CHAPTER 4

POLYMER SYNTHESIS AND CHARACTERIZATION

4.1 Homopolymerization and Copolymerization of Glycolide and δ-Valerolactone

4.1.1 Synthesis Procedure

The polymerization reactions were carried out using monomer mole ratios, initiators, temperatures and times as detailed in Table 4.1.

Glycolide alone, δ-valerolactone alone, or a comonomer mixture of the two were accurately weighed and placed in a 5 ml screw-cap bottle with a magnetic stirrer bar in a dry nitrogen atmosphere glove box at room temperature. 0.1 mole % of the initiator was then added with a capillary tube to the mixture and the bottle was tightly closed. The bottle was removed from the glove box and immersed in a silicone oil bath with stirring (see Fig. 4.1) at the appropriate temperature for the required time period. At the end of the polymerization period, the bottle was allowed to cool to room temperature. The crude product was ground up into a fine powder and dried to constant weight in a vacuum oven at 60°C before purification. The physical appearances of both the crude and purified products were as described in Table 4.1.

4.1.2 Purification of Poly(δ-Valerolactone) by Reprecipitation

The crude poly(δ-valerolactone), PVL, was purified by dissolving in warm chloroform at about 40°C and reprecipitating the polymer by dropwise addition with efficient stirring into ice-cooled n-hexane, an appropriate non-solvent, as shown in Fig. 4.2. The white powdery precipitate was filtered off into a sintered glass filter (porosity 4) and dried in a vacuum oven at room temperature for 8 hours before being finally stored in a vacuum desiccator. The purified products obtained are described in Table 4.1 in terms of their physical appearances and % yields.

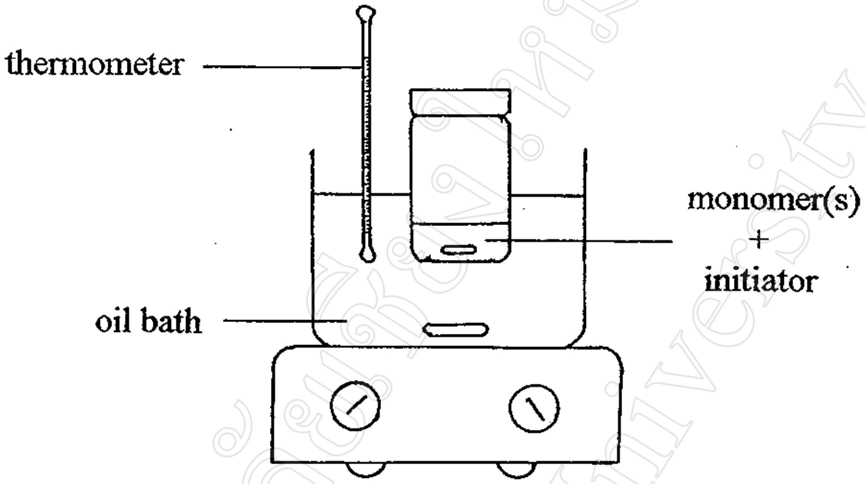


Fig. 4.1 : Apparatus used for homopolymerization and copolymerization reactions.

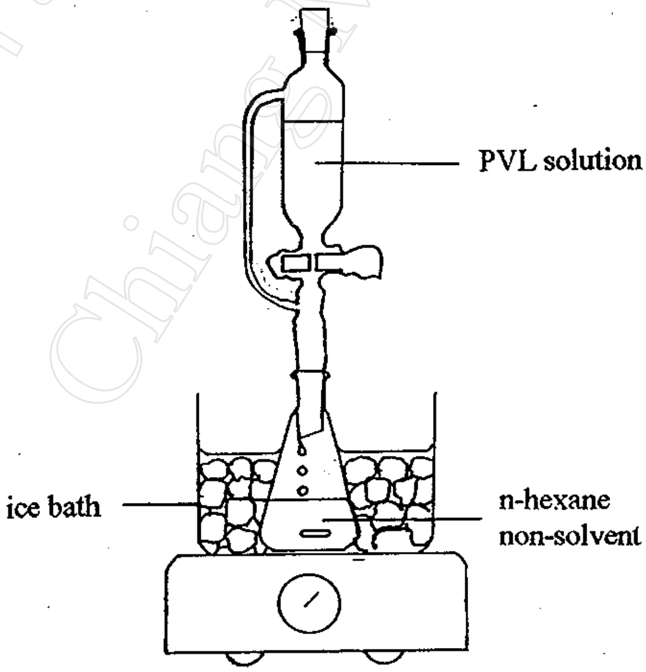


Fig. 4.2 : Apparatus used for the purification of poly(δ-valerolactone) by reprecipitation.

4.1.3 Purification of Poly(glycolic acid)

Using the apparatus shown in Fig. 4.3, an accurately weighed amount of crude poly(glycolic acid), PGA, previously ground up into a fine powder, was refluxed in absolute ethanol with efficient stirring at 77-78°C for 12 hours. The purified polymer was then filtered off, washed with more hot absolute ethanol and dried to constant weight in a vacuum oven at 60°C. The purified products obtained are each described in Table 4.1 in terms of their physical appearances and % yields.

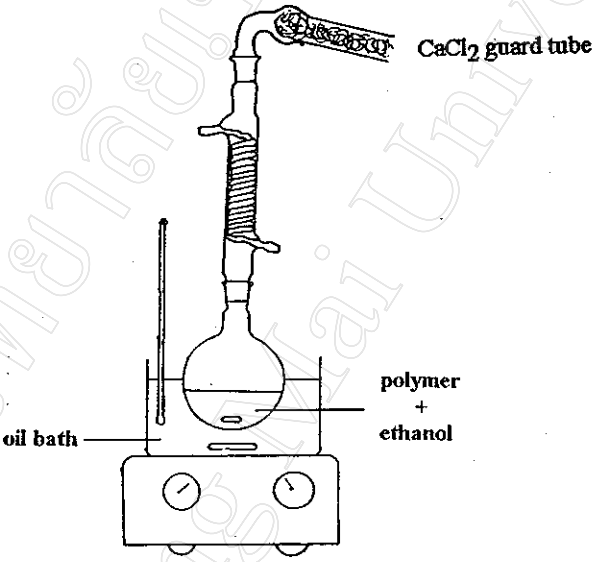


Fig. 4.3 : Apparatus used for the purification of the crude PGA and P(GA-co-VL) products by ethanol extraction.

4.1.4 Purification of Poly(glycolic acid-co-valerolactone)

The purification procedure used for the poly(glycolic acid-co-valerolactone), P(GA-co-VL), products was similar to that described above for PGA, using the apparatus shown in Fig. 4.3. The purified products obtained are described in Table 4.1 in terms of their physical appearances and % yields.

The reason why the crude PGA and P(GA-co-VL) products were purified by hot alcohol extraction rather than by reprecipitation was because of their insolubilities in all common organic solvents. The only effective solvent was hot dimethyl sulphoxide (DMSO) which had the disadvantage for purification of being very difficult to remove completely from the reprecipitated polymer. Thus, hot alcohol extraction was used instead to remove any remaining monomer and initiator residues.

From the results shown in Table 4.1, the purified poly(glycolic acid) and poly(glycolic acid-co-valerolactone) products obtained using stannous octoate (SO) as initiator at 150°C for 12 hours and the poly(δ-valerolactone) product obtained using SO as initiator at 100°C for 8 hours were chosen as the subjects for subsequent characterization because of their superior physical appearances and high % yields.

4.2 Characterization of Purified Polymer Products and Discussion of Results

4.2.1 Infrared Spectroscopy (IR)

The infrared spectra of the purified poly(glycolic acid), poly(δ-valerolactone) and poly(glycolic acid-co-valerolactone) (comonomer mole ratios 1:1 and 2:1) products chosen for characterization are shown, together with a poly(δ-valerolactone) reference spectrum, in Figs. 4.4 - 4.8. The major vibrational peaks are compared in Table 4.2. The product spectra were obtained with the samples prepared in the form of KBr discs.

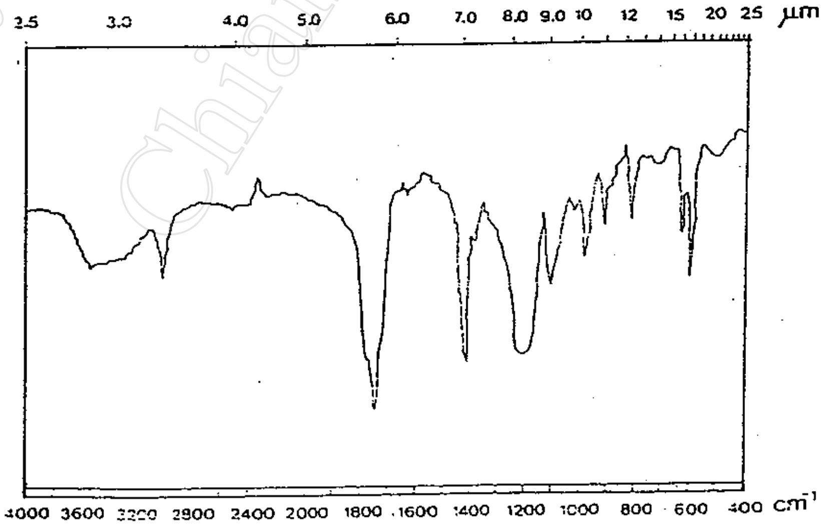


Fig. 4.4 : **Infrared spectrum of poly(glycolic acid) synthesized at 150°C for 12 hours using SO as initiator.**

Table 4.1 : Conditions used in homopolymerizations and copolymerizations of glycolide and δ-valerolactone.

Polymer	Copolymer	Monomer (1) (g)	Monomer (2) (g)	Mole Ratio of Monomers	Initiator	Temp. (°C)	Time (hrs.)	Physical Appearance of Product		% Yield of Purified Product
								Crude	Purified	
PGA	-	G (2.320)	-	-	SO	100	8	white solid	white powder	56.2
PVL	-	-	VL (2.010)	-	SO	100	8	white waxy solid	white powder	87.3
-	P(GA-co-VL)	G (2.320)	VL (2.010)	1:1	SO	100	8	white waxy solid	white powder	66.9
-	P(GA-co-VL)	G (2.320)	VL (1.001)	2:1	SO	100	8	white waxy solid	white powder	71.4
-	P(GA-co-VL)	G (1.161)	VL (2.002)	1:2	SO	100	8	white paste	white paste	49.8

Table 4.1 : **(continued)**

Polymer	Copolymer	Monomer (1) (g)	Monomer (2) (g)	Mole Ratio of Monomers	Initiator	Temp. (°C)	Time (hrs.)	Physical Appearance of Product		% Yield of Purified Product
								Crude	Purified	
PGA	-	G (2.321)	-	-	SO	150	8	white solid	white powder	75.1
PVL	-	-	VL (2.001)	-	SO	150	8	white waxy solid	white powder	65.8
-	P(GA-co-VL)	G (2.321)	VL (2.010)	1:1	SO	150	8	white waxy solid	white powder	73.9
-	P(GA-co-VL)	G (2.321)	VL (1.001)	2:1	SO	150	8	white waxy solid	white powder	86.4
-	P(GA-co-VL)	G (1.161)	VL (2.002)	1:2	SO	150	8	white paste	white paste	38.2

Table 4.1 : **(continued)**

Polymer	Copolymer	Monomer (1) (g)	Monomer (2) (g)	Mole Ratio of Monomers	Initiator	Temp. (°C)	Time (hrs.)	Physical Appearance of Product		% Yield of Purified Product
								Crude	Purified	
PGA	-	G (2.321)	-	-	SO	150	12	white solid	white powder	78.4
PVL	-	-	VL (2.001)	-	SO	100	12	white waxy solid	white powder	65.0
-	P(GA-co-VL)	G (2.321)	VL (2.010)	1:1	SO	150	12	white waxy solid	white powder	88.1
-	P(GA-co-VL)	G (2.321)	VL (1.001)	2:1	SO	150	12	white waxy solid	white powder	86.4

Table 4.1 : (continued)

Polymer	Copolymer	Monomer (1) (g)	Monomer (2) (g)	Mole Ratio of Monomers	Initiator	Temp. (°C)	Time (hrs.)	Physical Appearance of Product		% Yield of Purified Product
								Crude	Purified	
PGA	-	G (2.321)	-	-	BF_3Et_2O	150	8	white solid	white powder	59.2
PVL	-	-	VL (2.001)	-	BF_3Et_2O	100	8	white waxy solid	white powder	82.8
-	P(GA-co-VL)	G (2.321)	VL (2.010)	1:1	BF_3Et_2O	150	8	white waxy solid	white powder	76.1
-	P(GA-co-VL)	G (2.321)	VL (1.001)	2:1	BF_3Et_2O	150	8	white waxy solid	white powder	89.6

ABBREVIATIONS :

G = glycolide **PGA = poly(glycolic acid)**
VL = δ-valerolactone **PVL = poly(δ-valerolactone)**
P(GA-co-VL) = poly(glycolic acid-co-valerolactone)
SO = stannous octoate
BF_3Et_2O = boron trifluoride etherate

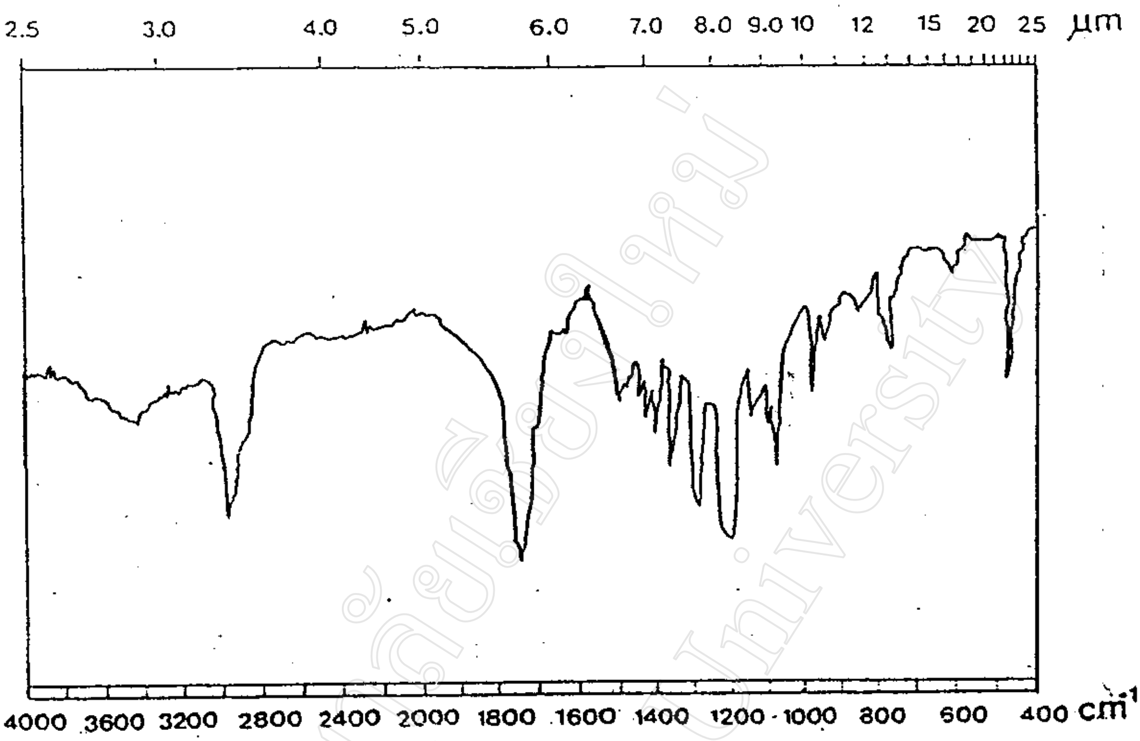


Fig. 4.5 : Infrared spectrum of poly(δ-valerolactone) synthesized at 100°C for 8 hours using SO as initiator.

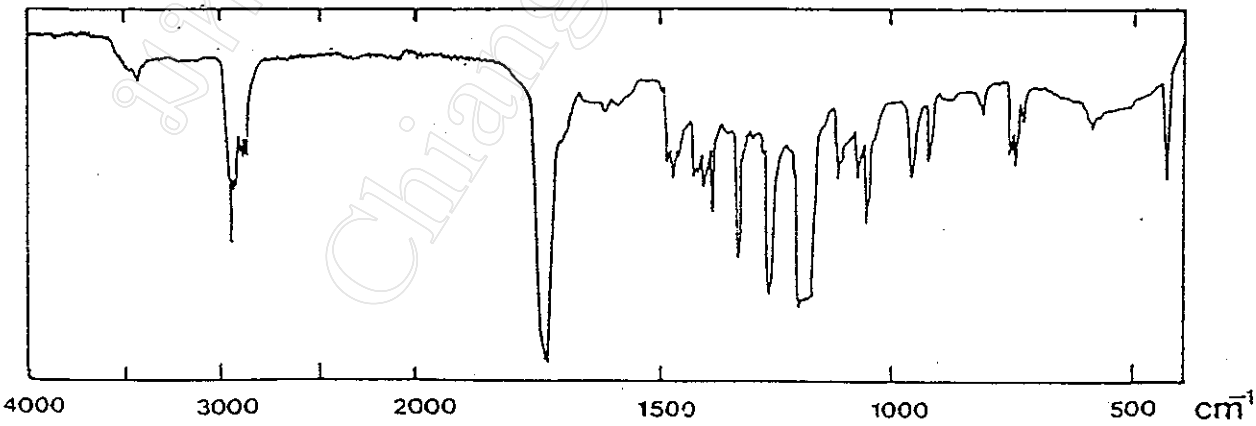


Fig. 4.6 : Reference infrared spectrum of poly(δ-valerolactone) [37].

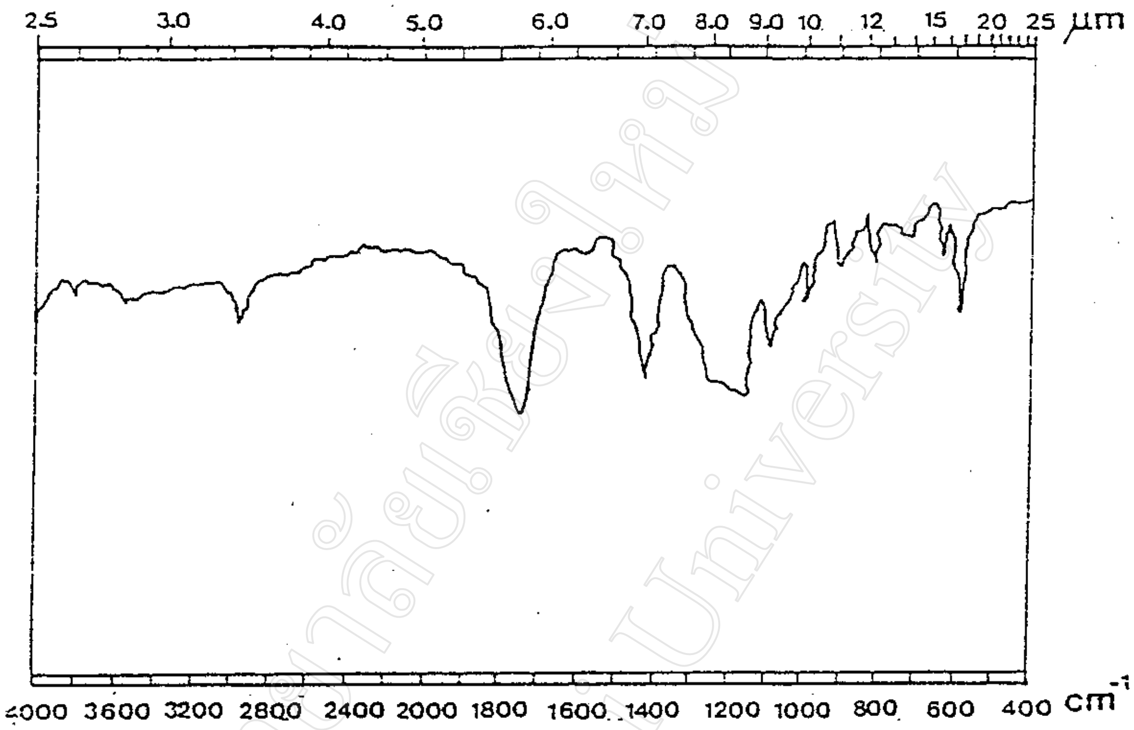


Fig. 4.7 : Infrared spectrum of poly(glycolic acid-co-valerolactone), comonomer mole ratio 1:1, synthesized at 150° C for 12 hours using SO as initiator.

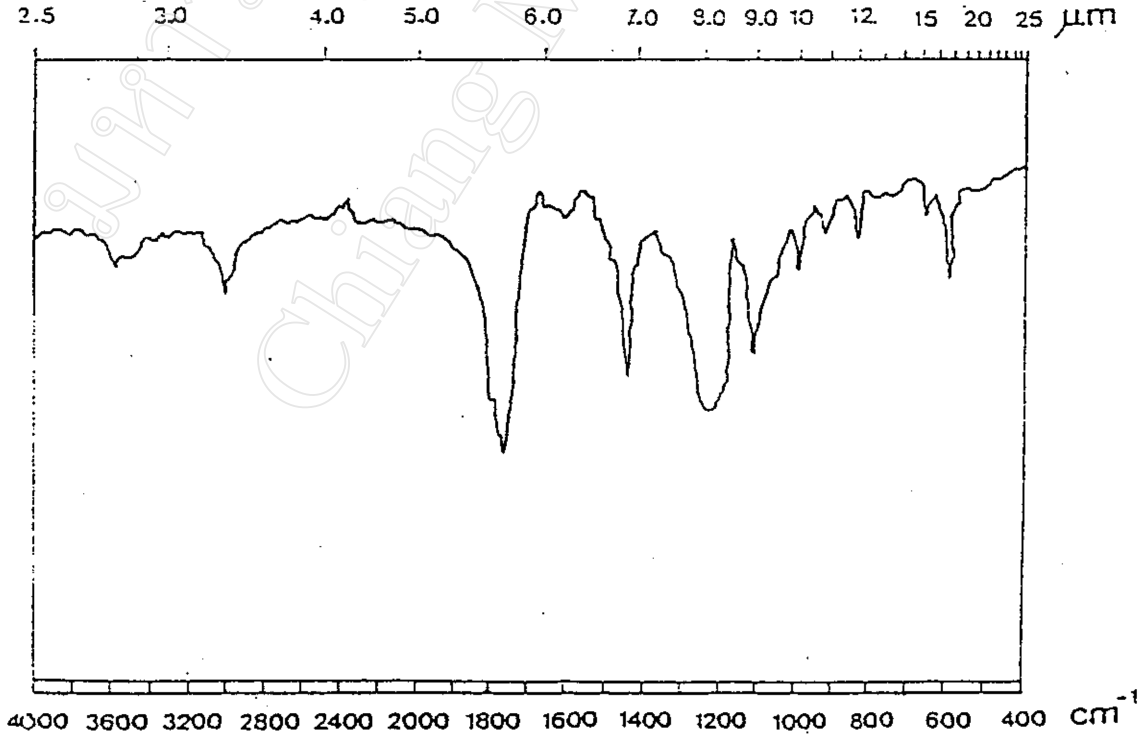


Fig. 4.8 : Infrared spectrum of poly(glycolic acid-co-valerolactone), comonomer mole ratio 2:1, synthesized at 150° C for 12 hours using SO as initiator.

Table 4.2 : Comparison of the main IR vibrational frequencies of synthesized poly(glycolic acid), poly(δ-valerolactone) and poly(glycolic acid-co-valerolactone).

Vibrational Assignment	Wavenumber (cm^{-1})			
	PGA	PVL	P(GA-co-VL) 1:1	P(GA-co-VL) 2:1
O-H stretching, in OH and / or COOH	3700-3300	3600-3300	3600-3400	3700-3300
C-H stretching, in CH_2	2980	2970	2950	3000
C=O stretching	1750	1720	1750	1760
C-H bending, in CH_2	1420	1420-1380	1420	1440
C-O stretching, acyl-oxygen	1240-1180	1320, 1260 1170	1250-1140	1250-1170
C-O stretching, alkyl-oxygen	1090	1100-1050	1080	1100

Not surprisingly, since GA is the major component, the P(GA-co-VL) copolymer spectra in Figs. 4.7-4.8 closely resemble that of the PGA homopolymer in Fig. 4.4. However, one notable difference is that the relatively sharp acyl C-O stretching band in the PGA spectrum at about 1240-1180 cm^{-1} is seen to be considerably broader in the P(GA-co-VL) 1:1 copolymer spectrum (1250-1140 cm^{-1}), presumably due to its overlap with the corresponding C-O band from the incorporated valerolactone segments. However, when compared with the P(GA-co-VL) 2:1 copolymer (1280-1170 cm^{-1}), there was no significant difference in this band, indicative that there is relatively little valerolactone in its more GA-rich copolymer chain. Apart from this, the differences between the IR spectra of the PGA and P(GA-co-VL) products are so small as to render it impossible to drawn any firm conclusions about the exact composition of the copolymers. Consequently, it is still unclear from these IR results alone as to whether the P(GA-co-VL) is a genuine random copolymer or a mixture containing mainly homopolymeric fractions, particularly PGA. More conclusive evidence regarding copolymer composition and microstructure will be presented in the following sections.

4.2.2 C-13 Solid-State Nuclear Magnetic Resonance Spectrometry (C-13 Solid-State NMR)

Combined copolymer composition and monomer sequence distribution analysis of the P(GA-co-VL) copolymers was carried out from 50.3 MHz C-13 solid-state NMR spectra obtained using a Chemagnetics CMX-200 spectrometer under conditions of cross-polarization, high power proton decoupling and magic-angle spinning (CP/MAS). The spectra are shown in Figs. 4.9-4.12 and the corresponding chemical shifts tabulated in Tables 4.3-4.6.

The main purpose of this C-13 solid-state NMR investigation was to try to obtain microstructural information about the copolymers which the IR spectra were unable to provide. The C-13 NMR spectra of most copolyesters show, like those of poly(esteramide)s [53] and copolyamides [54], that the carbonyl (C=O) signals are more sensitive to sequence effects than the signals of the aliphatic carbons (methyl, methylene and methine signals).

The spectra of the PGA and PVL homopolymers each show well defined peaks due to the methylene carbons (CH_2) in the range 12-56 ppm and to the carbonyl carbons (C=O) at 159.0 ppm (PGA) and 165.2 ppm (PVL). The small peaks in the range 70-90 ppm are side bands of the main carbonyl peak and appear in every spectrum.

When compared with these two homopolymer spectra, the spectrum of the copolymer P(GA-co-VL), comonomer mole ratio 2:1, appears to be essentially the same as that of the PGA. Only a very small carbonyl peak at around 165 ppm suggests the presence of VL units in the copolymer.

In contrast to this, the P(GA-co-VL), comonomer mole ratio 1:1, spectrum shows three poorly defined peak maxima in the range 12-23 ppm and a small peak at 164.6 ppm, coincident with those for the VL units in PVL, in addition to the two main GA peaks. The ratio of the intensities of the carbonyl peaks is about 10:1, indicating this ratio of GA:VL units in the copolymer. Furthermore, there are no extra peaks in the carbonyl region, suggesting that the copolymer is blocky in nature. However owing to the low intensity of the VL component, this latter suggestion cannot be confirmed.

These NMR spectra would therefore seem to reinforce the view that the P(GA-co-VL) copolymers contain much less VL than their initial comonomer feeds. This is undoubtedly due to the much lower reactivity of the δ-valerolactone monomer compared with that of the glycolide. This would also account for a tendency towards block formation, with the glycolide polymerizing first followed by the δ-valerolactone towards the end of the reaction. This is an interesting study in itself which warrants further investigation.

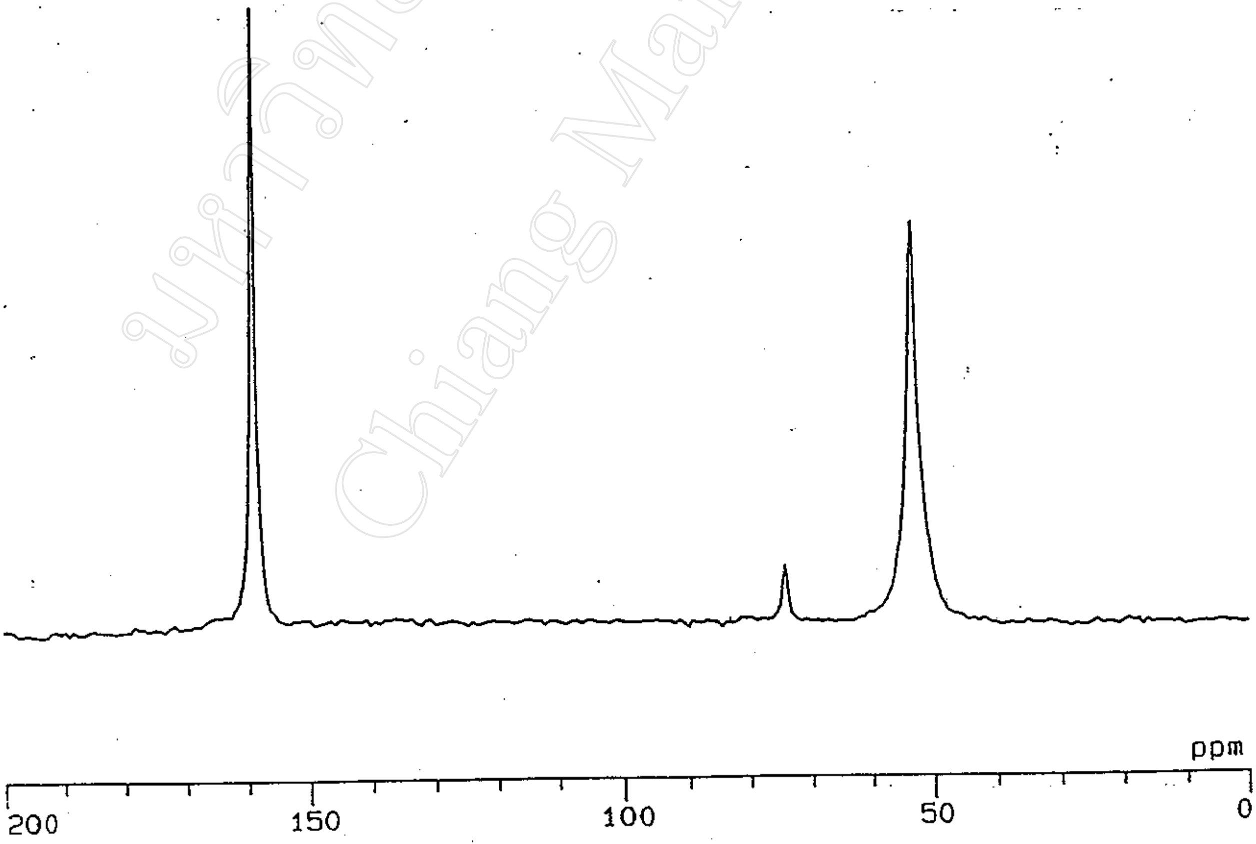
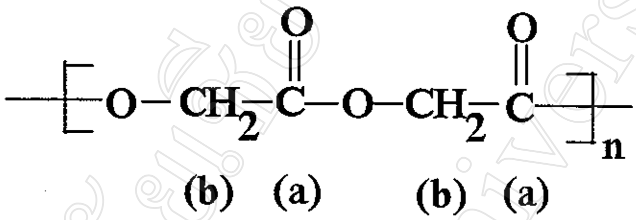


Fig. 4.9 : 50.3 MHz C-13 solid-state NMR spectrum of PGA synthesized at 150°C for 12 hours using SO as initiator.

Table 4.3 : **Interpretation of the C-13 solid-state NMR spectrum of PGA synthesized at 150°C for 12 hours using SO as initiator.**



$$-\!\!\left[\,O-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-O-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}\,\right]_n\!\!-$$

C-13 Assignment	Chemical Shift (ppm)
a	159.001
b	53.582

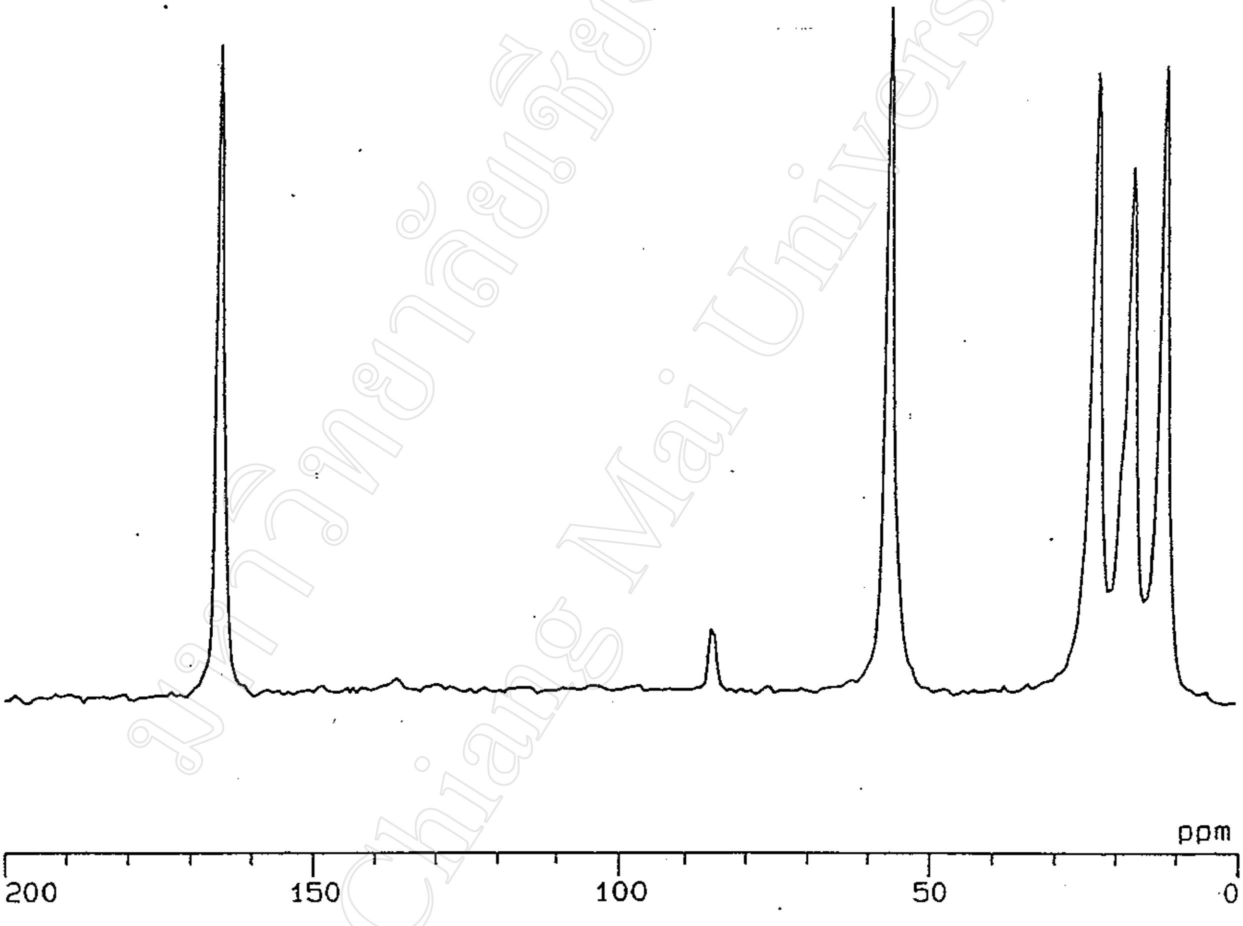
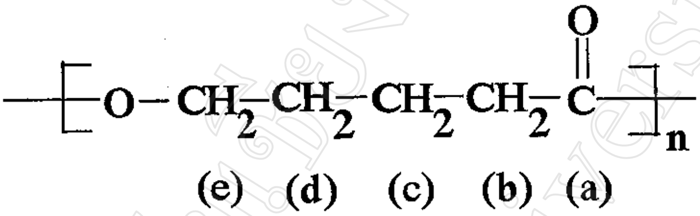


Fig. 4.10 : 50.3 MHz C-13 solid-state NMR spectrum of PVL synthesized at 100°C for 8 hours using SO as initiator.

Table 4.4 : Interpretation of the C-13 solid-state NMR spectrum of PVL synthesized at 100°C for 8 hours using SO as initiator.



$$-\left[O-CH_2-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}\right]_n-$$

C-13 Assignment	Chemical Shift (ppm)
a	165.20
e	56.989
b	23.711
d	17.772
c	12.531

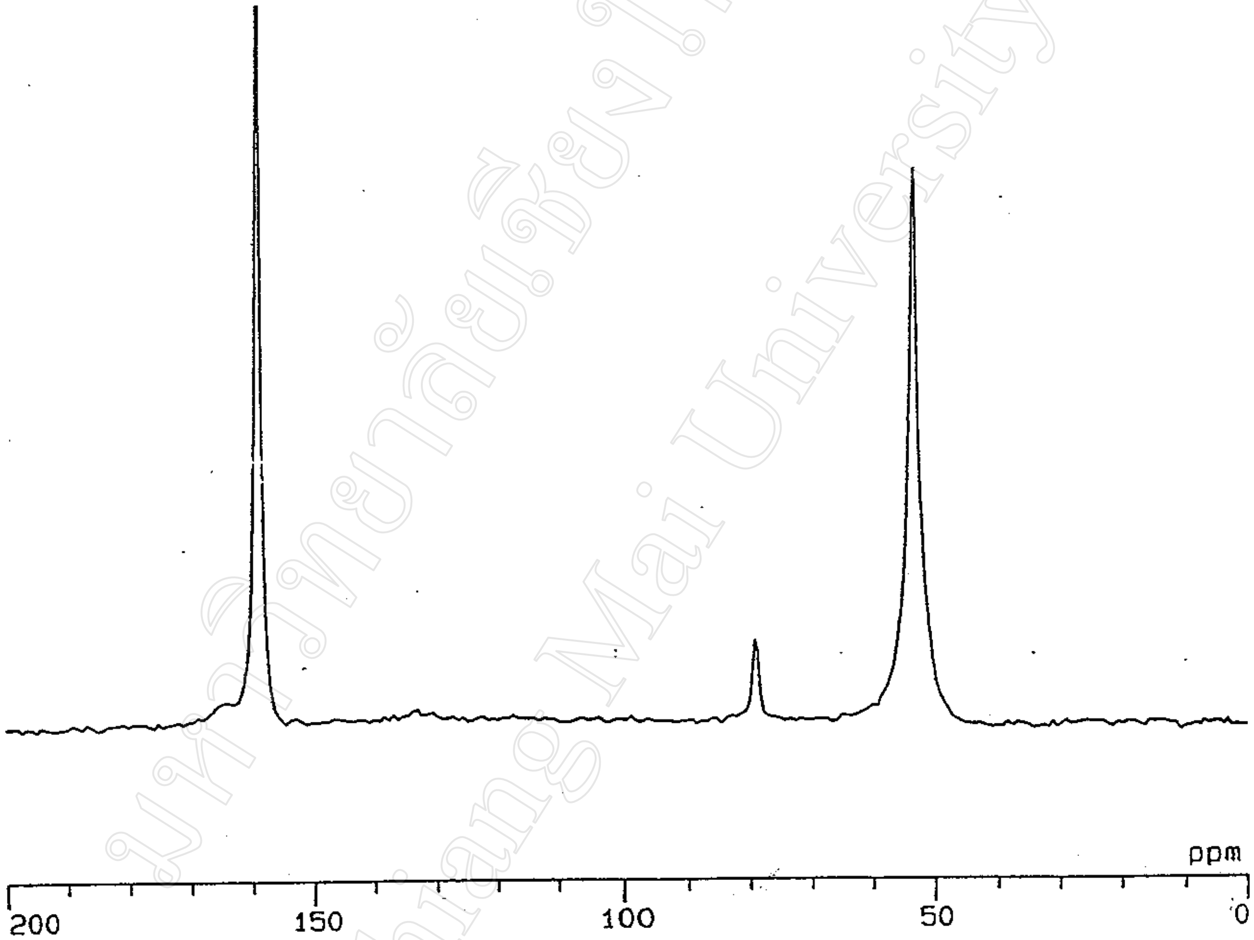
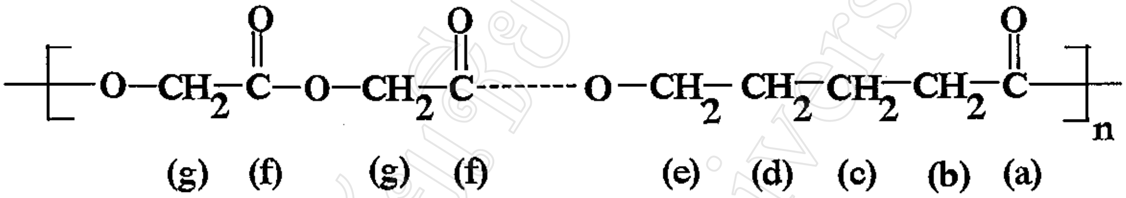


Fig. 4.11 : **50.3 MHz C-13 solid-state NMR spectrum of P(GA-co-VL), comonomer mole ratio 2:1, synthesized at 150°C for 12 hours using SO as initiator.**

Table 4.5 : **Interpretation of the C-13 solid-state NMR spectrum of P(GA-co-VL), comonomer mole ratio 2:1, synthesized at 150°C for 12 hours using SO as initiator.**



$$\left[-O-\underset{(g)}{CH_2}-\underset{(f)}{\overset{O}{\overset{\|}{C}}}-O-\underset{(g)}{CH_2}-\underset{(f)}{\overset{O}{\overset{\|}{C}}}\cdots\cdots O-\underset{(e)}{CH_2}-\underset{(d)}{CH_2}-\underset{(c)}{CH_2}-\underset{(b)}{CH_2}-\underset{(a)}{\overset{O}{\overset{\|}{C}}}- \right]_n$$

C-13 Assignment	**Chemical Shift (ppm)**
a	approx.165*
f	159.001
g	53.670

* a very small peak, inconclusive in its assignment

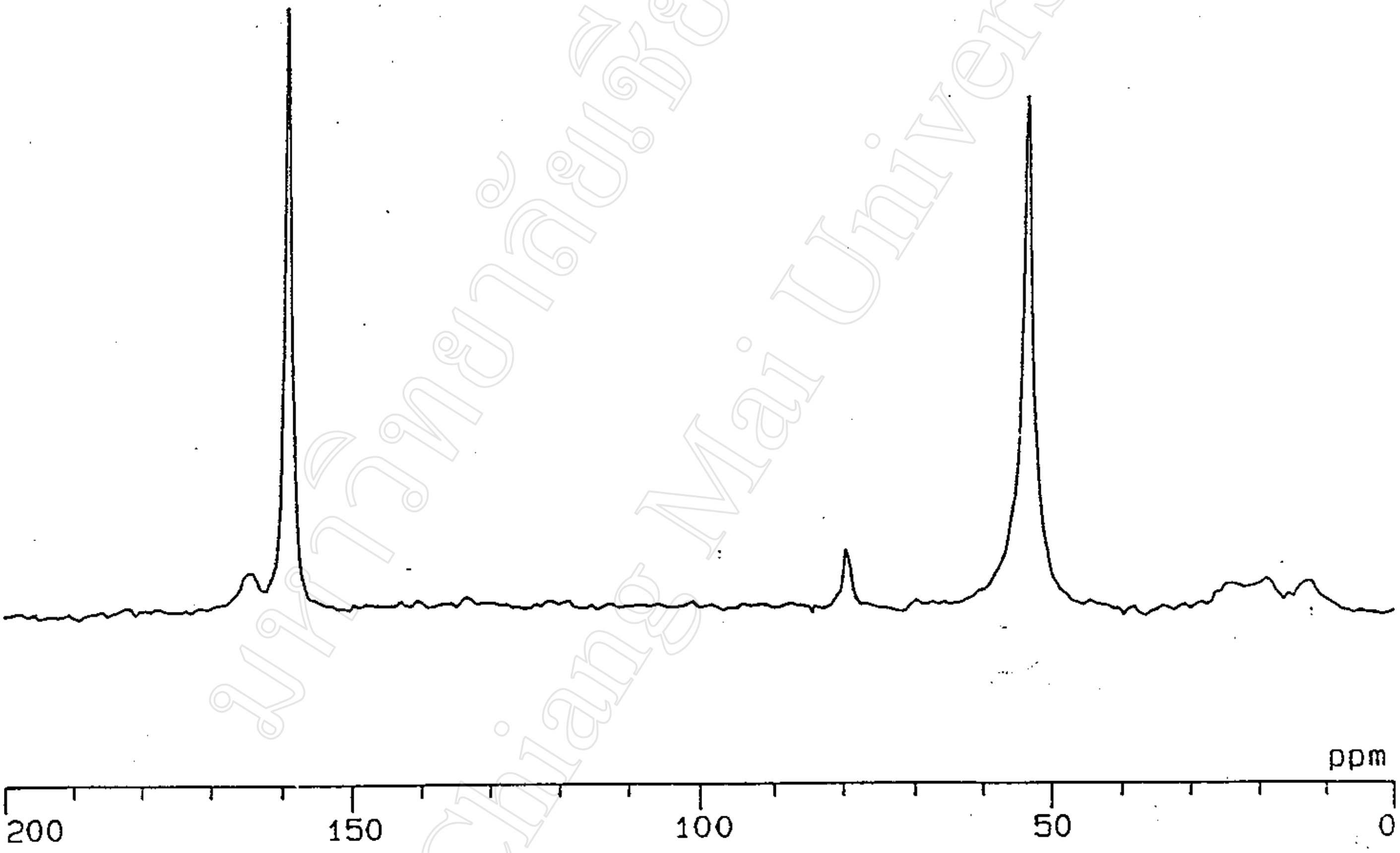
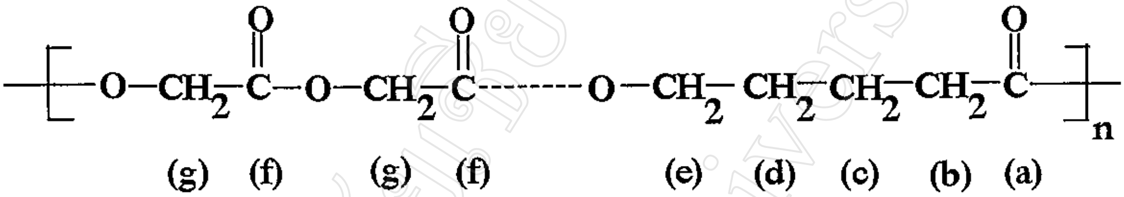


Fig. 4.12 : **50.3 MHz C-13 solid-state NMR spectrum of P(GA-co-VL), comonomer mole ratio 1:1, synthesized at 150°C for 12 hours using SO as initiator.**

Table 4.6 : **Interpretation of the C-13 solid-state NMR spectrum of P(GA-co-VL), comonomer mole ratio 1:1, synthesized at 150°C for 12 hours using SO as initiator.**



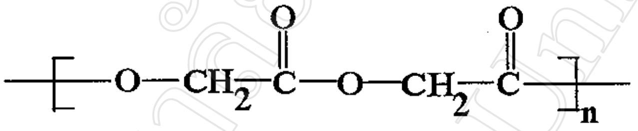
C-13 Assignment	Chemical Shift (ppm)
a	164.591
f	158.911
g	53.670
b	22.925
c	19.169
d	12.444

4.2.3 Elemental (CHNS/O) Analysis

The PGA, PVL and P(GA-co-VL) products were characterized by elemental (CHNS/O) analysis using a Perkin-Elmer PE-2400 Series II CHNS/O Elemental Analyzer.

The theoretical elemental compositions (% C, % H, and % O by weight) for various copolymer compositions can be calculated from the molecular formulae of the GA and VL repeat units as shown below.

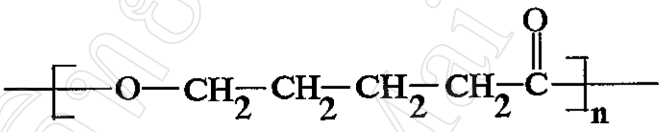
PGA



$$-\!\!\left[-O-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-\overset{\overset{O}{\|}}{C}-\right]_n\!\!-$$

mol. wt. = 116.08

PVL



$$-\!\!\left[-O-CH_2-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-\right]_n\!\!-$$

mol.wt. = 100.13

Atomic Weights : C = 12.01, H = 1.01, O = 16.00

Sample Calculation of the Theoretical Elemental Composition of a P(GA-co-VL) Copolymer of Known Composition

In 100 g of a P(GA-co-VL) copolymer containing 10% VL by weight :

Calculation of % Carbon

in the GA units = 90% by weight = $\frac{48.04}{116.08} \times 90 = 37.25$ g of carbon

in the VL units = 10% by weight = $\frac{60.05}{100.13} \times 10 = 6.00$ g of carbon

Therefore, the P(GA-co-VL) copolymer contains 37.25 + 6.00 = 43.25% C

Calculation of % Oxygen

in the GA units = 90% by weight = $\frac{64.00}{116.08} \times 90 = 49.62$ g of oxygen

in the VL units = 10% by weight = $\frac{32.00}{100.13} \times 10 = 3.20$ g of oxygen

Therefore, the P(GA-co-VL) copolymer contains 49.62 + 3.20 = 52.82% O

From these calculations, the theoretical % weights of carbon and oxygen are plotted against the % valerolactone in the form of calibration curves, as shown in Fig. 4.13.

RELATIONSHIPS BETWEEN % VALEROLACTONE AND % CARBON AND % OXYGEN IN P(GA-co-VL)

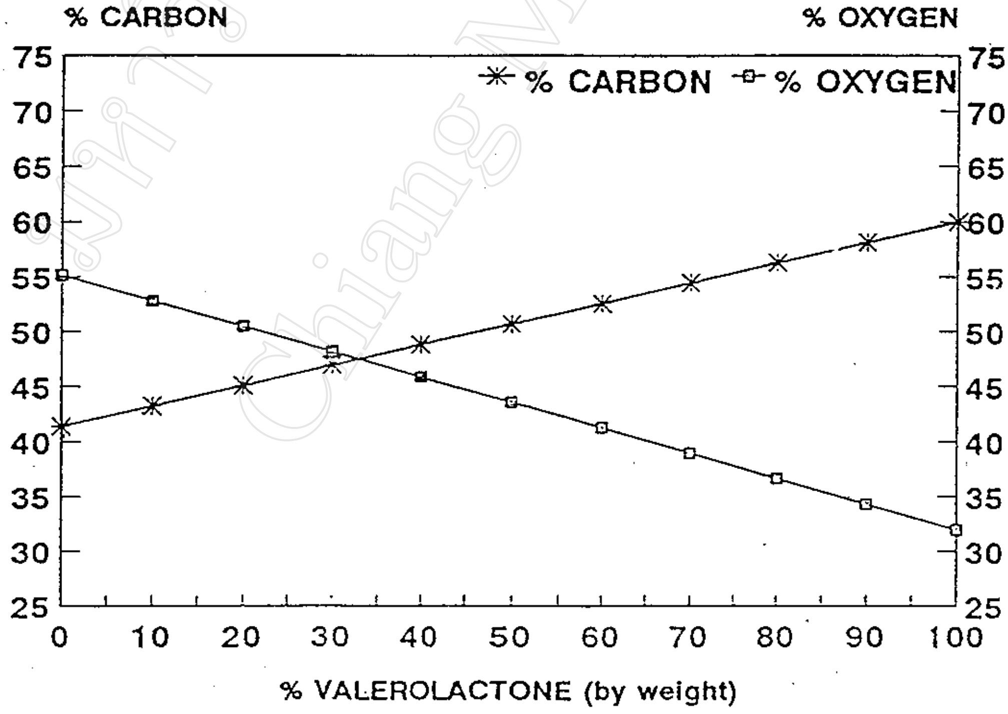


Fig. 4.13 : Theoretical calibration curves of % carbon and % oxygen (by weight) against % valerolactone (by weight) in P(GA-co-VL).

The experimental % weights of carbon, hydrogen and oxygen from elemental (CHNS/O) analysis are shown in Table 4.7. The % valerolactone in the copolymers can be determined from either of the two calibration curves in Fig. 4.13.

Table 4.7 : Copolymer compositions of P(GA-co-VL) from elemental (CHNS/O) analysis.

Polymer	C* (found) (wt %)	H* (found) (wt %)	O** (found) (wt %)	% Valerolactone***	
				(wt%)	(mole %)
PGA (cf., theoretical)	41.05 (41.39)	3.93 (3.48)	55.02 (55.13)	-1.85 1.64	-2.19 1.90
PVL (cf., theoretical)	59.62 (59.97)	8.90 (8.07)	31.48 (31.96)	98.10 101.65	99.19 101.34
P(GA-co-VL) 1:1	43.33	2.91	53.76	10.42 6.99	11.54 7.75
P(GA-co-VL) 2:1	41.44	3.51	55.05	0.25 1.51	0.28 1.70

* from CHNS analysis mode

** from oxygen analysis mode

*** upper value obtained from % CARBON calibration curve
lower value obtained from % OXYGEN calibration curve

From the results in Table 4.7 for the two homopolymers, PGA and PVL, of known elemental composition, this elemental analysis technique provides data which is in good agreement (i.e., to within ± 2 %) with the theoretical values. The small discrepancies between the experimental and theoretical values can be ascribed to various sources of error inherent in both the technique (incomplete combustion, instrumental precision) and the sample (initiator residues, other impurities). Even small errors will be magnified due to the narrow % C and % O ranges in the calibration curves.

The copolymer results in the Table 4.7 are consistent with the previous IR/NMR conclusions. The P(GA-co-VL) 1:1 copolymer contains about 7-12% VL by mole, which agrees with the previous 10% estimate obtained from the intensity ratio of the carbonyl peaks in the C-13 NMR spectrum (Fig. 4.12 on page 77). Similarly, the P(GA-co-VL) 2:1 copolymer is confirmed in Table 4.7 as containing negligible VL, again as previously suggested by its IR/NMR spectra.

4.2.4 Molecular Weight Determination by Vapour Pressure Osmometry

In this study, a Knauer Vapour Pressure Osmometer of the type shown in Fig. 3.16 (see page 51) was used.

4.2.4.1 PVL in Chloroform

The standard analytical procedure was based on the following conditions :

thermistor probe : universal bead thermistor (25-75°C)
color code = brown
calibration standard: benzil (mol. wt. = 210.22)
solvent : distilled chloroform ($CHCl_3$)
temperature : 45.0°C
sensitivity : 128
concentration range: 3-15 g/kg solvent

The calibration standard, benzil, was dissolved in the $CHCl_3$ solvent at ambient temperature and then heated in the osmometer at 45.0°C for about 30 minutes. The sample of lowest concentration was measured first, as soon as equilibrium had been attained. Measurements were recorded after 2 minutes and repeated every 30 seconds in order to determine the most reliable value for the balancing resistance (ΔR). This was eventually taken as the mean of the 3 most similar readings.

Calibration in $CHCl_3$ as Solvent at 45.0°C

Table 4.8 : Balancing resistance (ΔR) for different solution concentrations of benzil (calibrant) in $CHCl_3$ at 45.0°C.

Conc. (g/kg)	ΔR^* (scd)	$\Delta R/c$ (scd.kg/g)
3.640	16.5	4.53
6.918	31.5	4.55
10.250	50.0	4.88
13.641	67.0	4.91

NOTES :
* = mean of the 3 most similar readings
scd = scale divisions (as read from the osmometer)

Calculation :

The calibration constant, K, is calculated from the results in Table 4.8 by plotting the graphs shown in Fig. 4.14. Then, knowing the value of ($\Delta R/c$) at c=o and the equation :

$$(\Delta R/c)_{c=o} = K/\overline{M}_n$$

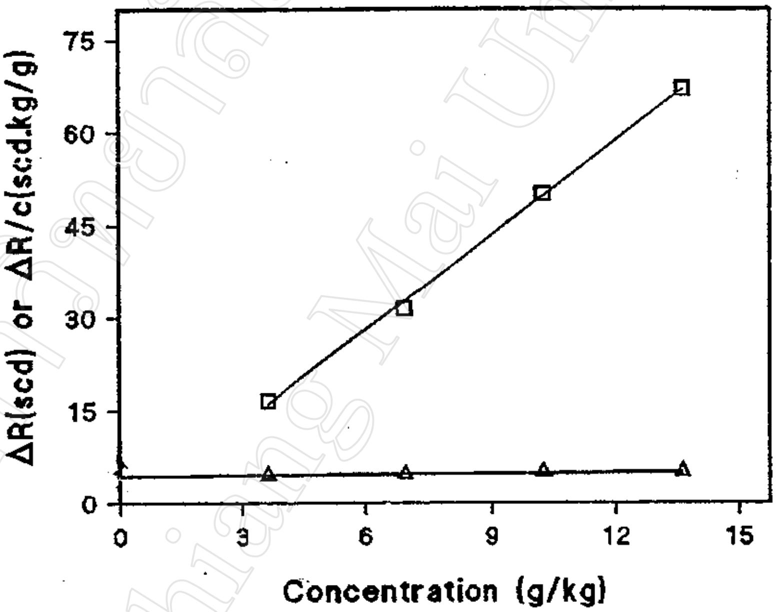
and replacing $\overline{M}_n$ by M (molecular weight of the benzil standard), the equation becomes

$$(\Delta R/c)_{c=o} = K/M$$

From Fig. 4.14, $(\Delta R / c)_{c=o}$ of benzil standard = 4.338 scd.kg/g
molecular weight of benzil, M= 210.22 g/mol

Therefore,

$$\boxed{K = 911.9 \text{ scd.kg/mol}}$$



□ = ΔR Δ = ΔR/c
intercept $(\Delta R / c)_{c=o}$ = 4.338

Fig. 4.14 : Extrapolation of ΔR and ΔR/c to infinite dilution (c=0) for the standard solutions of benzil in $CHCl_3$ at 45°C.

The value of a polymer's number-average molecular weight, $\overline{M}_n$, is then calculated using the above calibration constant, K = 911.9 scd.kg/g. For example, from the following Fig. 4.15 for the PVL polymer :

$$(\Delta R / c)_{c=o} = 0.450 \text{ scd.kg/g}$$

Therefore, $\overline{M}_n$ of this PVL sample = 911.9/ 0.450 g/mol

$$\boxed{\overline{M}_n = 2.03 \times 10^3 \text{ g/mol}}$$

which corresponds to a degree of polymerization of :

$$\boxed{\overline{DP}_n \approx 20}$$

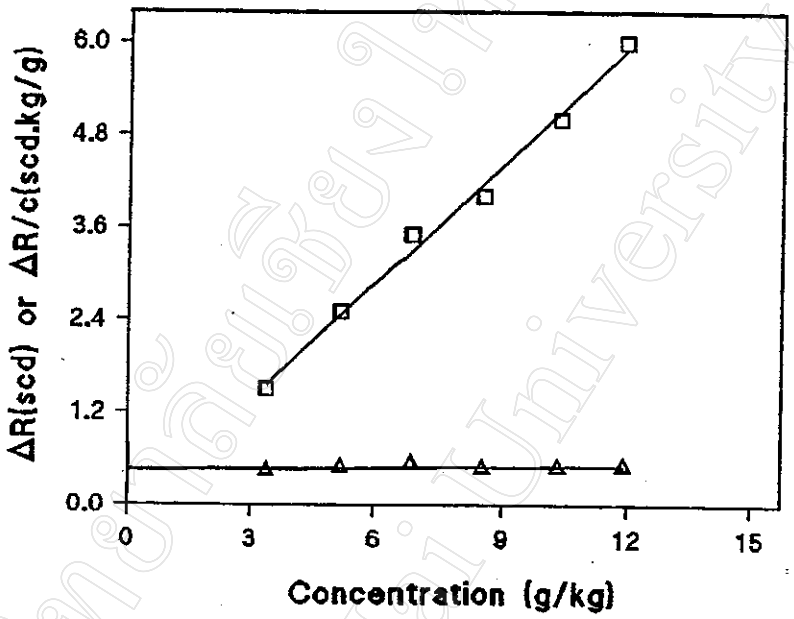
Table 4.9 : Balancing resistance (ΔR) for different solution concentrations of PVL in $CHCl_3$ at 45.0°C.

Conc. (g/kg)	ΔR* (scd)	ΔR/c (scd.kg/g)
3.396	1.5	0.44
5.192	2.5	0.48
6.788	3.5	0.52
8.518	4	0.47
10.324	5	0.48
11.905	6	0.50

NOTES :

* = mean of the 3 most similar readings

scd = scale divisions



□ = ΔR Δ = ΔR/c

intercept $(\Delta R/c)_{c=o}$ = 0.450 scd.kg/g

Fig. 4.15 : **Extrapolation of ΔR and ΔR/c to infinite dilution (c=0) for PVL in $CHCl_3$ at 45.0°C.**

4.2.4.2 PGA and P(GA-co-VL) in DMSO

The conditions used for these determinations were :

thermistor probe : universal bead thermistor (70-130°C)
color code = blue
calibration standard : benzil (mol. wt. = 210.22)
solvent : distilled dimethyl sulfoxide (DMSO)
temperature : 110.0°C
sensitivity : 128
concentration range : 3-15 g/kg solvent

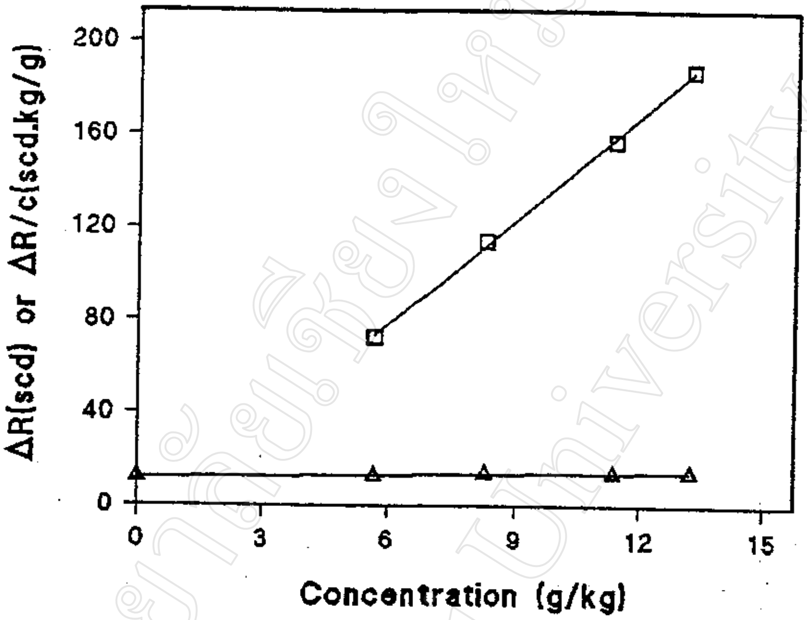
The calibrant standard, benzil, was dissolved in the DMSO solvent at ambient temperature and then heated in the osmometer at 110°C for about 30 minutes. However, the PGA and P(GA-co-VL) samples needed to be dissolved at 120-130°C before placing in the osmometer at 110°C. The measurement procedure was as mentioned before for the PVL sample. A problem encountered during the course of this procedure was the increasing tendency towards PGA or P(GA-co-VL) precipitation (particularly the former) at the measuring temperature of 110°C as the concentration of the polymer sample increased. This effect, whenever it occurred, was noticeable through the development of a slight cloudiness in the polymer solution during its residence time in the osmometer. For this reason, ΔR measurements on the PGA and P(GA-co-VL) solutions were carried out as quickly as possible following thermal equilibration (15 mins) in the osmometer.

Calibration in DMSO as Solvent at 110.0°C

<u>Table 4.10</u> : Balancing resistance (ΔR) for different solution concentrations of benzil (calibrant) in DMSO at 110.0°C.

Conc. (g/kg)	ΔR* (scd)	ΔR/c (scd.kg/g)
5.687	72.5	12.75
8.269	114.1	13.80
11.353	157.2	13.85
13.226	187.5	14.18

NOTES : * = mean of the 3 most similar readings
scd = scale divisions



□ = ΔR Δ = ΔR/c
intercept $(\Delta R/c)_{c=o}$ = 12.026 scd.kg/g

Fig. 4.16 : Extrapolation of ΔR and ΔR/c to infinite dilution (c=0) for the standard solutions of benzil in DMSO at 110.0°C.

From Fig. 4.16, $(\Delta R/c)_{c=o}$ of benzil standard = 12.026 scd.kg/g
molecular weight of benzil, M = 210.22 g/mol

Therefore,

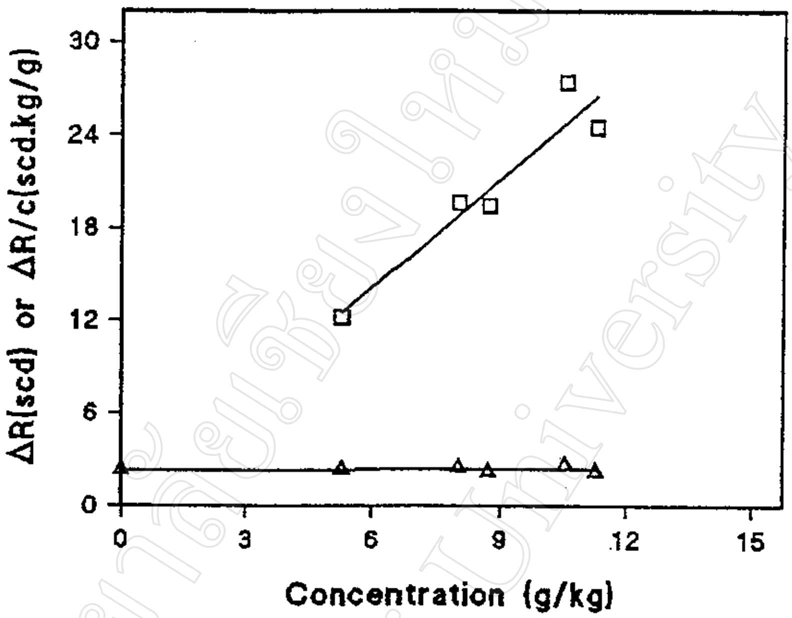
$$\boxed{K = 2528.2 \text{ scd.kg/mol}}$$

The values of the number-average molecular weights, $\overline{M}_n$, of the PGA and P(GA-co-VL) copolymers are now calculated from this value of K = 2528.2 scd.kg/g.

Table 4.11 : Balancing resistance (ΔR) for different solution concentrations of PGA in DMSO at 110.0°C.

Conc. (g/kg)	ΔR* (scd)	ΔR/c (scd.kg/g)
5.298	12.2	2.30
7.985	19.6	2.45
8.710	19.4	2.23
10.540	27.4	2.60
11.269	24.5	2.18

NOTES : * = mean of the 3 most similar readings
scd = scale divisions



□ = ΔR   Δ = ΔR/c

intercept $(\Delta R / c)_{c=o}$ = 2.304 scd.kg/g

Fig. 4.17 : Extrapolation of ΔR and ΔR/c to infinite dilution (c=0) for PGA in DMSO at 110.0°C.

Therefore, $\overline{M}_n$ of this PGA sample = 2528.2/ 2.304 g/mol

$$\boxed{\overline{M}_n = 1.10 \times 10^3 \text{ g/mol}}$$

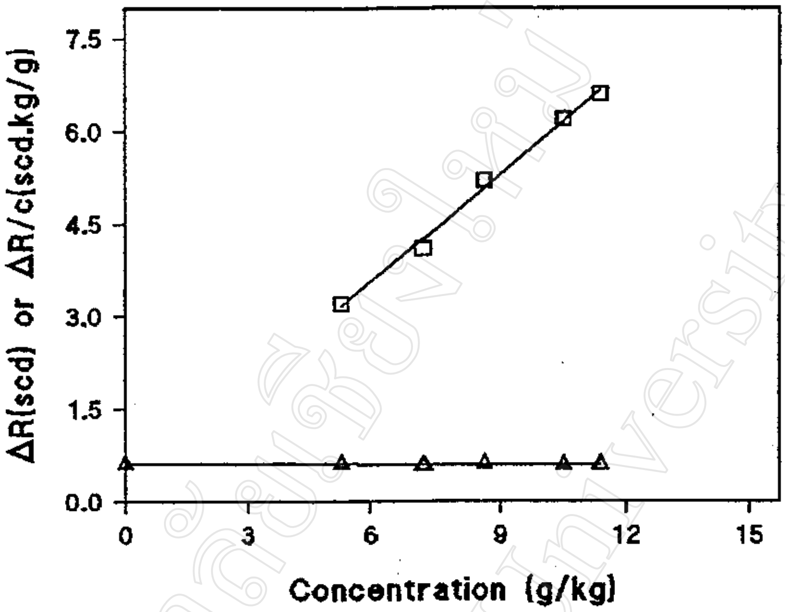
which corresponds to a degree of polymerization of :

$$\boxed{\overline{DP}_n \approx 10}$$

Table 4.12 : Balancing resistance (ΔR) for different solution concentrations of P(GA-co-VL), comonomer mole ratio 1:1.

Conc. (g/kg)	ΔR* (scd)	ΔR/c (scd.kg/g)
5.311	3.2	0.603
7.193	4.1	0.570
8.618	5.2	0.603
10.500	6.2	0.591
11.380	6.6	0.580

NOTES :
* = mean of the 3 most similar readings
scd = scale divisions



□ = ΔR   Δ = ΔR/c

intercept $(\Delta R / c)_{c=o}$ = 0.603 scd.kg/g

Fig. 4.18 : Extrapolation of ΔR and ΔR/c to infinite dilution (c=0) for P(GA-co-VL) 1:1 copolymer in DMSO at 110°C.

Therefore, $\overline{M}_n$ of this P(GA-co-VL) 1:1 sample = 2528.2 / 0.603 g/mol

$$\boxed{\overline{M}_n = 4.19 \times 10^3 \text{ g/mol}}$$

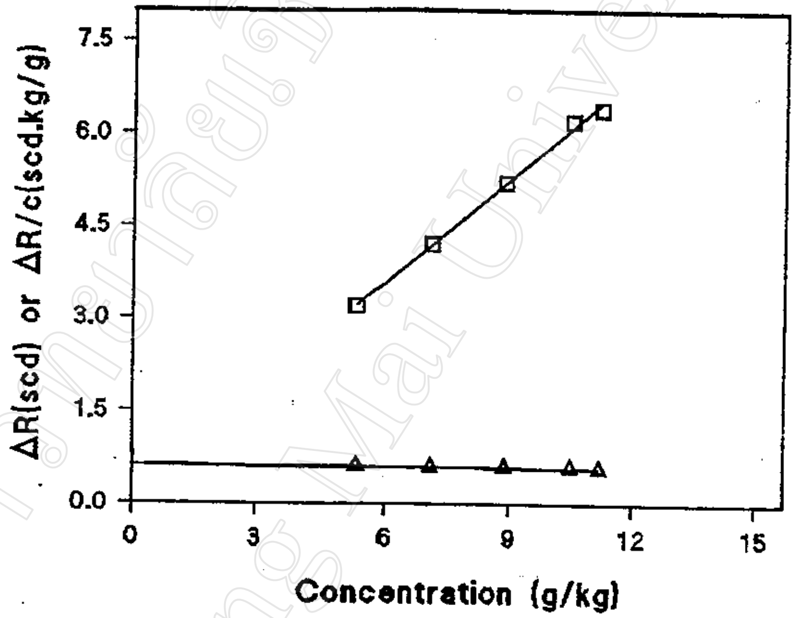
Table 4.13 : Balancing resistance (ΔR) for different solution concentrations of P(GA-co-VL), comonomer mole ratio 2:1.

Conc. (g/kg)	ΔR* (scd)	$\Delta R/c$ (scd.kg/g)
5.358	3.2	0.596
7.075	4.2	0.591
8.868	5.2	0.582
10.471	6.2	0.590
11.182	6.4	0.570

NOTES : * = mean of the 3 most similar readings
scd = scale divisions

Therefore, $\overline{M}_n$ of this P(GA-co-VL) 2:1 sample = 2528.2 / 0.613 g/mol

$$\boxed{\overline{M}_n = 4.12 \times 10^3 \text{ g/mol}}$$



□ = ΔR   Δ = ΔR/c

intercept $(\Delta R / c)_{c=o}$ = 0.613 scd.kg/g

Fig. 4.19 : Extrapolation of ΔR and ΔR/c to infinite dilution (c=0) for P(GA-co-VL) 2:1 copolymer in DMSO at 110.0°C.

Table 4.14 : Comparison of the number-average molecular weights, $\overline{M}_n$, and the degrees of polymerization, $\overline{DP}_n$, of the polymer products determined by vapour pressure osmometry.

Homopolymer or Copolymer	$\overline{M}_n$	$\overline{DP}_n$
PVL	2.03×10^3	20
PGA	1.10×10^3	10
P(GA-co-VL) 1:1	4.19×10^3	36*
P(GA-co-VL) 2:1	4.12×10^3	35*

* approximate values taking into account the copolymer compositions

The $\overline{M}_n$ values in Table 4.14 are all relatively low as far as synthetic polymers are concerned and would be too low for, say, surgical suture applications ($\overline{M}_n > 20{,}000$). Further work therefore needs to done in order to increase $\overline{M}_n$ by at least an order of magnitude, for example by further reducing the initiator concentration used.

4.2.5 Differential Scanning Calorimetry (DSC)

The DSC thermograms in Figs. 4.20-4.22 and the data in Table 4.15 compare the melting characteristics of the purified poly(glycolic acid), poly (δ-valerolactone) and poly(glycolic acid-co-valerolactone) products.

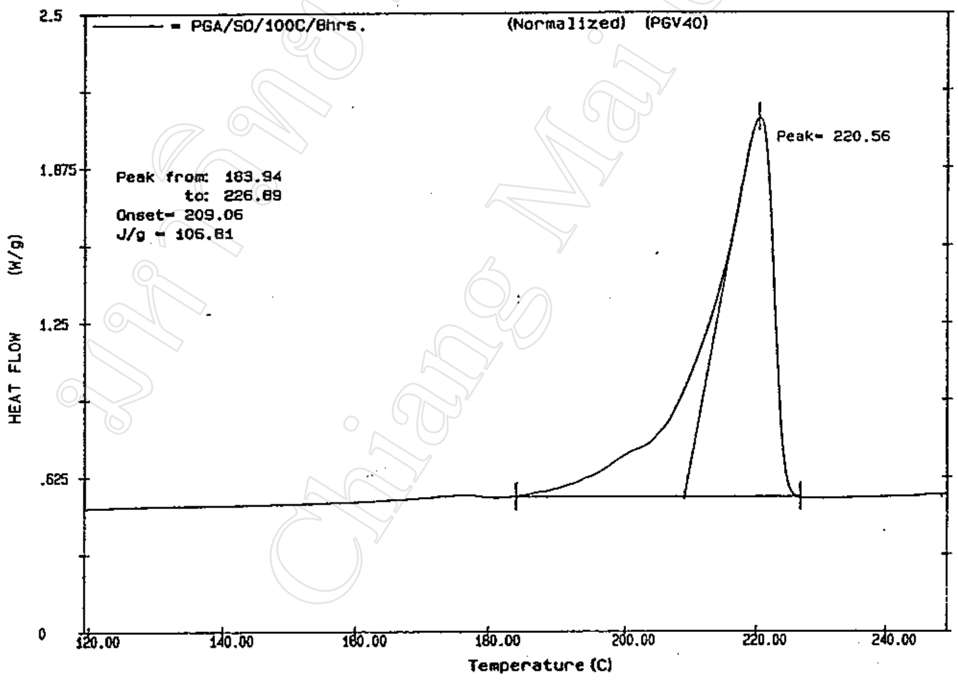


Fig. 4.20 : DSC thermogram of purified PGA synthesized at 150°C for 12 hours using SO as initiator.

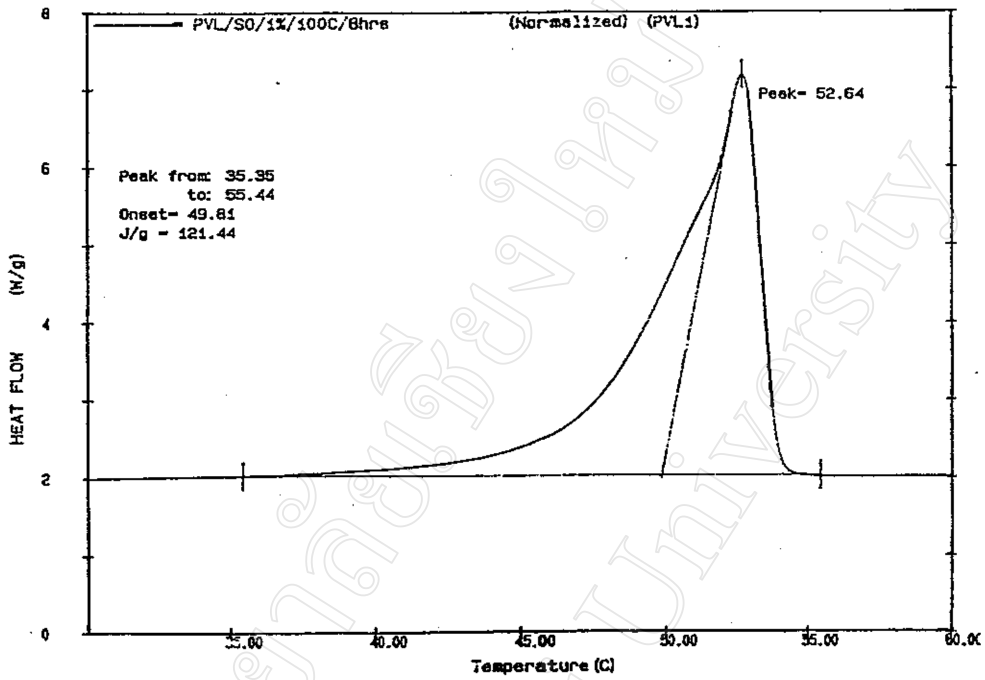


Fig. 4.21 : DSC thermogram of purified PVL synthesized at 100°C for 8 hours using SO as initiator.

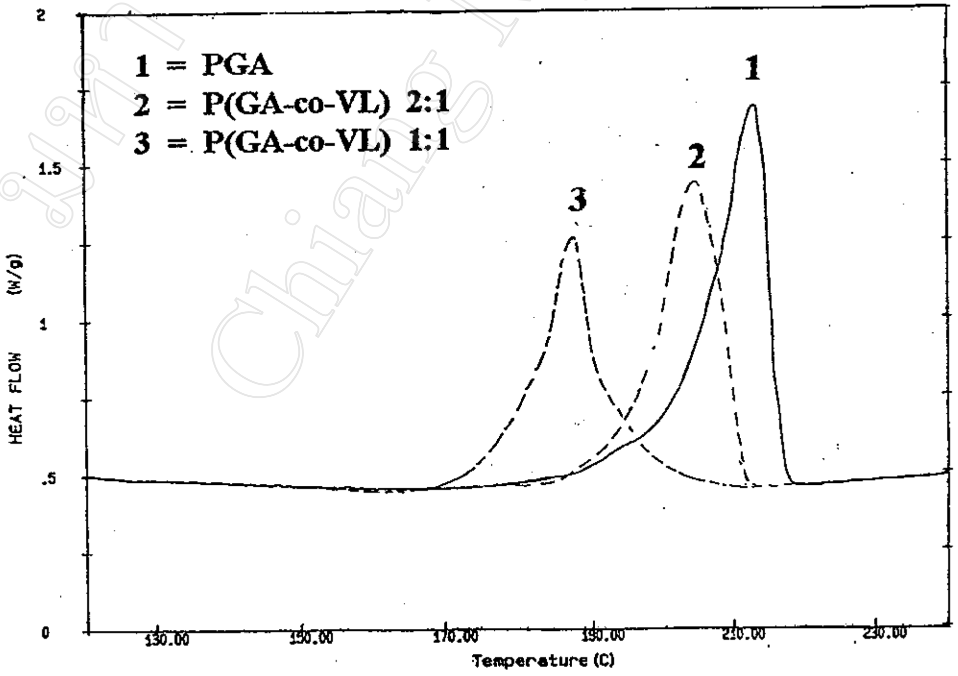


Fig. 4.22 : Comparison of the DSC thermograms of the purified PGA and P(GA-co-VL) products synthesized at 150°C for 12 hours using SO as initiator.

Table 4.15 : DSC melting peak parameters for poly(glycolic acid), poly(δ-valerolactone), and poly(glycolic acid-co-valerolactone) products using SO as initiator.

Homopolymer or Copolymer	DSC Melting Parameters*		
	Onset (°C)	Peak (Max) (°C)	Heat of Fusion (J/g)
PGA	209.06	220.56	106.81
PVL	49.81	52.64	121.44
P(GA-co-VL) 2:1	195.32	205.15	57.87
P(GA-co-VL) 1:1	176.84	180.67	66.89

* values computed by the Perkin-Elmer DSC 7's peak analysis software

From the DSC thermograms in Figs. 4.20 and 4.21, the PGA and PVL homopolymers exhibit quite different melting ranges. PVL has a low melting range with a peak maximum at 52.64°C (c.f., lit.[37] m.p. = 53-55° C), as shown in Fig. 4.21. In marked contrast to this, PGA exhibits a much higher peak maximum at 220.56°C (c.f., lit.[37] m.p. = 220°C).

From the DSC thermograms in Fig. 4.22, the most obvious feature is that the melting peaks of the P(GA-co-VL) copolymers have melting ranges at significantly lower temperatures than that of the PGA homopolymer. Since each P(GA-co-VL) sample shows only a single peak, below that of PGA synthesized under the same conditions, this provides at least some qualitative evidence to suggest that they are indeed genuine copolymers. As the mole % VL in the comonomer feed increases from 33.3 to 50.0 mole %, the melting range of the copolymer decreases, as would be expected if there were increasing amounts of VL units in the copolymer structures, even if these amounts are relatively minor (≤ 10%) in proportion. It is also significant to note that copolymerization drastically reduces the heat of fusion and, thus, the % crystallinity. Again, this is as would be expected due to the increased structural disorder in the copolymer chain.

4.2.6 Thermogravimetry (TG)

The TG thermograms in Fig. 4.23 compare the thermal degradation characteristics of the poly(glycolic acid), poly(δ-valerolactone) and poly (glycolic acid-co-valerolactone) products. From this and the DSC thermograms, the thermal degradation ranges and melting ranges respectively are compared in Table 4.16.

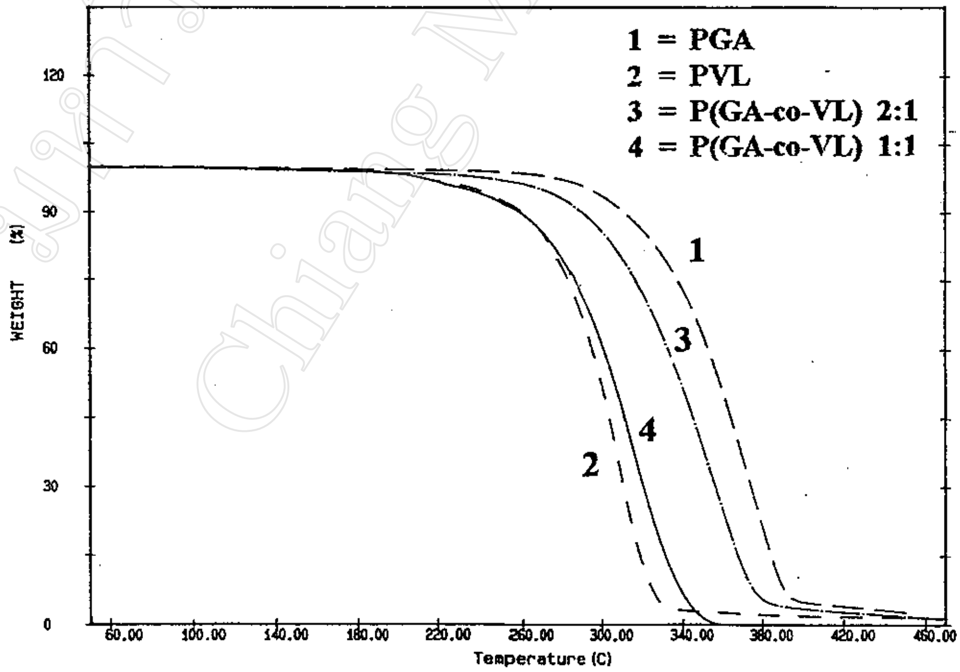


Fig. 4.23 : Comparison of the TG thermograms of the PGA, PVL and P(GA-co-VL) products synthesized using SO as initiator.

Table 4.16 : The melting and thermal degradation ranges of poly(glycolic acid), poly(δ-valerolactone) and poly(glycolic acid-co-valerolactone) synthesized using SO as initiator.

Homopolymer or Copolymer	Temperature Range		ΔT**
	Tm (°C)*	Td (°C)	(°C)
PGA	210-230	250-400	20
PVL	50-55	190-340	135
P(GA-co-VL) 2:1	195-210	240-360	30
P(GA-co-VL) 1:1	175-180	240-390	60

* Tm range = Tm(onset) - Tm(final) (from DSC)

** ΔT calculated as the difference between the lower limit of the Td range and the upper limit of the Tm range

ΔT = Td(min) - Tm(max)

From the TG curves of the PGA, PVL and P(GA-co-VL) products, the temperature ranges of decomposition appear between 180-400°C. When the TG and DSC data are taken together, they give some indication of the melt stability range of the polymer. This is particularly relevant to melt processing since the temperature range Td (min) - Tm(max) encompasses the limits of the "processing window" within which the polymer can be safely processed. Normally, the temperature used in melt processing needs to be at least 10°C higher than Tm (max) and, preferably, not less than 40-50°C lower than Td (min). Hence, ΔT = Td (min.) -Tm (max) should be a positive value of at least 50°C if possible. From the results in Table 4.16, the ΔT values of PGA and the P(GA-co-VL) copolymers are all below or around 50°C which would necessitate extremely careful temperature control in a melt processing operation. Clearly, the incorporation of VL units into the copolymer chain is an advantage in this respect. Increasing the VL content lowers the melting range more than the decomposition range, thereby increasing ΔT and widening the "processing window". This is one of the advantages to be gained from PGA chain modification by random copolymerization. Other advantages include increased solubility and (for suture applications) increased chain flexibility.

However, just as there are advantages to be gained from copolymerization, there are invariably disadvantages too. One disadvantage in incorporating VL units into the PGA chain is that the biodegradability (hydrolysability) of the polymer is decreased. This is a consequence of the fact that the VL units are much more hydrophobic than the GA units. This, of course, has wide-ranging implications for a polymer which is to be used in a biomedical application such as an absorbable suture material. The effect of polymer structure on the in vitro biodegradability of the homopolymers and copolymers studied in this project has formed the subject of the final part of this research project. The results are now described in the following Chapter 5.