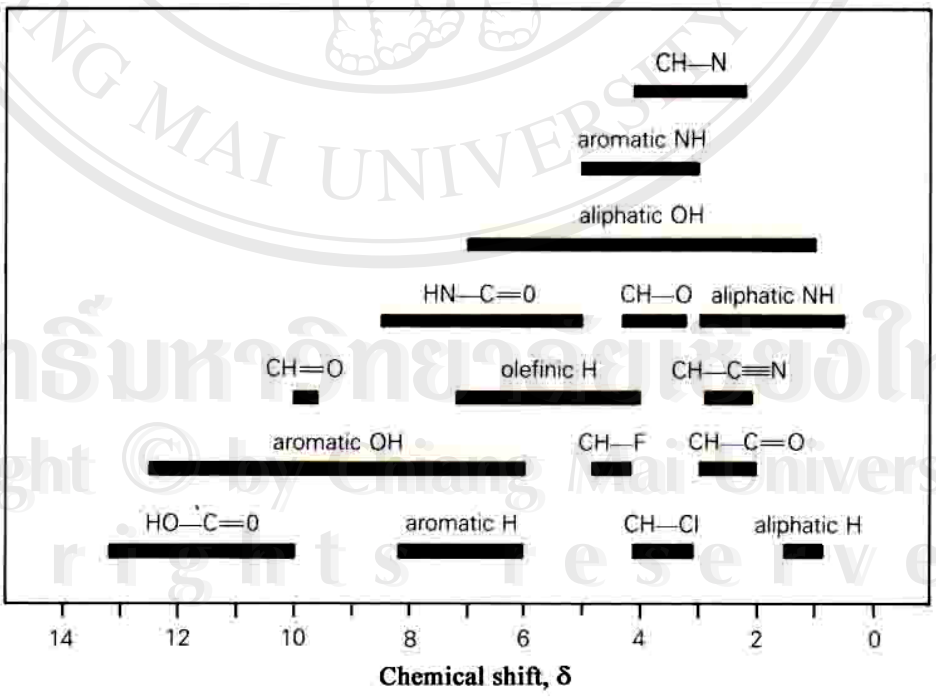


Fig. 2.10 Approximate chemical shifts for protons in various functional groups relative to TMS [10].

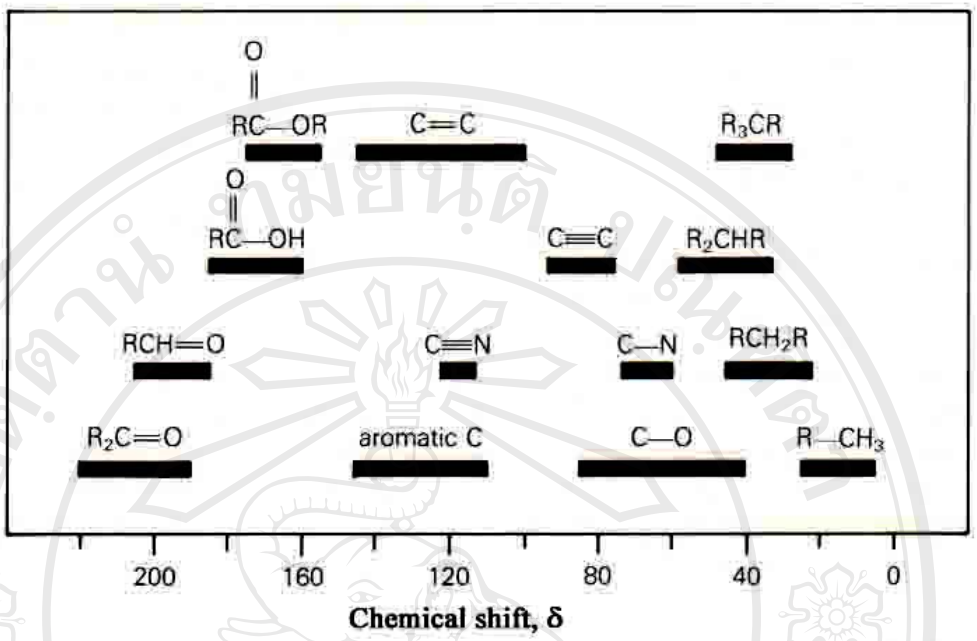


Fig. 2.11 Approximate chemical shifts for ^{13}C-NMR in various functional groups relative to TMS [10].

2.5.5 Differential scanning calorimetry (DSC)

Thermal behaviors of polymers may be investigated by the techniques of DSC. In DSC, there are two modes of measuring some property changes in the sample as a function of time and temperature namely isothermal (constant temperature) and non-isothermal (increasing temperature), respectively. DSC result obtained as a curve from either of the two modes is called a thermogram. In the particular, the thermal properties of the terpolymers such as glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) of polymers, together with their corresponding heats of transitions observed in this research were measured by non-isothermal mode.

In the mode of non-isothermal, the sample and a reference substance are also subjected to a continuously increasing temperature. Heat is added to the sample or to reference as necessary to maintain the two at identical temperatures. The added heat, which is recorded, compensates for that lost or gained as a consequence of

endothermic or exothermic processes occurring in the sample [34]. The non-isothermal DSC thermogram is illustrated in Fig. 2.12.

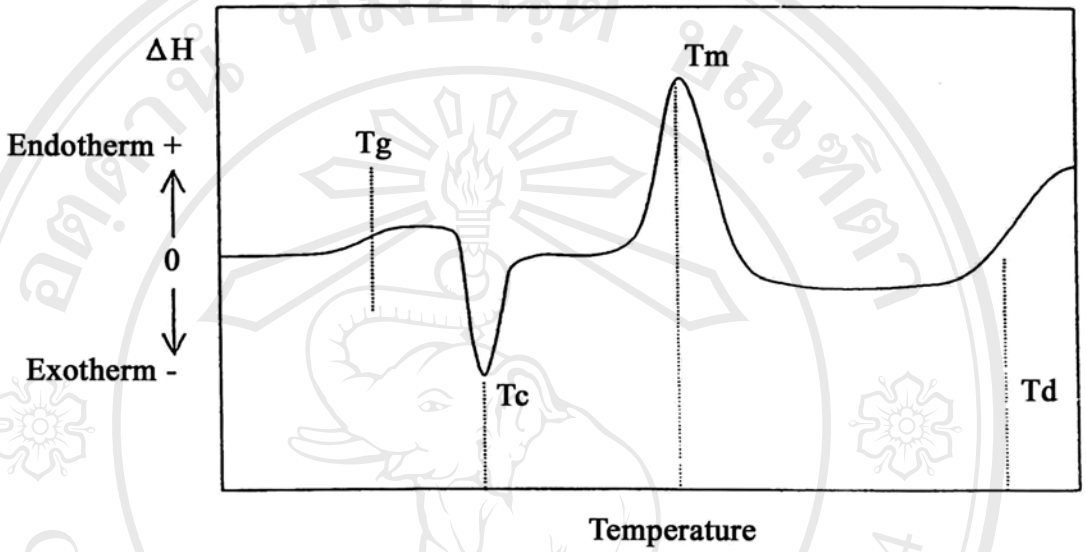


Fig. 2.12 DSC thermogram of polymer

The T_g of a polymer appears as an endothermic shift from the baseline. Such a change results from an increase in heat capacity due to the increased molecular motions in the material.

For crystallization temperature (T_c), transition is observed between the T_g and T_m values. This temperature is at which ordering and production of the crystalline regions occur. The polymer chains have sufficient mobility at this particular temperature to crystallize and an exothermic peak in then observed.

T_m of a polymer corresponds to a change from the solid to liquid state. This transition gives rise to an endothermic peak in the DSC curve. Such a peak enables the melting point and the heat of fusion to be determined by using this technique. The width of the melting peak provides an indication of the range of crystal sizes and also their perfection. Above the T_m, the polymer will degrade at the degradation temperature (T_d) [31].

The accuracy in temperature measurement is attained by observing the following :

(1) Precise calibration of the instrument
(2) Small sample size (< 5 mg)
(3) Proper encapsulation of the sample
(4) Slow scanning rate (< 10°C/min)

For precise measurements for heats of transition, it is necessary to add two further considerations:

(1) Precise weighing (± 0.01 mg)
(2) Precise calculation of the peak area lying under the endotherm or exotherm caused by the transition

In this research project, the instruments used were a Perkin-Elmer DSC2 and DSC7 Differential Scanning Calorimeter. Nitrogen gas (99.99% purity) was used as the purge gas. The heating rate used was 10 and 20°C/min with a sample size in range of 3-5 mg.

2.5.6 Thermogravimetry (TG)

TG involves the measurement of the change in weight of a sample either as a function of time at constant temperature (isothermal thermogravimetry) or as a function of temperature as the system temperature changes at a constant heating rate (non-isothermal thermogravimetry). The record is usually in the form of weight as a function of time (t) or temperature (T). A typical non-isothermal TG curve is illustrated in Fig. 2.13. The sample may either lose weight to the atmosphere or gain weight by reaction with the atmosphere. The loss weight indicates decomposition or evaporation of the sample. The temperature, at which no weight loss takes place, indicates stability of the material. In addition it enables to determine the composition of a compound and to follow the reactions involved in its decomposition [37-38].

Non-isothermal thermogravimetry thermograms of the terpolymers in this project were obtained using a Perkin-Elmer TGA7 Thermogravimetry Analyzer. Nitrogen

gas (99.99% purity) was used as the purge gas. The heating rate used was 20°C/min with initial sample weights in the range of 5-10 mg.

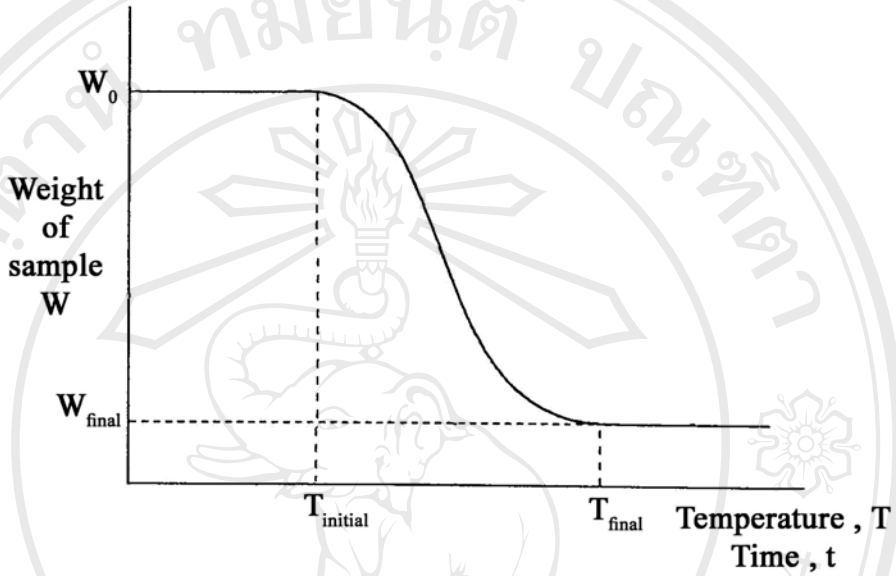


Fig. 2.13 A typical non-isothermal TG thermogram for a polymer.

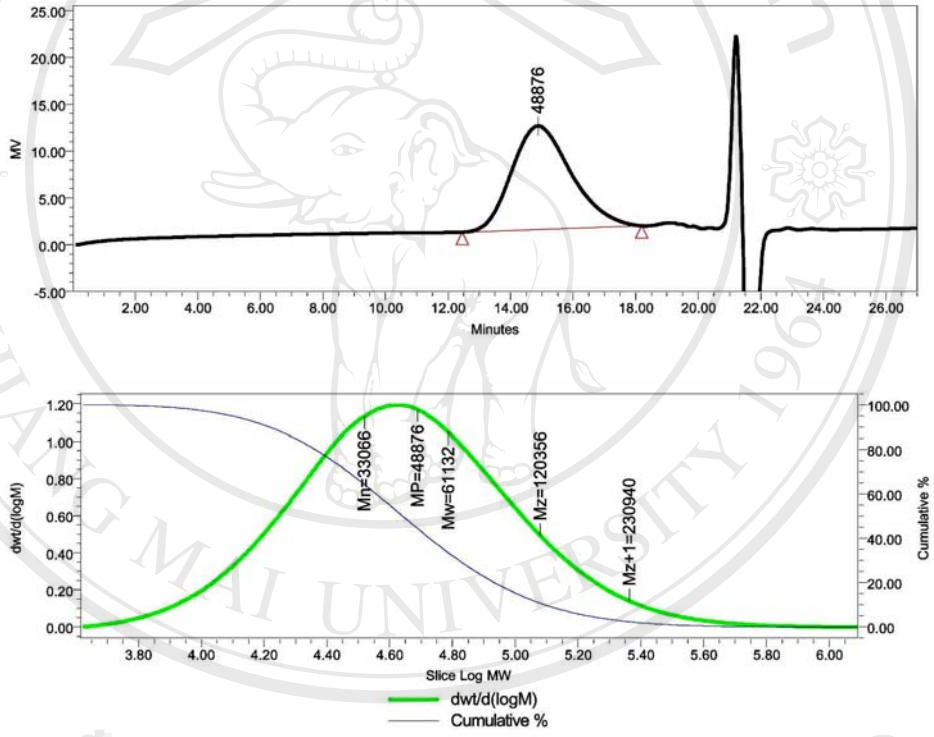
2.6 Polymer characterization

The terpolymer products were characterized by a combination of techniques: average molecular weights by GPC and dilute-solution viscometry, chemical structure by FT-IR, chemical composition by ^{1}H-NMR, chemical microstructure by ^{13}C-NMR, thermal transitions by DSC and thermal stability by TG. The results from all of these techniques are now described.

2.6.1 Average molecular weight determination

The average molecular weights and molecular weight distributions of the terpolymer products were determined by GPC. The GPC measurements were performed in THF as eluent (1 ml/min) using a Waters 717 plus Autosampler Gel Permeation Chromatography equipped with an Styragel® HR 5E and HR 4E THF

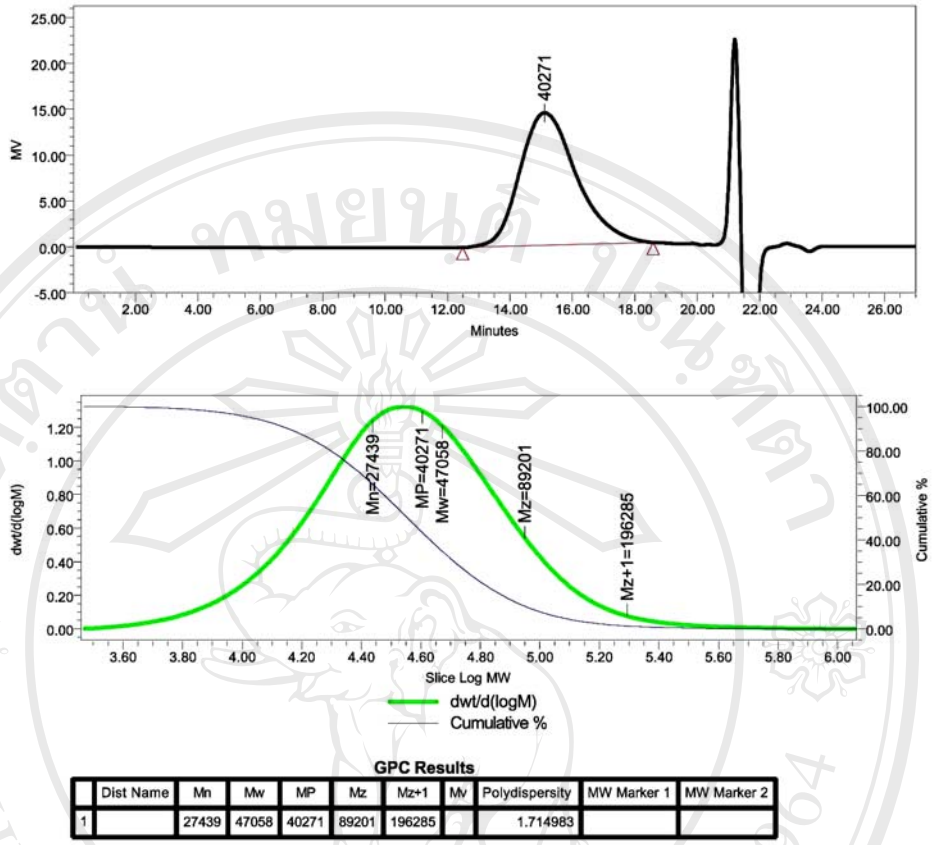
column operating at 40°C and employing a refractive index detector with polystyrene standard calibration. Typical GPC curves and the related print-outs are shown in Figs. 2.14 – 2.15. The number-average molecular weight ($\overline{M_n}$) of the random terpolymer is ~ 33,000 with polydispersity index ($\overline{M_w}/\overline{M_n}$) of 1.85. For the block terpolymer, $\overline{M_n}$ ~ 27,000 with $\overline{M_w}/\overline{M_n}$ of 1.71. Single almost symmetric profiles observed for both of their GPC curves suggested that the terpolymers contained no oligomer or residual monomers.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		33066	61132	48876	120356	230940		1.848804		

Fig. 2.14 GPC curve of the random terpolymer



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	MV	Polydispersity	MW Marker 1	MW Marker 2
1		27439	47058	40271	89201	196285		1.714983		

Fig. 2.15 GPC curve of the block terpolymer

2.6.2 Intrinsic viscosity determination

The intrinsic viscosity, $[\eta]$, of prepolymer and terpolymer products were measured in chloroform as solvent at 30°C with a Ubbelohde viscometer over the concentration range of 0.0 – 0.5 g/dl. Each solution concentration was separately prepared in order to eliminate any dilute errors.

The reduced and inherent viscosities over a range of concentration were obtained. Their linear plots are extrapolated back to their intercept at zero concentration to give $[\eta]$ which are shown in Figs. 2.16 – 2.18. The intrinsic viscosity values of the random terpolymer, prepolymer and block terpolymer are 1.27, 0.85 and 0.97 dl/g, respectively.

The intrinsic viscosity values follow the same trend as the $\overline{M}_n$ values from GPC. The prepolymer sample could not be determined by GPC because the prepolymer sample degraded before investigated. The block terpolymer had intrinsic viscosity higher than its prepolymer. This confirms that the monomers added in the second-step reaction polymerized to both ends of the prepolymer rather than just polymerized by themselves.

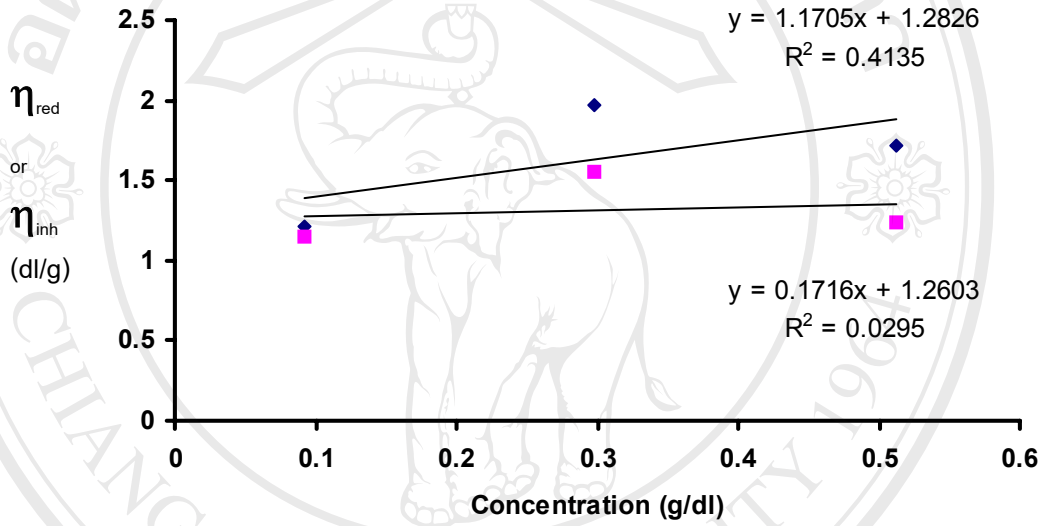


Fig. 2.16 Reduced and inherent viscosity-concentration plots for the random terpolymer in chloroform as solvent at 30°C.

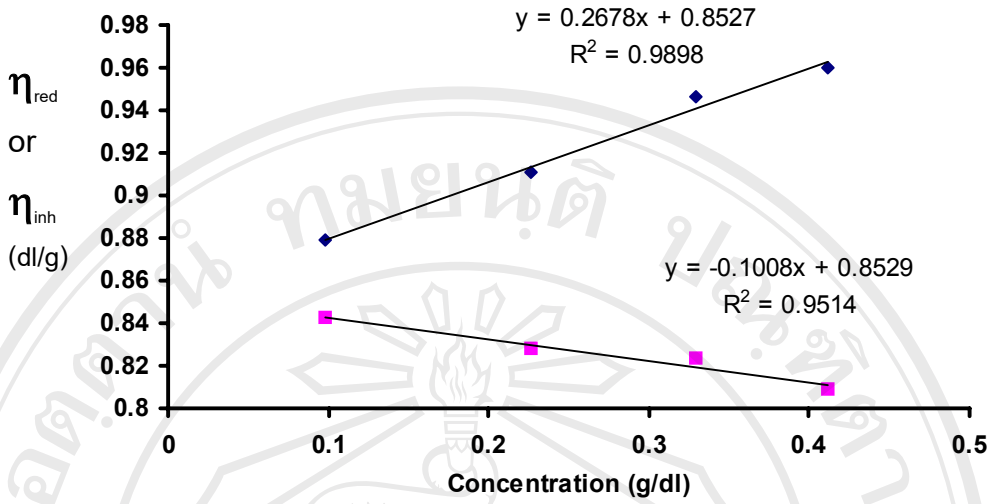


Fig. 2.17 Reduced and inherent viscosity-concentration plots for the prepolymer, (P(LL-co-CL), in chloroform as solvent at 30°C.

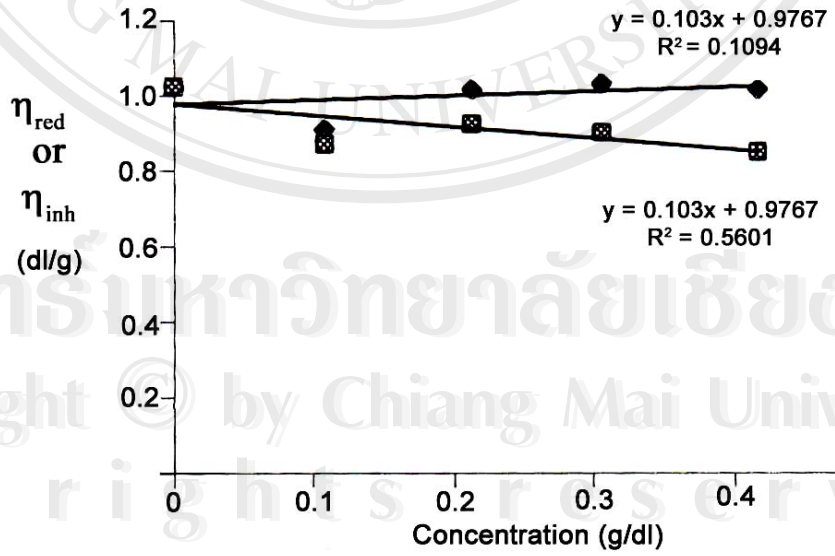


Fig. 2.18 Reduced and inherent viscosity-concentration plots for the block terpolymer in chloroform as solvent at 30°C.

2.6.3 Structural characterization

The reference homopolymer infrared spectra are shown in Figs. 2.19–2.21 and can be compared with the spectra of terpolymer products in Figs. 2.22–2.23. The terpolymer spectra were all obtained from samples prepared in the form of thin films cast from solution in chloroform onto NaCl discs. The major vibrational peak assignments are listed in Table 2.4.

The infrared spectra of poly(L-lactide), poly(ε-caprolactone) and poly(glycolide) homopolymers are very similar in appearance, as would be expected from their similar chemical structures. Consequently, the infrared spectra of terpolymer products contained all the characteristic absorption bands of the three homopolymers, as to render it impossible to detect their compositional and microstructural differences. The NMR spectroscopy will be used to give more information about terpolymer composition and microstructure as now describe in the following section.

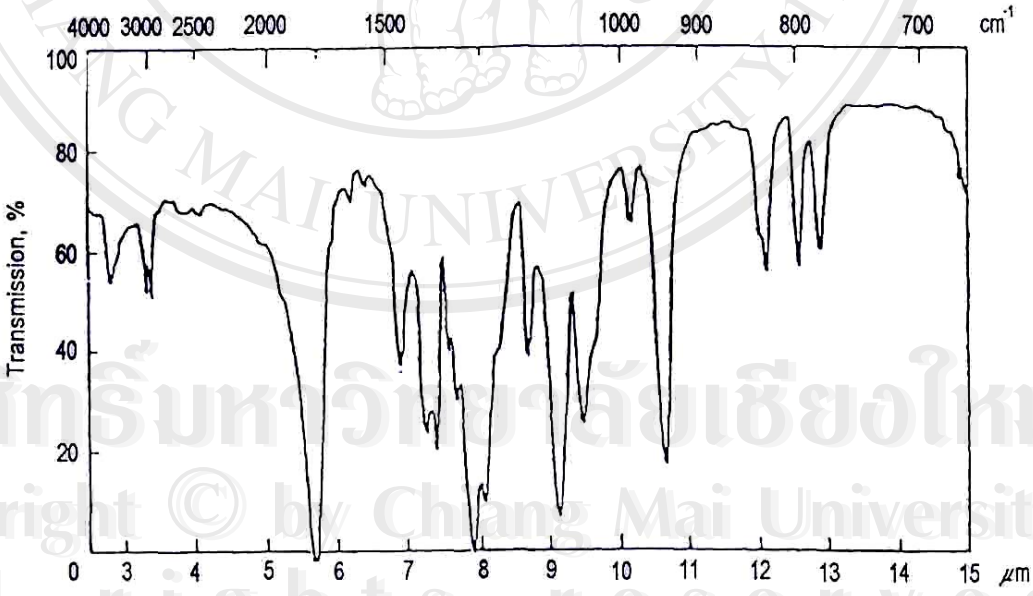


Fig. 2.19 Reference infrared spectrum of poly(L-lactide) [39].

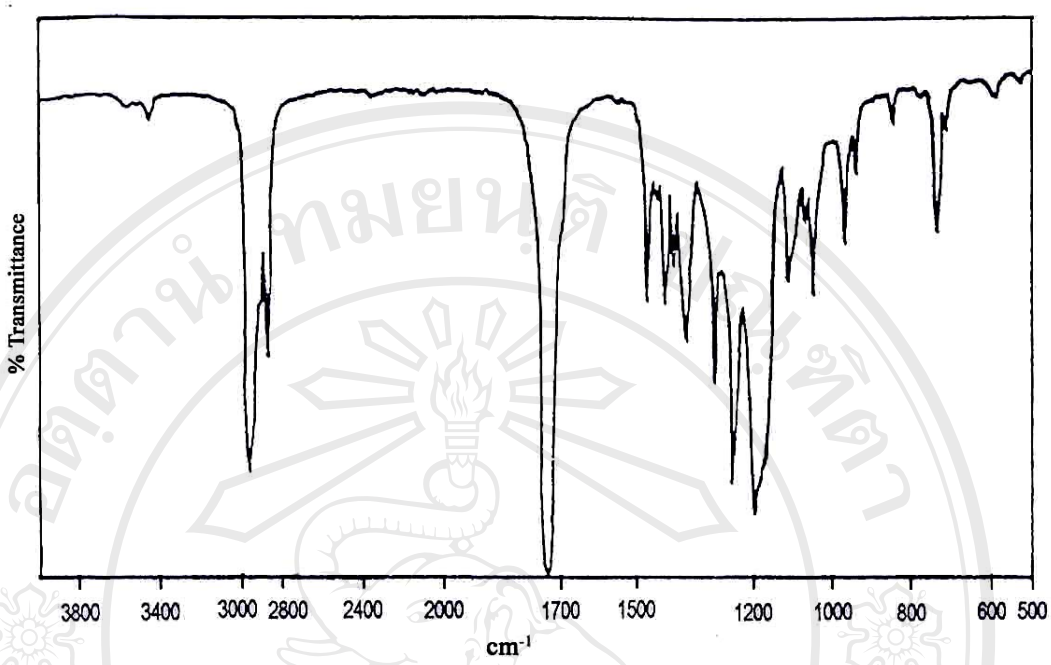


Fig. 2.20 Reference infrared spectrum of poly(ε-caprolactone) [40].

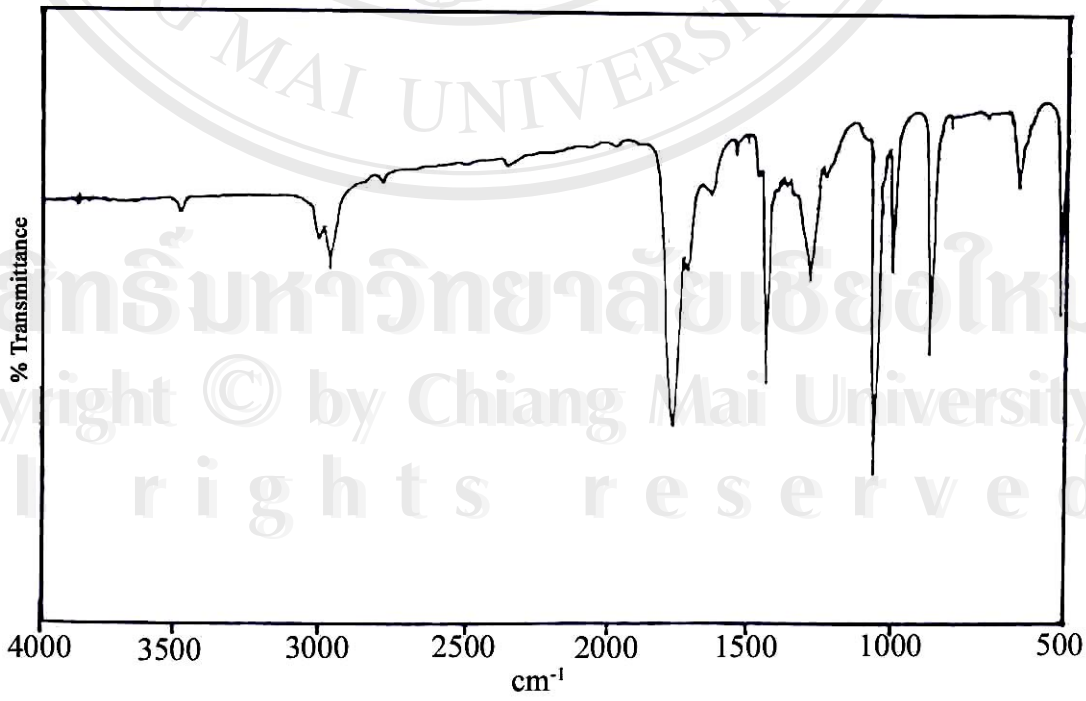


Fig. 2.21 Reference infrared spectrum of poly(glycolide) [6].

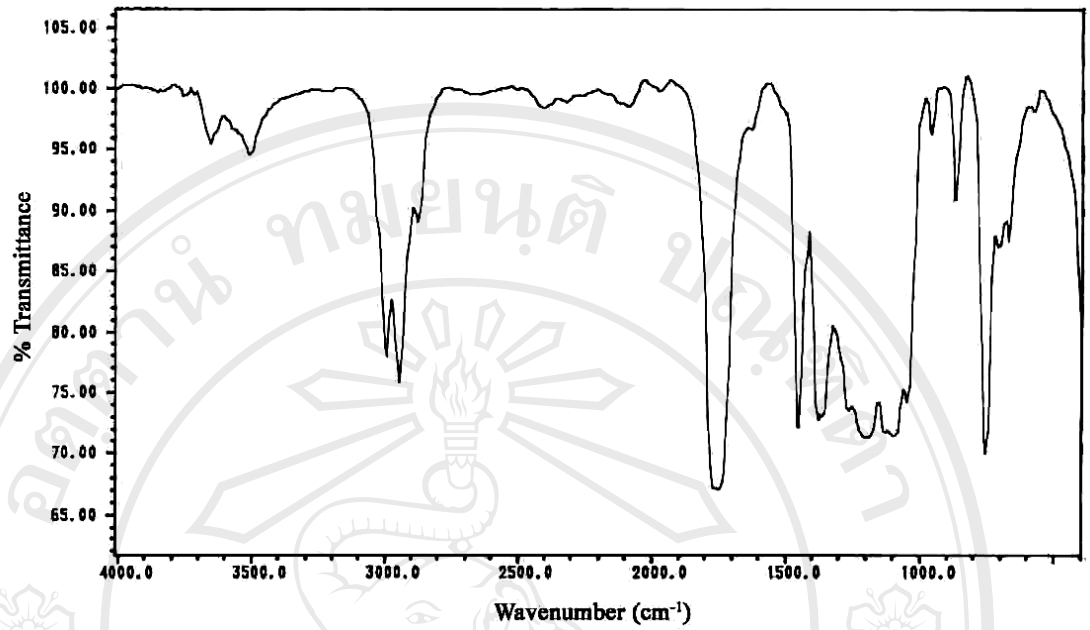


Fig. 2.22 Infrared spectrum of the random terpolymer.

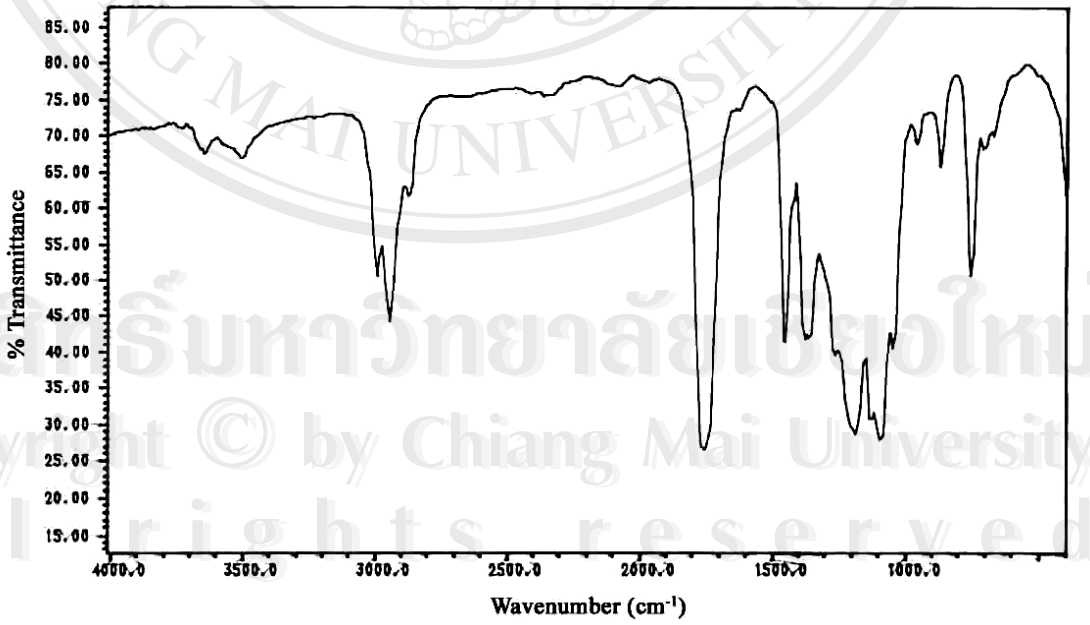


Fig. 2.23 Infrared spectrum of the block terpolymer.

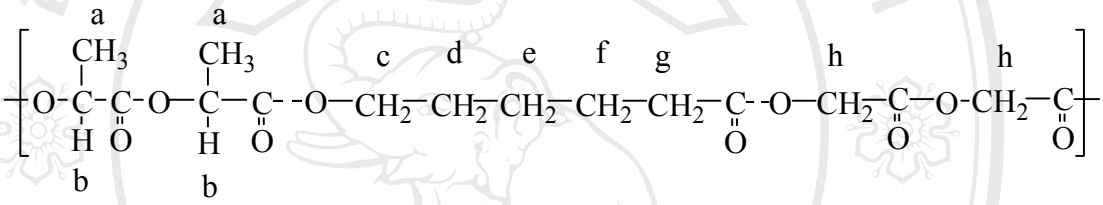
Table 2.4 Vibrational peak assignments and frequencies in the homopolymer and terpolymer products infrared spectra.

Vibrational Assignment	Wavenumber (cm^{-1})				
	Poly(L-lactide)	Poly(ε-caprolactone)	Poly(glycolide)	random terpolymer	block terpolymer
O-H stretching in OH and/or COOH	3600 – 3400 (W)	3600 – 3400 (W)	3600 – 3300 (W)	3700 – 3400 (W)	3700 – 3400 (W)
C-H stretching in CH, CH_2, CH_3	3000, 2950 (M)	2936, 2861 (S)	2980 (M)	3000, 2980 (S)	3000, 2980 (S)
C=O stretching	1750 (S)	1723 (S)	1745 (S)	1750 (S)	1750 (S)
C-H bending in CH, CH_2, CH_3	1450 – 1380 (M)	1470 – 1400 (M)	1450 – 1400 (S)	1450 – 1380 (S)	1450 – 1380 (S)
C-O stretching in acyl-oxygen	1280 (S)	1250, 1200 (S)	1240 (W)	1200 (W)	1220 (W)
C-O stretching in akyl-oxygen	1090 (S)	1060 (M)	1082 (S)	1090 (W)	1090 (W)
CH_2 bending (rocking)	-	720 (S)	-	750 (S)	750 (S)

W = weak, M = medium, S = strong (Peak intensity)

2.6.4 Identification and monomer composition determination

The nuclear magnetic resonance spectrometry was used to identify the monomers in the polymers and also determine monomer compositions, as described in this section. The ^{1}H-NMR spectra of the terpolymers were recorded at 250 MHz with a Bruker Advance DPX250 in a 5 mm sample tube. Deuterium Chloroform ($CDCl_3$) was used as a solvent and tetramethylsilane (TMS) was used as an internal standard. The spectra obtained at 294K are shown in Figs. 2.24–2.25. Peak assignments and their corresponding chemical shifts are shown in Table 2.5.



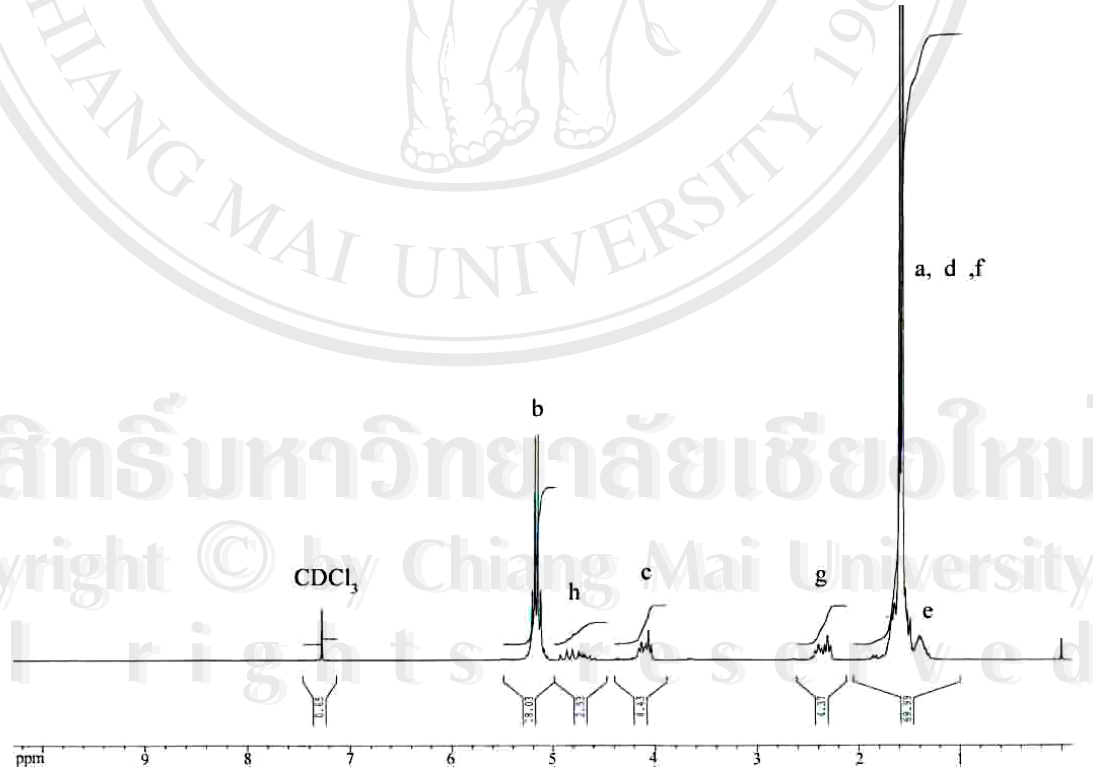


Fig. 2.24 250 MHz ^{1}H-NMR spectrum of the random terpolymer.

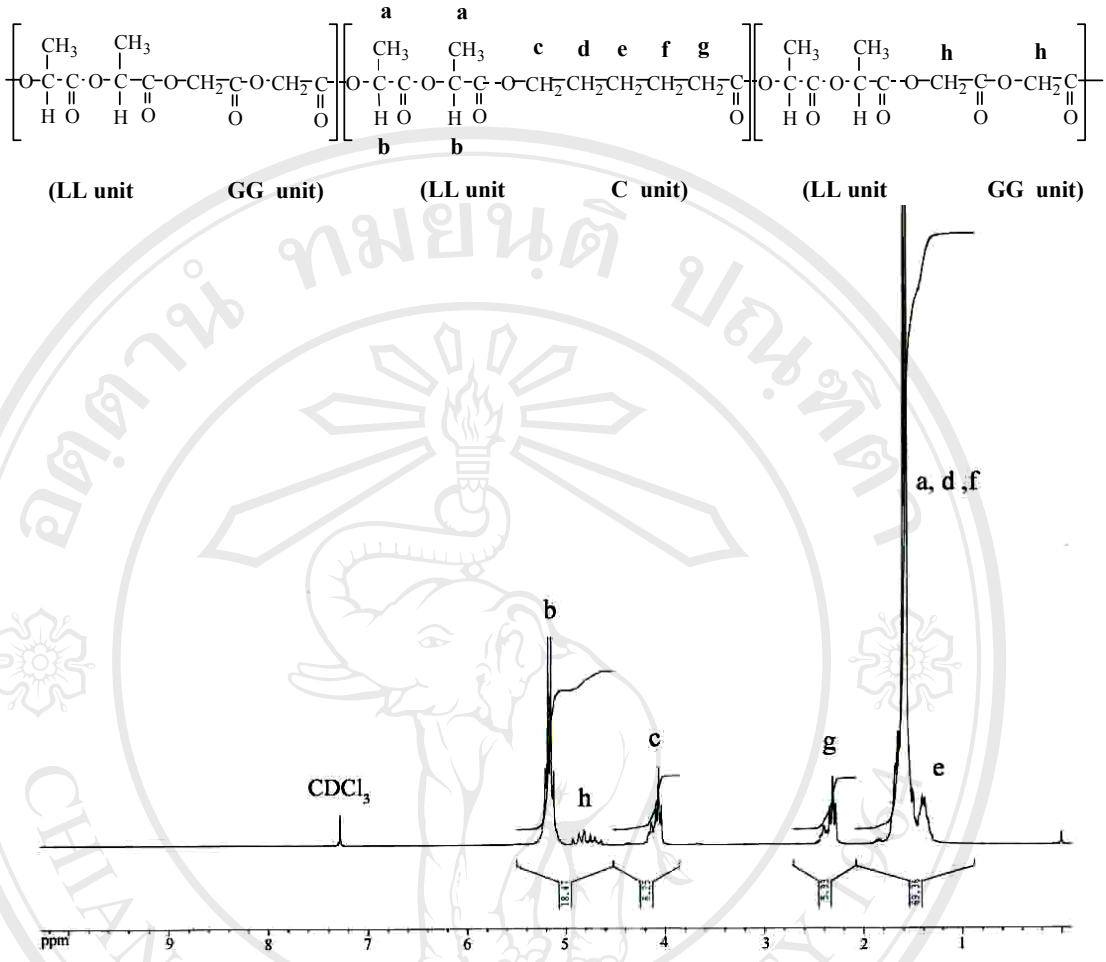


Fig. 2.25 250 MHz ^{1}H-NMR spectrum of the block terpolymer.

Table 2.5 Peak assignments and corresponding chemical shifts in ^{1}H-NMR spectra of the random and block terpolymers.

Proton assignment	Chemical shift range, δ (ppm)	
	random terpolymer	block terpolymer
b	5.3 – 5.0	5.3 – 5.0
h	4.9 – 4.6	4.9 – 4.6
c	4.2 – 4.0	4.2 – 4.0
g	2.6 – 2.2	2.6 – 2.2
a, d, f	1.7 – 1.4	1.8 – 1.5
e	1.4 – 1.2	1.5 – 1.2
$CDCl_3$ solvent	7.3	7.3

The monomer compositions of the terpolymers products were determined from the peak area integration in the ^{1}H-NMR spectra [25], the peak at δ = 5.0 - 5.3 ppm corresponding to the methine hydrogen (C-H) in the LL units, at δ = 4.0 – 4.2 ppm corresponding to methylene hydrogen (ε-CH_2) attached to the oxygen in a repeating CL unit and the peak at δ = 4.6 – 4.9 corresponding to methylene hydrogen (CH_2) in the G units. Therefore, peak area integrations in ^{1}H-NMR spectra in the range of 5.3 – 4.0 ppm are useful to evaluate the relative compositions of the monomers. Figs. 2.26-2.27 show the expanded ^{1}H-NMR spectra of the terpolymers in this range. Table 2.6 shows the relative peak area integrations for the three peak assignments.

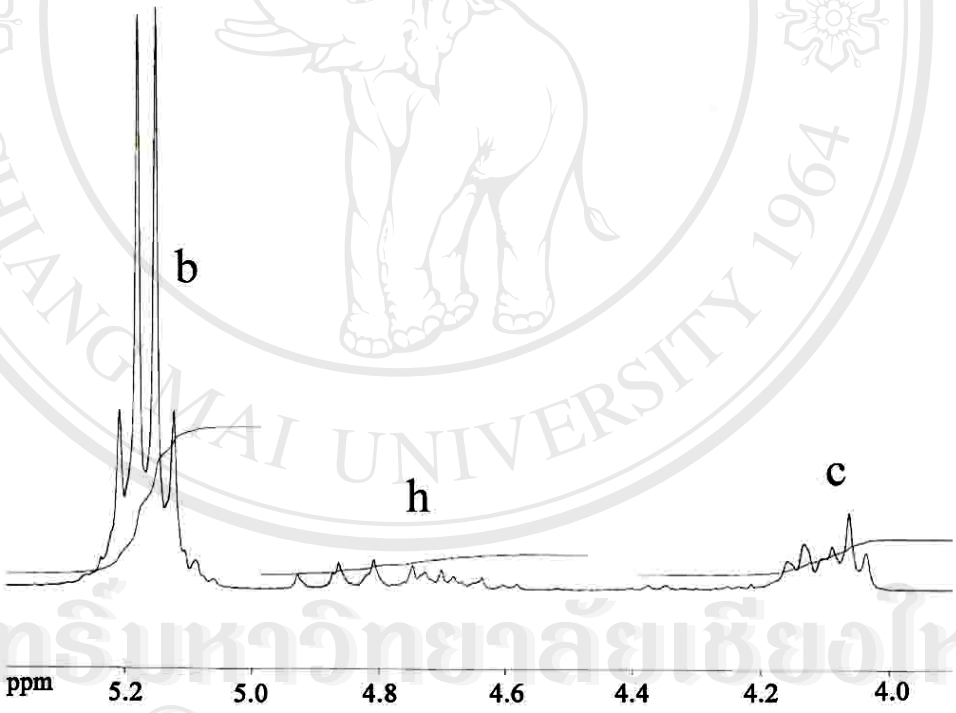


Fig. 2.26 The expanded ^{1}H-NMR spectrum of the random terpolymer in the range of 5.3 - 4.0 ppm.

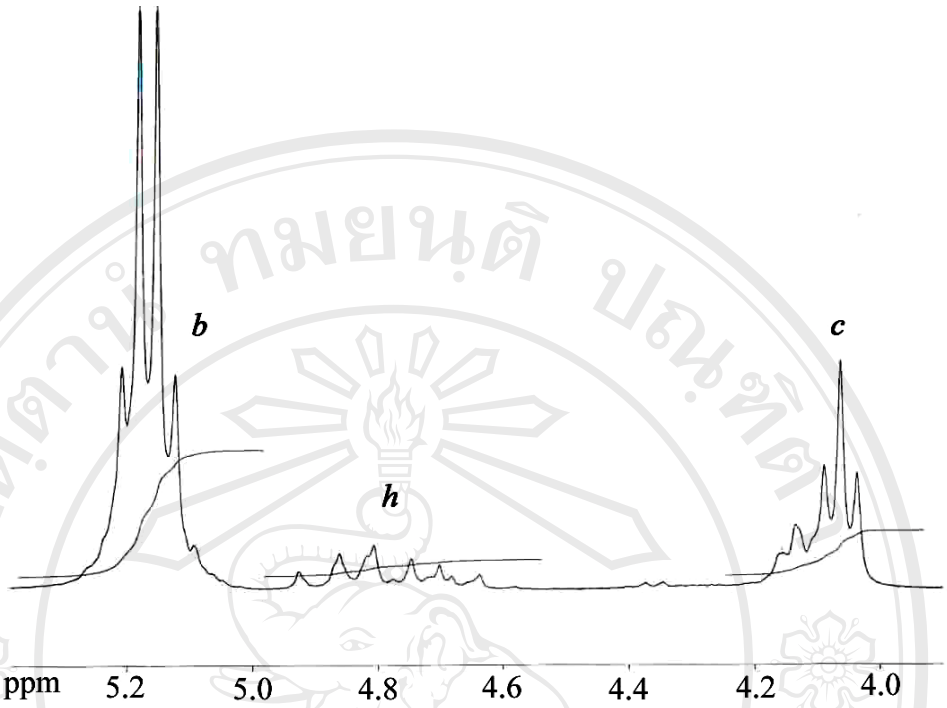


Fig. 2.27 The expanded ^{1}H-NMR spectrum of the block terpolymer in the range of 5.3 - 4.0 ppm.

Table 2.6 Peak assignments and peak area integrations in ^{1}H-NMR spectra for the random and block terpolymers.

Proton assignment	**Peak area integrations**	
	random terpolymer	**block terpolymer**
b	18.04	18.04
h	2.53	2.25
c	4.43	6.36

The monomer compositions are calculated as shown below for the random terpolymer.

Peak integration of Methine protons (2H/LL unit)		Peak integration of ε-methylene protons (2H/CL unit)		Peak integration of methylene protons (4H/G unit)
$\frac{18.04}{2}$	:	$\frac{4.43}{2}$	:	$\frac{2.53}{4}$
9.020	:	2.22	:	0.632

Thus, the terpolymer composition is as follows:

LL : CL : G = 9.020 : 2.22 : 0.632

= 75.99 : 18.7 : 5.32 mol%

= 76 : 19 : 5 mol%

The monomer composition of the block terpolymer was calculated similarly from the data in Table 2.6. It was found to be 71 : 25 : 4 mol%

The initial monomer feed ratio and the final composition ratio of the block terpolymer are similar. In the case of the random terpolymer, LL presented more while CL appeared less. It might be considered as a consequence of their different reactivities for polymerization. LL is more reactive than CL [24, 41-42].

2.6.5 Monomer sequences of terpolymers

The monomer sequences of the terpolymers were analyzed using ^{1}H-NMR and ^{13}C-NMR. The ^{1}H-NMR spectra provide information not only about the terpolymer compositions but also about the chain microstructure. Recent reports describing the ^{1}H-NMR spectra of copolymers of glycolide with L-lactide [43-44], glycolide with ε-caprolactone [30, 45-47], L-lactide with ε-caprolactone [48-49] and terpolymer of L-lactide, ε-caprolactone and glycolide [50-51] were used to assign the ^{1}H-NMR spectra line of our terpolymers. For simplicity, ^{1}H-NMR spectra in Figs. 2.26 - 2.27 are shown here as Figs. 2.28 - 2.29 to illustrate the monomer sequence assignments.

Table 2.7 shows chemical shifts along with their peak intensities and the monomer sequence assignments in the ^{1}H-NMR spectra of the random and block terpolymers. In the range of 4.0 – 4.2 ppm there are the signals due to ε-methylene protons of the caproyl unit, whereas in the range of 4.6-4.9 ppm there are the signals of methylene protons of the glycolidyl unit and in the range of 5.0 – 5.3 ppm the signals are of the methine protons of lactidyl unit.

For simplicity to explain the monomer sequence after this point onwards. We designated the L-lactide unit (lactidyl unit) as LL (A) :

$$-O-CH(CH_3)-CO-O-CH(CH_3)-CO- \qquad \text{(A)}$$

whereas the ε-caprolactone unit (caproyl unit) will be referred to as C (B) :

$$-O-\overset{\varepsilon}{C}H_2-\overset{\delta}{C}H_2-\overset{\gamma}{C}H_2-\overset{\beta}{C}H_2-\overset{\alpha}{C}H_2-CO- \qquad \text{(B)}$$

and the glycolide unit (glycolidyl unit) will be referred to as GG (C) :

$$-O-CH_2-CO-O-CH_2-CO- \qquad \text{(C)}$$

In addition, L represents only a half-L-lactide unit (lactyl unit) and G is also a half-glycolide unit (glycolyl unit).

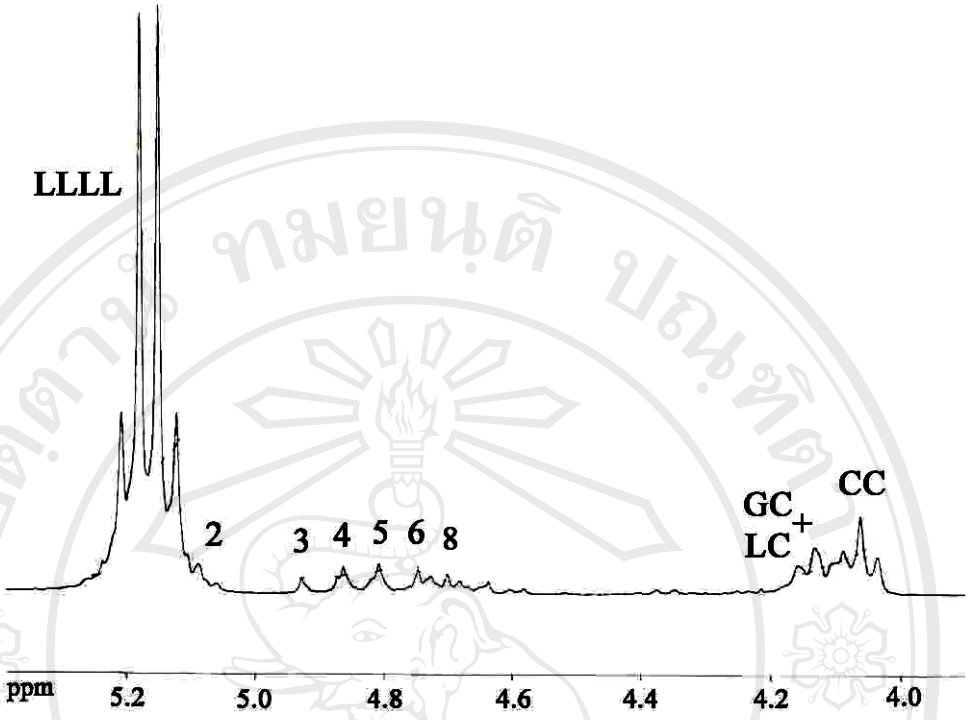


Fig. 2.28 ^{1}H-NMR spectra of the random terpolymer.

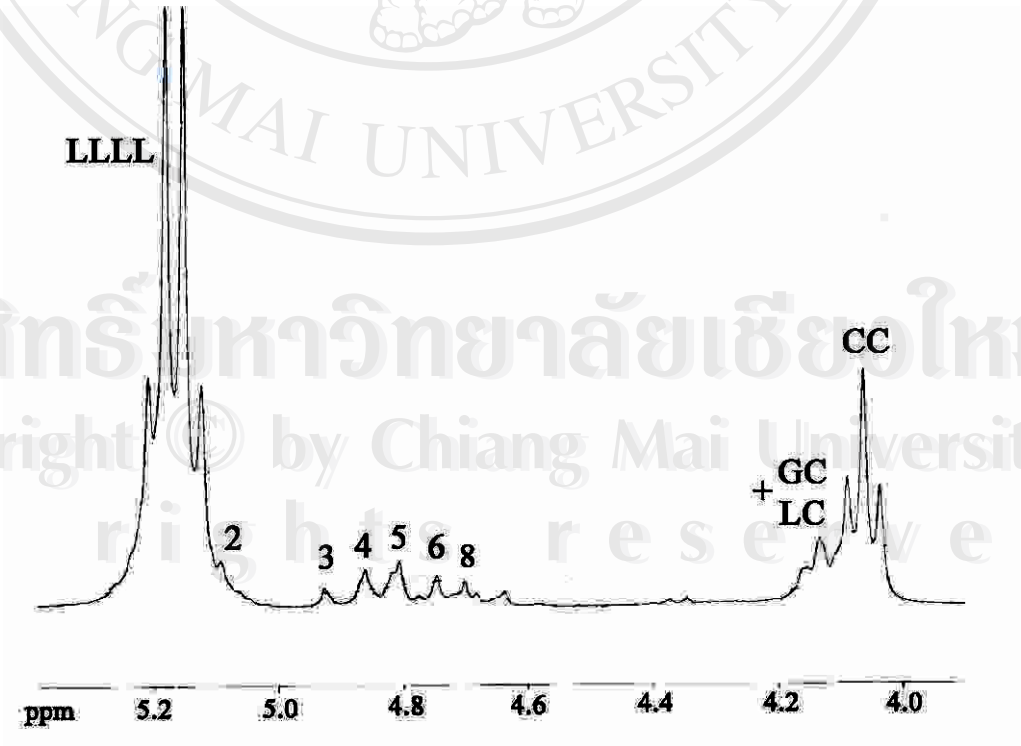


Fig. 2.29 ^{1}H-NMR spectra of the block terpolymer.

Table 2.7 Chemical shifts, peak intensities and monomer sequences in the ^{1}H-NMR spectra of the random and block terpolymers.

No.	Sequence	Random terpolymer		Block terpolymer	
		δ (ppm)	Intensity	δ (ppm)	Intensity
1	LLLL	5.16	50.07	5.16	58.77
2	LLGG + LLC + CLL + GGLL	5.09	0.97	5.09	1.63
3	CGGGG+GGGGC	4.93	0.49	4.93	0.69
4	CGGGC	4.86	0.90	4.86	1.30
5	LGL	4.81	1.03	4.81	1.61
6	GGGGC	4.75	0.80	4.75	1.13
7	CGGGG + CGGGC	4.73	0.60	-	-
8	CLC	4.70	0.67	4.70	0.89
9	CGC	4.64	0.42	4.64	0.55
10	GC + LC	4.13	1.59	4.13	2.31
11	CC	4.06	5.40	4.06	16.75

^{13}C-NMR spectra of the terpolymers in $CDCl_3$ at 294 K were recorded at resonance frequency of 100 MHz on a Bruker Advance AMX400 spectrometer. The ^{13}C-NMR spectra of the terpolymer products are shown in Figs. 2.30 – 2.31. Table 2.8 shows peak assignments and corresponding chemical shifts of the terpolymers. As we can see that the ^{13}C-NMR spectral range is spread over a much wider than that of ^{1}H-NMR. It therefore makes possible to draw information of chain microstructure, as described below.

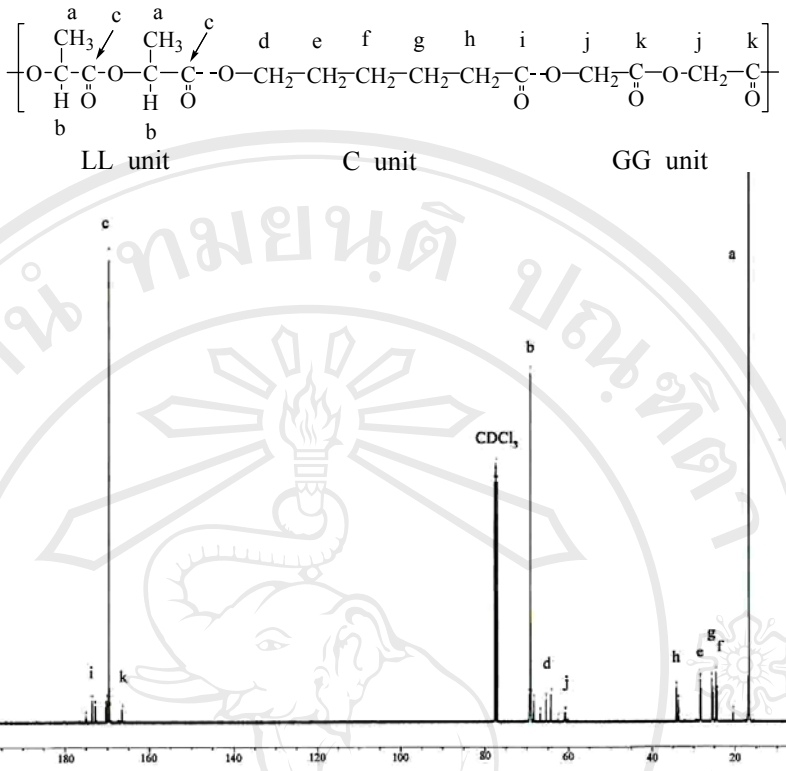


Fig. 2.30 100 MHz ^{13}C-NMR spectrum of the random terpolymer in $CDCl_3$ as solvent at 294 K.

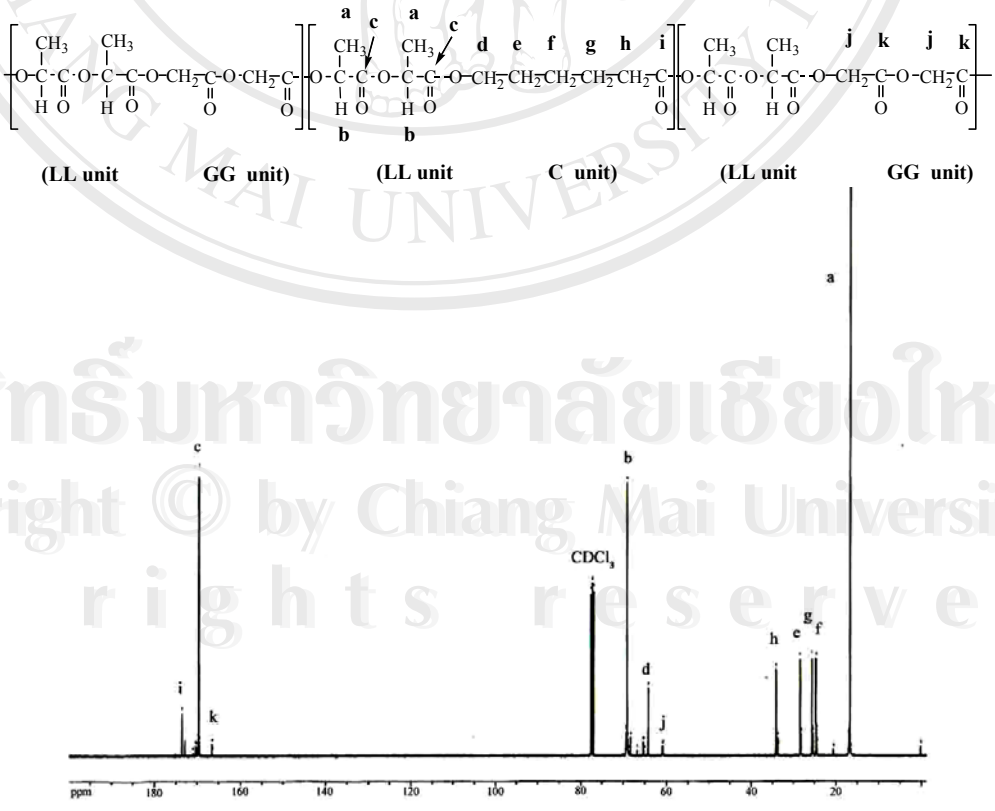


Fig. 2.31 100 MHz ^{13}C-NMR spectrum of the block terpolymer in $CDCl_3$ as solvent at 294K.

Table 2.8 Peak assignments and corresponding chemical shifts in ^{13}C-NMR spectra of the random and block terpolymers.

^{13}C assignment	Chemical shift range, δ (ppm)	
	random terpolymer	block terpolymer
i	173.5	173.5
c	169.56	169.56
k	166.46	166.46
b	68.8	69.0
d	64.1, 65.3	64.1, 65.3
j	60.7, 60.9	60.7, 60.9
h	34.1, 33.6	33.7, 34.1
e	28.1, 28.3	28.2, 28.3
g	25.1, 25.5	25.5
f	24.4, 24.5	24.7
a	16.7	16.6
$CDCl_3$ solvent	76.9, 77.2, 77.5	76.9, 77.2, 77.5

A particular region in the range of 166-175 ppm has been found very useful [41, 51-55]. This is the carbonyl carbon (C=0) region which is sensitive to sequencing variations. Figs 2.32 – 2.33 show expanded spectra in the region of the random and block terpolymers respectively. Assigning spectral lines to corresponding comonomeric sequences has been performed by analogy on the basis of recent research describing spectra of the copolymers of glycolide, lactide and ε-caprolactone [41, 51-55], as shown in Figs. 2.32 – 2.33. Table 2.9 shows chemical shifts along with their intensities in the spectra. The analysis makes use of the carbonyl signals from the ester units; for sequences containing only ε-caprolactone, a singlet is observed at 173.5 ppm while lactate-based system the homopolymer shows a signal at 169.6 ppm [48] (These chemical shifts are quoted from the appropriate publications, these values may vary slightly with for example change of solvent; the relative

positions should remain unchanged). The situation is made more complex for the lactidyl and glycolidyl units by the fact that once the symmetry is reduced by the presence of comonomer units, the two carbonyls in the repeat unit have different chemical shifts. The presence of transesterification in the polymer can be detected by the presence of isolated lactidyl (lactyl) or isolated glycolidyl (glycolyl)units in the polymer [55].

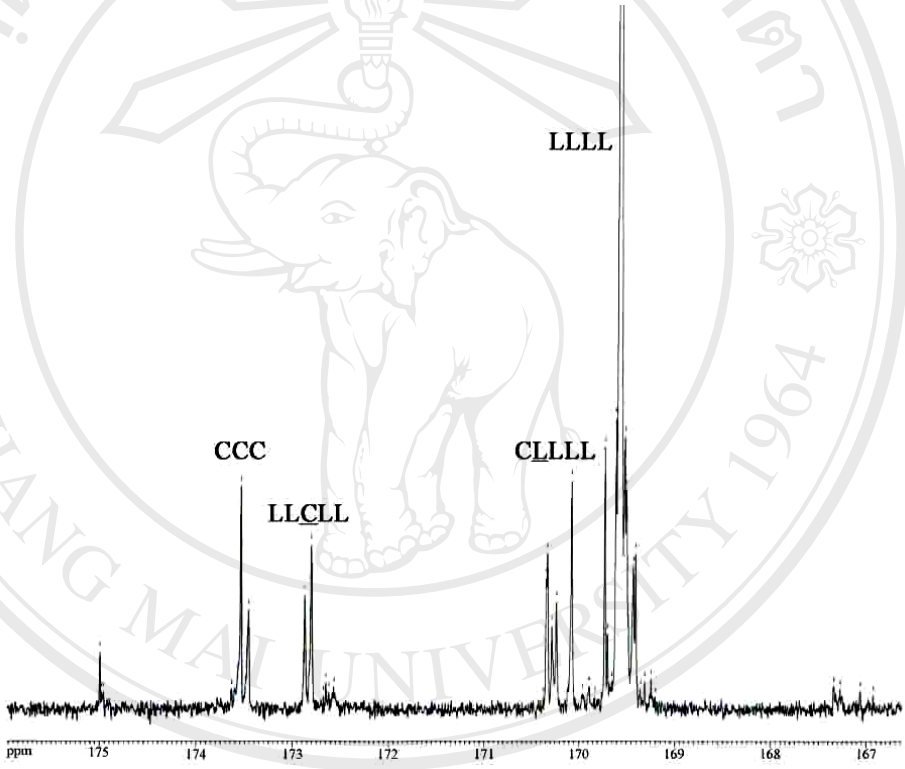


Fig. 2.32 Expanded carbonyl region of the ^{13}C-NMR spectrum of the random terpolymer.

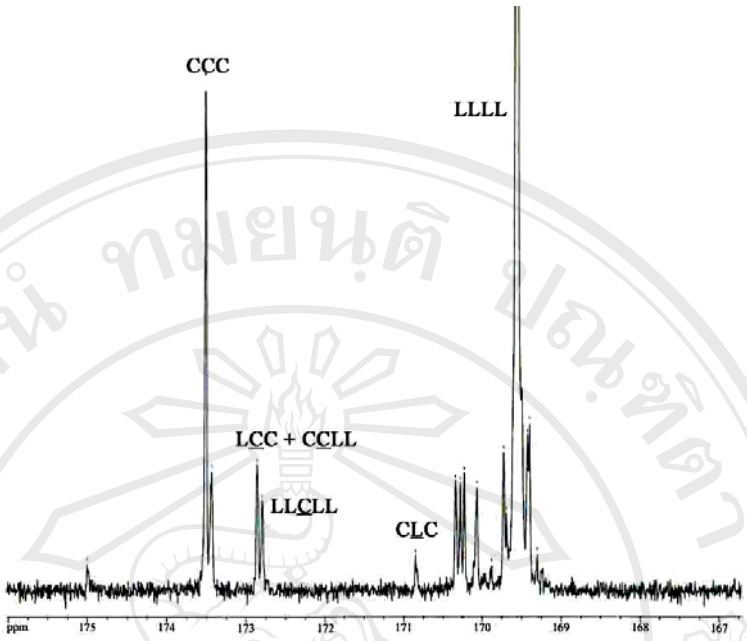


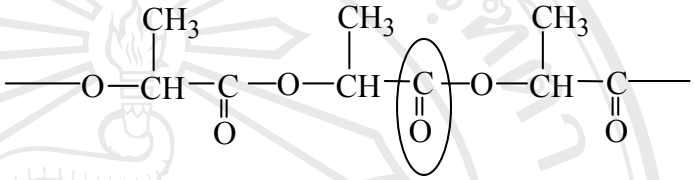
Fig. 2.33 Expanded carbonyl region of the ^{13}C-NMR spectrum of the block terpolymer.

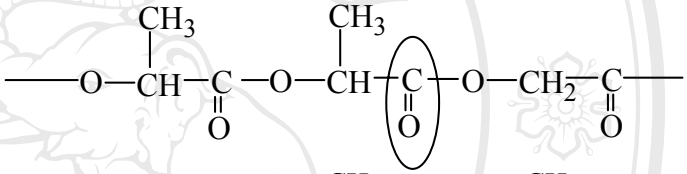
Table 2.9 Chemical shifts along with their intensities of the terpolymer sequences in the ^{13}C-NMR spectra of random and block terpolymers in the carbonyl atom regions.

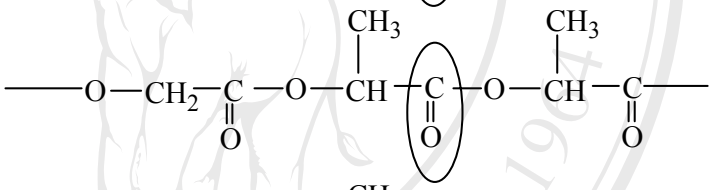
No.	Sequence	Random terpolymer		Block terpolymer	
		δ (ppm)	Intensity	δ (ppm)	Intensity
1	CCC	173.53	0.88	173.51	19.62
2	LLCC	173.45	0.40	173.43	4.63
3	LCC + CCLL	172.87	0.45	172.85	4.85
4	LLCLL	172.80	0.65	172.79	3.47
5	CLC	-	-	170.85	1.37
6	LLLLC + CLLLC	170.32	0.62	170.34	4.24
7	CLLC	170.28	0.33	170.28	4.15
8	CLLC	170.23	0.43	170.22	4.54
9	CLLLL	170.07	0.90	170.06	4.02
10	LLLLC	169.72	1.03	169.72	5.35
11	CLLLC + LLGG	169.69	0.30	169.69	3.00
12	LLLLLL + CLLLL	169.56	18.67	169.56	129.35
13	GLG	169.50	0.87	169.42	5.99

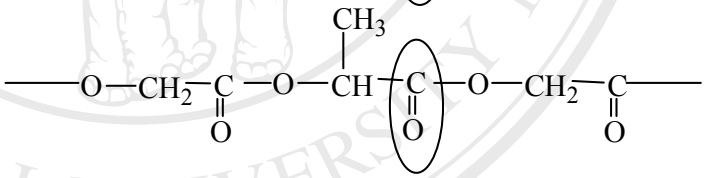
Below shows chemical structures to visualize influences of the monomer neighbours in different triad sequences. The spectral line corresponding to the C=O carbon of the middle unit is influenced by the neighbouring units on either side. Additional effect from further neighbours is also taken into account to enable all possible assignments to the spectral lines.

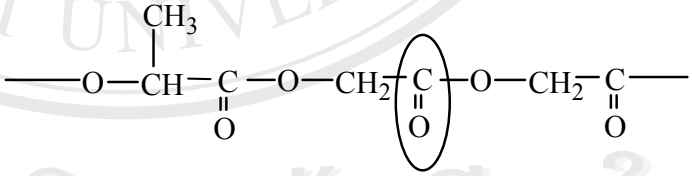
Triad Sequences **Corresponding Structures**

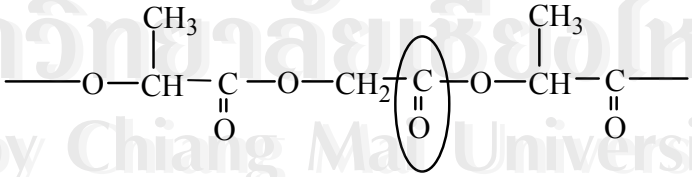
LLL 

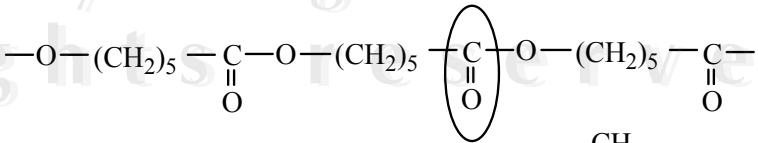
LLG 

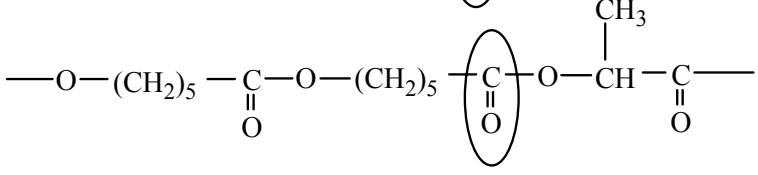
GLL 

GLG 

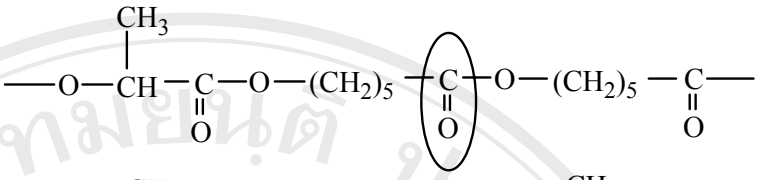
LGG 

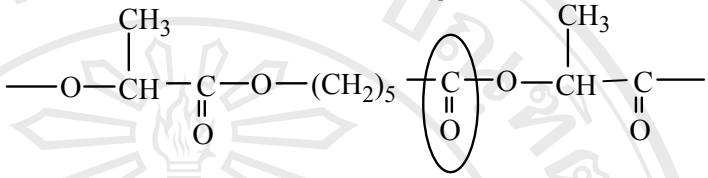
LGL 

CCC 

CCL 

Triad Sequences Corresponding Structures

LCC 

LCL 

The average block lengths of lactidyl, caproyl and glycolidyl, (l_{LL}, l_C, l_{GG}), can be determined from ^{13}C-NMR spectra using the Equations 2.1 – 2.3 [55].

$$l_{LL} = \frac{1}{2} \times \frac{LLL + LLX + XLL + XLX}{XLX + \frac{1}{2}(LLX + XLL)} \quad ; \quad X = G \text{ and } C \tag{2.1}$$

$$l_C = \frac{CCC + CCY + YCC + YCY}{YCY + \frac{1}{2}(CCY + YCC)} \quad ; \quad Y = L \text{ and } G \tag{2.2}$$

$$l_{GG} = \frac{1}{2} \times \frac{GGG + GGZ + ZGG + ZGZ}{ZGZ + \frac{1}{2}(GGZ + ZGG)} ; \quad Z = L \text{ and } C \tag{2.3}$$

Where the factor of $\frac{1}{2}$ is only suitable for the double monomer units in equation 2.1 and 2.3. This technique is sensitive to longer sequences, and this is particularly the case for ^{13}C-NMR, therefore the triad sequences need to be calculated from (for example pentad) sequences.

For instance, Kasperczyk, J. and Bero, M. [52, 55] demonstrated the calculation of average lengths of blocks l_{LL} and l_C of copolymer of L-lactide with ε-caprolactone as below:

$$l_{LL} = \frac{1}{2} \times \frac{LLL + LLC + CLL + CLC}{CLC + \frac{1}{2}(LLC + CLL)}$$

where :

$$LLL = \frac{1}{2}[CLLLL] + \frac{1}{2}[LLLLC] + \frac{1}{3}[CLLLC] + [LLLLLL]$$

$$LLC = \frac{1}{2}[CLLC] + \frac{1}{2}[LLLLC] + \frac{1}{3}[CLLLC]$$

$$CLL = \frac{1}{2}[CLLC] + \frac{1}{2}[CLLLL] + \frac{1}{3}[CLLLC]$$

$$CLC = [CLC]$$

$$l_C = \frac{LCL + CCL + LCC + CCC}{LCL + \frac{1}{2}(CCL + LCC)}$$

where :

$$LCL = [LLCLL] + [LLCLC] + [CLCLL] + [CLCLC]$$

$$CCL = [CCLC] + [CCLL]$$

$$LCC = [CLCC] + [LLCC]$$

$$CCC = [CCC]$$

The monomer sequence in parenthesis, $[seq.]$, indicate the contents of appropriate sequences in the copolymer chain represented by the intensities of suitable lines in the ^{13}C-NMR spectrum. In addition, for example the CLLC sequence contains 1 CLL and 1 LLC triad and must be weighted accordingly.

In the case of ^{1}H-NMR spectra the average block lengths of the lactidyl and glycolidyl, l_{LL} and l_{GG} can also be calculated in the same manner using equation 2.1 and 2.3, whereas the average block length of caproyl can be determined by equation 2.4

$$l_C = \frac{CC + YC}{YC}; \quad Y = L \text{ and } G \tag{2.4}$$

From both ^{1}H-NMR and ^{13}C-NMR spectra, we have analyzed the sequence lengths of l_{LL}, l_C, and l_{GG} as described above and the results obtained are shown in Table 2.10.

Table 2.10 The sequence distribution of the random and block terpolymers.

Terpolymer	Sequence Length		
	l_{LL}	l_C	l_{GG}
Random ^{1}H	9.0	2.3	0.85
Random ^{13}C	9.8	2.2	[a]
Block ^{1}H	8.1	3.8	0.79
Block ^{13}C	7.5	4.0	[a]

[a] Unable to assign peaks unambiguously hence no value available

The sequence lengths appear to largely reflect the distributions expected for random terpolymers with more or less equal reactivities. The main differences in the NMR between the so-called block and random samples is that the block sample clearly shows a much higher proportion of the CCC triad than is observed for the random sample with 60% for the block and 37% for the random. This of course is entirely in line with expectations based on the method used to synthesize the materials. In particular, since in the block terpolymer the ε-caprolactone is restricted to one of the blocks, the overall equivalent concentration appears contiguously in longer sequence lengths than broken up as in the random terpolymer. No conclusion could be drawn from the glycolidyl units from the ^{13}C-NMR because of difficulties assigning the NMR peaks unambiguously, however, the data from the ^{1}H-NMR is included. The only other particularly noticeable feature is a signal which can be assigned to a CLC triad is observed for the block sample, but not for the random sample. It is the presence of this unit that may in part explain the lower average

lactidyl sequence length for the block terpolymer. Apart from this peak, there is some evidence for anomalous CLC and GLG sequences; however, these are not a major feature of the NMR. Thus it would seem transesterification has little effect on the lactidyl units. The glycidyl units in contrast seem rather more effected by this process and a peak at 4.81 ppm in the ^{1}H-NMR which can be related to the presence of isolated glycidyl units is the most prominent in this region of the spectrum. As a consequence, the average sequence length for the glycidyl units is less than 1.

One final feature of the ^{1}H NMR which is worthy of note, is that while most of the spectrum is comparable to that given by Dobrzynski [51], the caprolactone region differs substantially. In particular the CC sequences are present in substantially higher concentrations than the GC and LC sequences; in the ^{1}H-NMR presented by Dobrzynski for a polymer of similar composition, the situation is reversed. This presumably relates to the different method of polymerization used.

In the case of the block terpolymer, there are two types of lactidyl sequences. The first are those involving the copolymerization of lactide with ε-caprolactone to form the macro-initiator or middle block and the second are those located in the end blocks copolymerized with glycolide. It is not possible to differentiate in the NMR spectra between these two types of sequences and as a consequence the estimate of the average sequence length involves an average over the two types. If we assume that for the centre block, the units are arranged randomly according to composition alone we can estimate that the sequence length of the lactide units in the two outer blocks is ~ 10. As the molecular weight data were obtained from GPC measurements calibrated with polystyrene standards, there will always be some doubt as to the absolute values. However, if we combine the GPC and NMR data, we can develop a picture of the block terpolymer with the middle block containing some 80 to 90 C and LL units, while the end blocks each contain some 50-60 units which are largely LL. The C units are restricted to this central block. Within the end blocks, the LL units exhibit an average sequence length of ~ 10, separated by glycolide units. In contrast, the random terpolymer contains LL sequences of some 9 units but which are distributed throughout the chain separated by either glycolide units or short sequences of caprolactone. The caprolactone units are distributed throughout the chain. However it is worth to mention here that, much higher composition of 76 mol% L-lactide in the random terpolymer analyzed from ^{1}H-NMR integration areas agrees

somehow to the observed rather long sequence length of lactidyl in the random terpolymer (9-9.8).

2.6.6 Thermal transition analysis

DSC analyses of the homopolymer and terpolymer products were conducted at a heating rate of 20°C/min under dry nitrogen atmosphere. The DSC thermograms are shown in Figs. 2.34 – 2.38 and the results compared in Table 2.11. Sample weights were typically in the range of 3 – 5 mg. Prior to measurement, the samples were melted and quenched by immersion in liquid nitrogen in order to make the material amorphous.

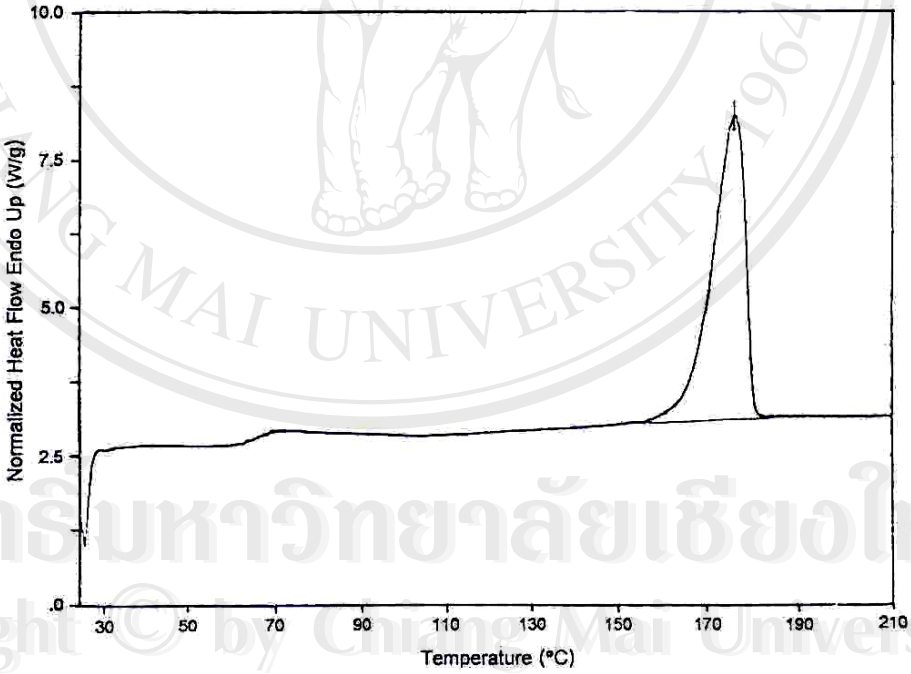


Fig. 2.34 DSC thermogram of poly(L-lactide) [32].

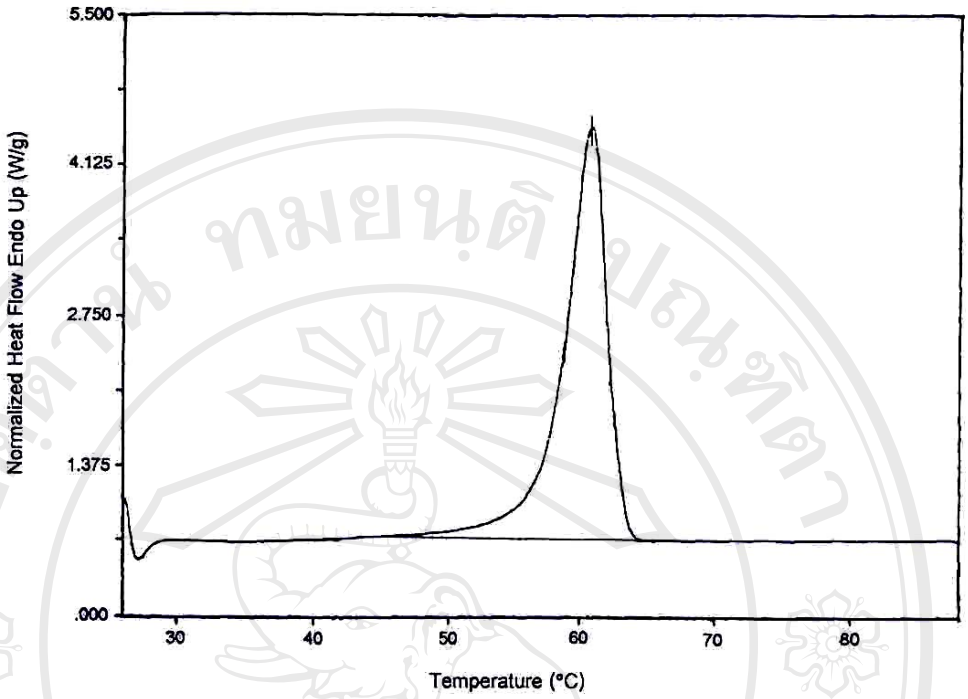


Fig. 2.35 DSC thermogram of poly(ε-caprolactone) [32].

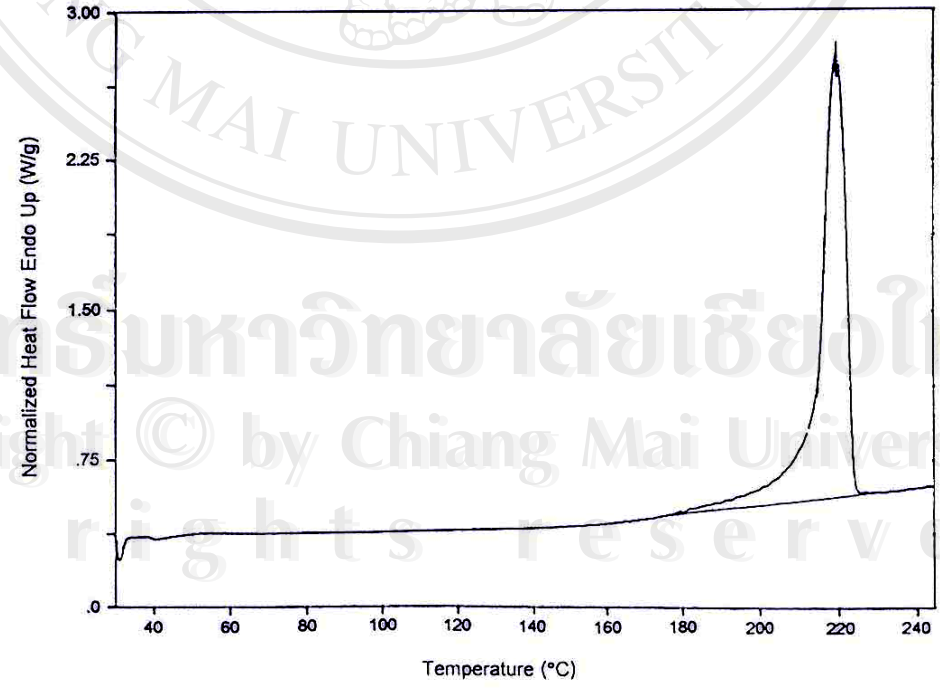


Fig. 2.36 DSC thermogram of poly(glycolide) [32].

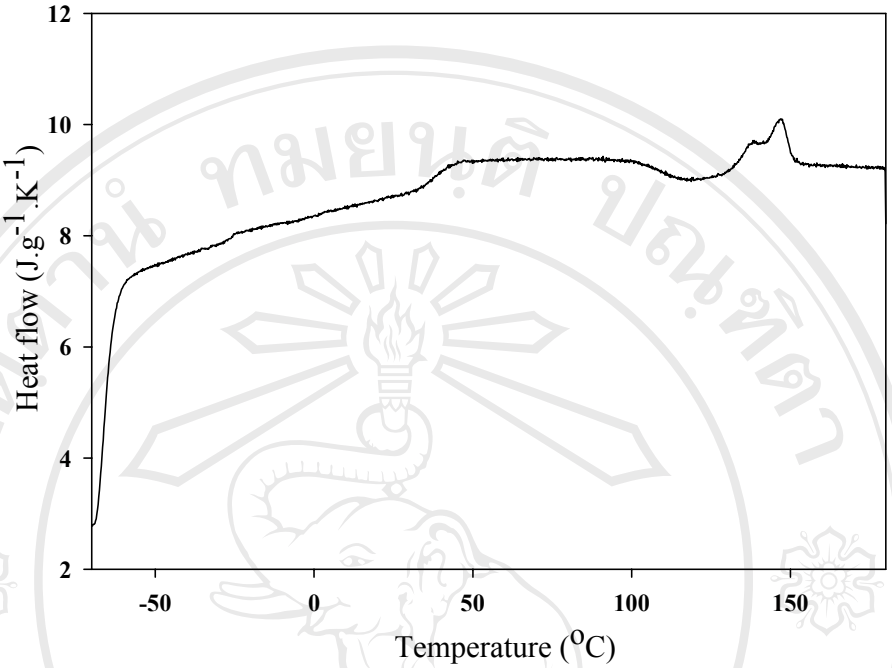


Fig. 2.37 DSC thermogram of the random terpolymer.

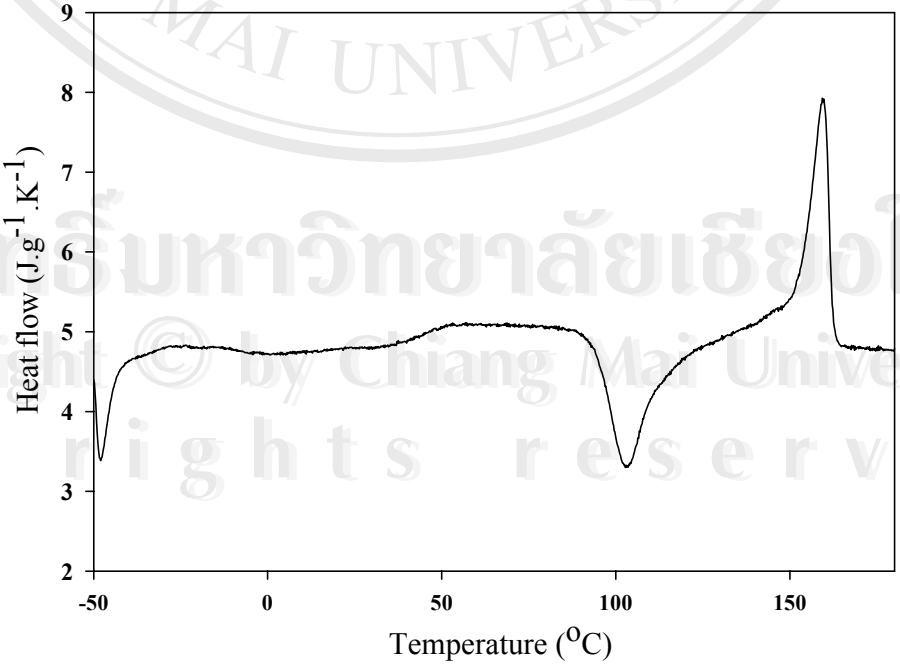


Fig. 2.38 DSC thermogram of the block terpolymer.

Table 2.11 DSC transition temperatures and heats of melting of the homopolymers and terpolymers.

Polymer	T_g[a] (°C)	T_m[b] (°C)	ΔH_m (J/g)
Poly(L-lactide)	65 (65)	176	46.7
Poly(ε-caprolactone)	nd (-60)	61	93.2
Poly(glycolide)	nd (35)	217	102.8
Random terpolymer	35 (35.4)[c]	144(143.4)[d]	7.65
Block terpolymer	42	156	25.2

[a] T_g taken as the mid-point of the glass transition

[b] T_m taken as the peak temperature of the melting range

[c] calculated T_g values in parentheses from Fox equation (see text)

[d] calculated T_m values in parentheses from Flory equation (see text)

nd : not determined or difficult to estimate (reference value in parentheses)

The glass transition temperature, T_g, for the random terpolymer can be compared with the weight-averaged values calculated from the Fox equation [56]:

$$\frac{W_L}{T_{g_{PLL}}} + \frac{W_{CL}}{T_{g_{PCL}}} + \frac{W_G}{T_{g_{PG}}} = \frac{1}{T_{g_{random\ terpolymer}}}$$

where W_{LL} is the weight fraction of L-lactide in the terpolymer

W_{CL} is the weight fraction of ε-caprolactone in the terpolymer

W_G is the weight fraction of glycolide in the terpolymer

and $T_{g_{PLL}}$, $T_{g_{PCL}}$ and $T_{g_{PG}}$ are the T_g (K) values of the respective homopolymers. W_{LL}, W_{CL} and W_G are calculated from the corresponding mole fraction m_{LL}, m_{CL} and m_G obtained from the ^{1}H-NMR spectra, as determined in section 2.6.4. W_{LL}, W_{CL} and W_G values calculated are 0.799, 0.158 and 0.042. The values of weight fractions and $T_{g_{PLL}}$, $T_{g_{PCL}}$ and $T_{g_{PG}}$ in Table 2.11 are substituted in Fox equation. A

value for $T_{g_{random\ terpolymer}}$ of 35.4°C is obtained, which agrees closely with the experimental value of 35°C.

Similarly, the T_m of the random terpolymers can be estimated from the Flory equation [57]:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_m^*} \ln m_{LL}$$

where m_{LL} is the mole fraction of the main L-lactide crystallizing component and T_m^0 and ΔH_m^* are the reference melting point and heat of melting of a 100% crystalline sample respectively of poly(L-lactide) homopolymer. Substituting values of m_{LL} = 0.76, T_m^0 = 175°C (448 K) and ΔH_m^* = 93.7 J/g [58] into the Flory equation yields the theoretical value for T_m of 143.4°C, which is in close agreement with the observed DSC value of 144°C.

DSC thermograms of the random terpolymer showed glass transition temperature (T_g) at 35°C. The melting range showed double peaks with the higher peak at 144°C, ΔH_m = 7.65 J/g. This is probably interpreted that two different crystal sizes appeared. The observed T_g and T_m values were close to the calculated values (as shown in parentheses in the Table 2.11). For the block terpolymer, its T_g and T_m appeared at 42°C and 156°C, respectively. The ΔH_m was 25.2 J/g, indicating the block terpolymer had much more crystalline than the random terpolymer.

2.6.7 Thermal stability analysis

TG thermograms of poly(L-lactide), poly(ε-caprolactone), poly(glycolide) and the terpolymer products obtained at a heating rate of 20°C/min under dry nitrogen are shown in Figs. 2.39 – 2.43 and the temperature ranges which the weight losses occur are shown in Table 2.12

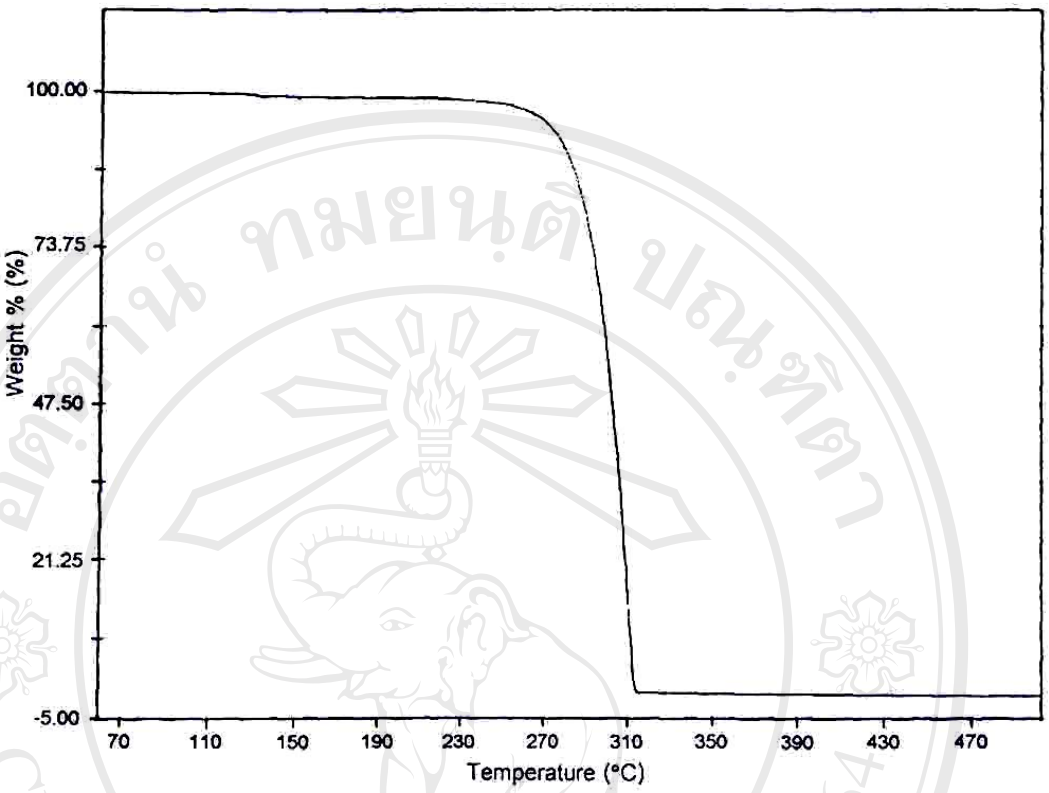


Fig. 2.39 TG thermogram of poly(L-lactide) [32].

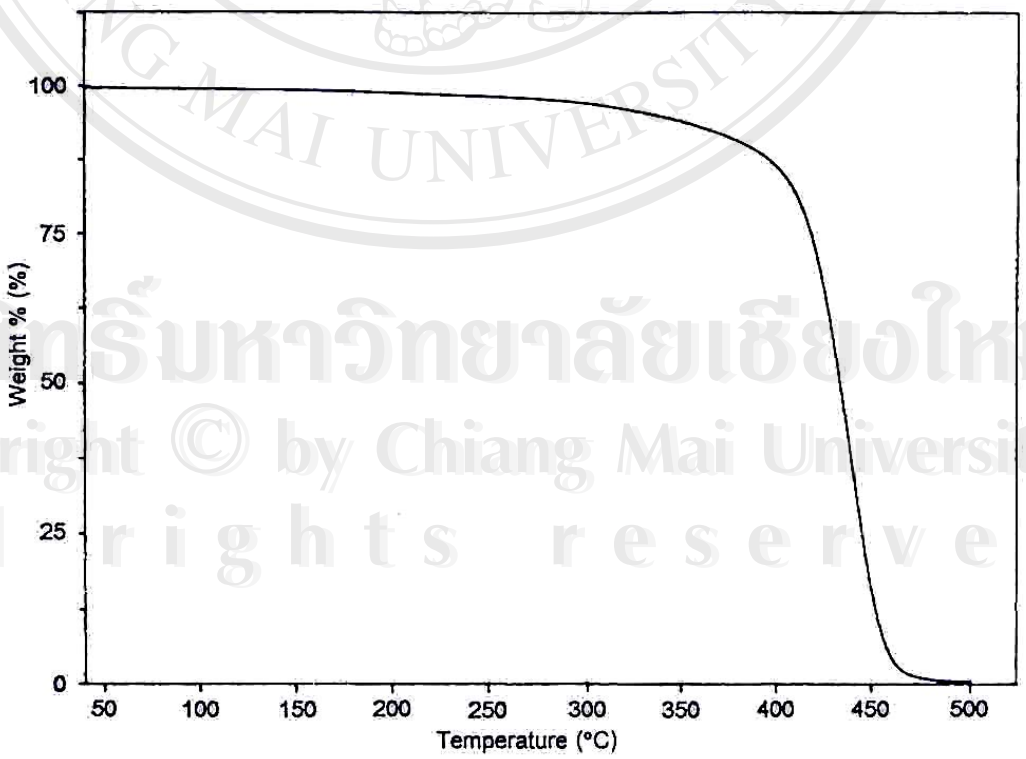


Fig. 2.40 TG thermogram of poly(ε-caprolactone) [32].

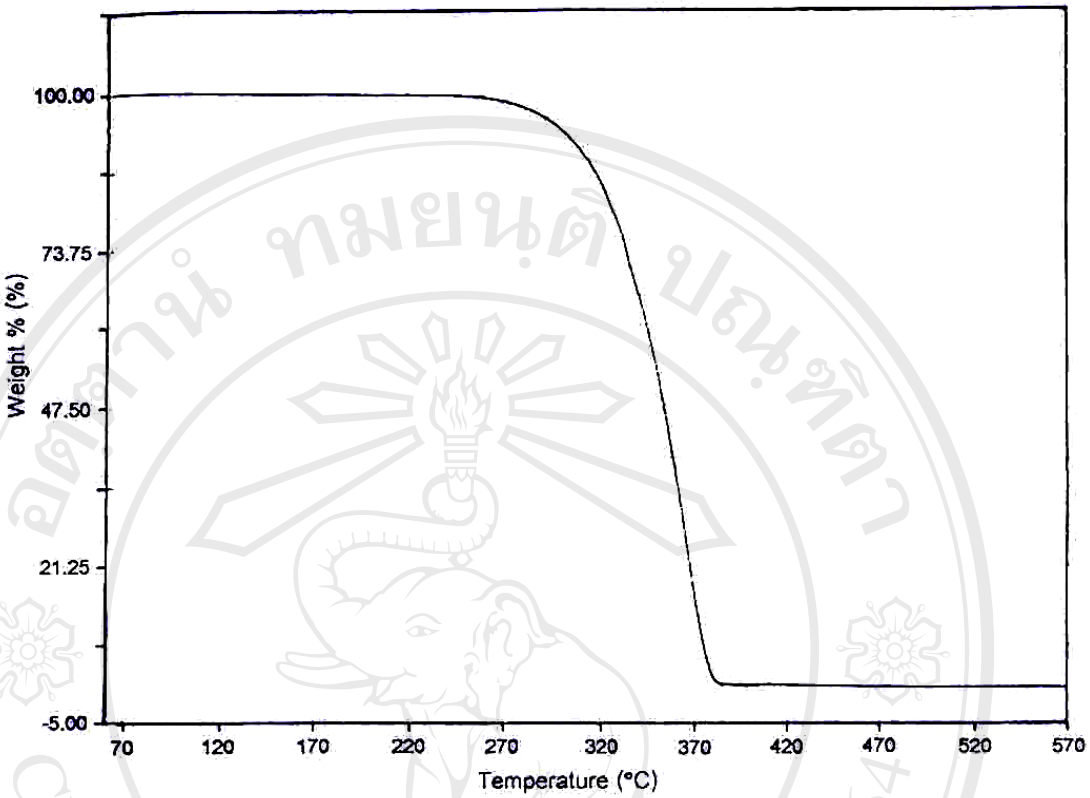


Fig. 2.41 TG thermogram of poly(glycolide) [32].

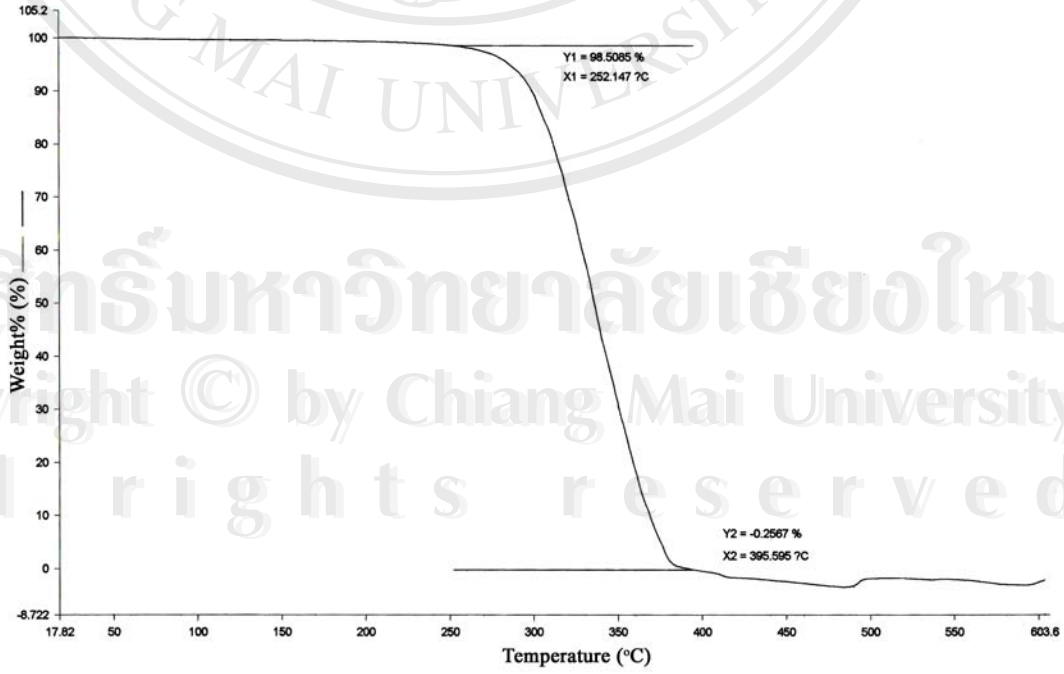


Fig. 2.42 TG thermogram of the random terpolymer.

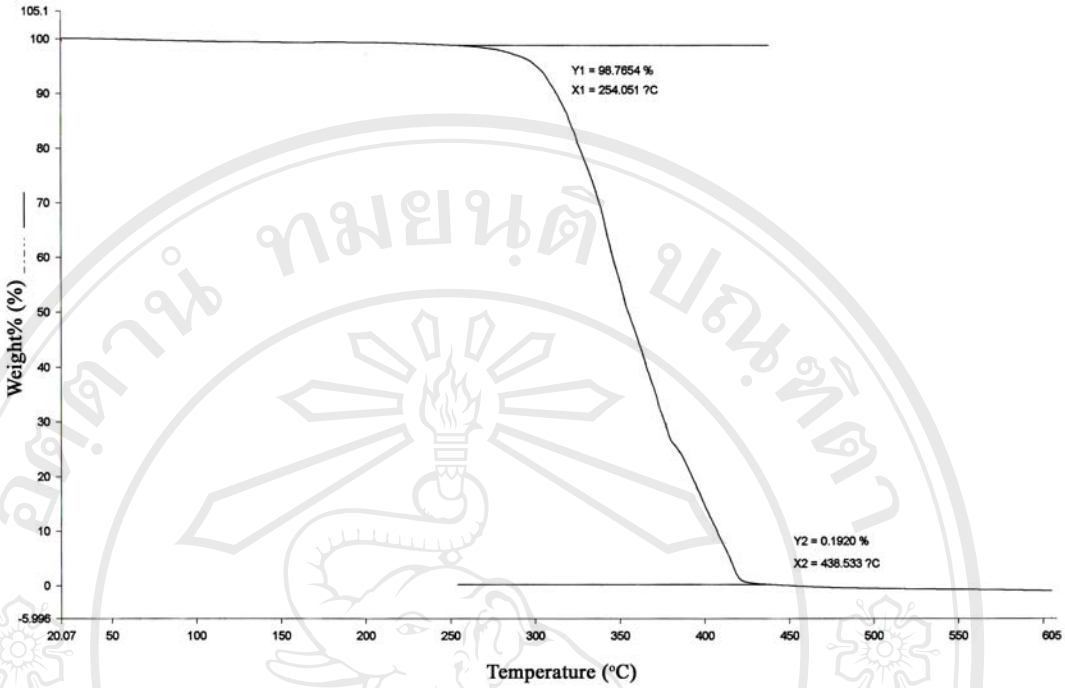


Fig. 2.43 TG thermogram of the block terpolymer.

Table 2.12 TG thermal degradation range for the homopolymers and terpolymer products.

Polymer	**Thermal degradation range (°C)**
Poly(L-lactide)	210-320
Poly(ε-caprolactone)	240-500
Poly(glycolide)	250-410
Random terpolymer	252-390
Block terpolymer	254-430

Thermogravimetric studies showed that the onset of significant degradation did not take place until ~ 250°C. The weight loss profiles showed single-step to complete (100%) with no involatile residue remaining. The initial temperatures of degradation are useful when combined with the DSC data to define the melting processing ranges of the polymers for fibre melt spinning as described in chapter 3.