CHAPTER 4

POLYMER SYNTHESIS AND CHARACTERISATION

4.1 Previous Reports on Poly(glycolic acid) Synthesis

It was reported [25] that poly(glycolic acid) was most conveniently prepared from glycolide which was obtained by heating glycolic acid at atmospheric pressure up to a temperature of 175-185 °C. The temperature was maintained at this level for 2 hours (or until water ceased to distill), the pressure was then reduced over a period of 1/2 hour to about 150 mm Hg, and the temperature maintained at 175-185 °C for an additional 2 hours. The residue obtained solidified to a white, brittle solid. This solid was the low molecular weight poly(glycolic acid) which was depolymerized to glycolide in the presence of antimony trioxide at a temperature of 270-285 °C and pressure of about 12-15 mm Hg. The poly(glycolic acid) was prepared by adding 0.03 % by weight of antimony trifluoride to the glycolide. The reaction was heated to 195 °C and stirred for 1 hour until it could not be stirred further. The mixture was heated for an additional 1 hour at this temperature, before the temperature was raised to 230 °C for 1/2 hour. The final polymer was obtained in a high molecular weight and could be fabricated into drawable films and fibers.

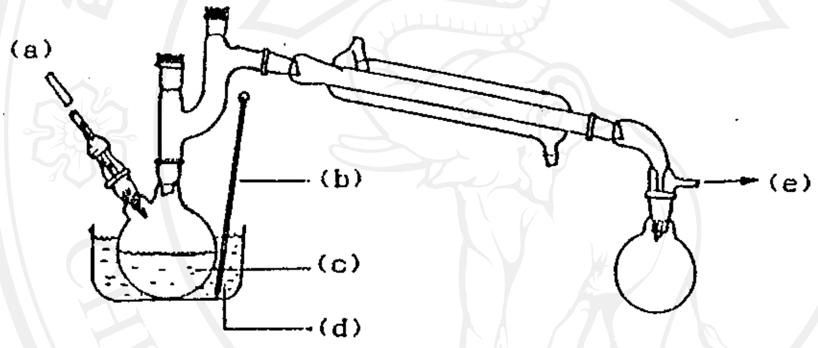
4.2 Synthesis of Glycolide

The experimental procedure described here is based on that given in an earlier literature report [25].

Approximately 20 g of glycolic acid were heated to 170-180 °C under a flowing atmosphere of dry N_2 in a two-necked round bottomed flask, connected as shown in Fig. 4.1. Heating was continued for over 2 hours until water ceased to distill. The pressure was then reduced to about 7 mbar while still maintaining the heating at 180 °C for a further 2 hours. At the end of this period, the residue in the heating flask was allowed to cool to room temperature. This intermediate product was a soft, white semi-solid substance which was presumed to be low molecular weight poly(glycolic acid) formed from the self-condensation of glycolic acid.

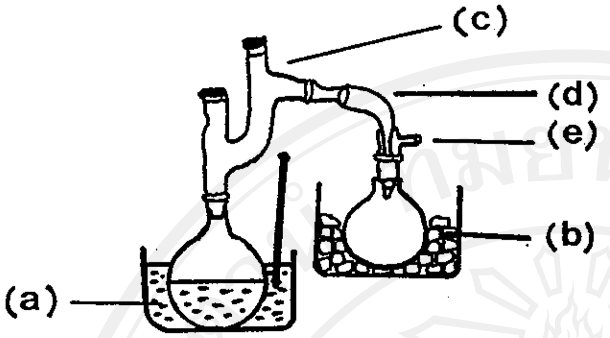
Then, 0.5 g of antimony trioxide were added to the flask as degradation catalyst and the apparatus re-assembled as shown in Fig. 4.2 . The mixture was heated to about 250 °C under a reduced pressure of about 4 mbar. When the temperature reached about 210 °C, the mixture melted to a yellow liquid. During continued heating to about 250 °C for 2 hours, a white crystalline solid collected in the receiving flask. When the residue in the reaction flask turned black, the heating was discontinued.

The pale yellow solid which had collected in the receiving flask was carefully removed and recrystallized from absolute ethanol. The resulting white crystals, obtained in about 35% yield, had a melting range of 80-83 °C (cf. glycolide: lit.[26] m.p. 82-84 °C). In this project, this preparation of glycolide was repeated 3 more times in order to obtain enough glycolide for the subsequent homopolymerisation and copolymerisation steps.



(a) = dry N_2
(b) = thermometer
(c) = glycolic acid
(d) = phosphoric acid
(e) = vacuum connection

Fig. 4.1: Apparatus used for the intermediate preparation of low molecular weight poly(glycolic acid).



(a) heating bath
(b) ice bath
(c) Claisen head
(d) receiver adapter
(e) vacuum connection

Fig. 4.2: Apparatus used for the preparation of glycolide.

4.3 Polymerisation and Copolymerisation of Glycolide

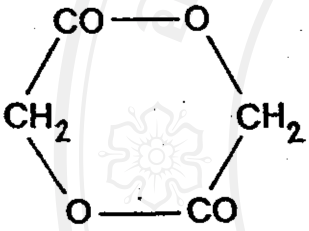
Either glycolide alone or glycolide and its comonomer in a 1:1 mole ratio (see Table 4.1), each purified by recrystallization or distillation, were placed in a reaction flask and heated to 150 °C under dry nitrogen for about 30 mins (see Fig. 4.3). Then, 1 ml of stannous octoate initiator was injected into the stirred mixture and the solution maintained at 150 °C for a further 30 mins. The mixture was cooled to room temperature and the product purified by dissolving in DMSO and precipitating in absolute ethanol. Finally, the product was filtered, washed with more ethanol, and dried to constant weight in a vacuum oven at 60 °C.

Altogether, three reactions were carried out via this procedure (see Table 4.1) :

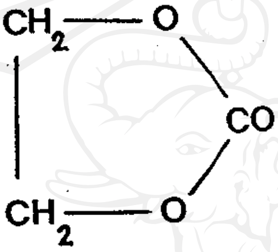
(1) polymerisation of glycolide alone

(2) copolymerisation of glycolide and ethylene carbonate

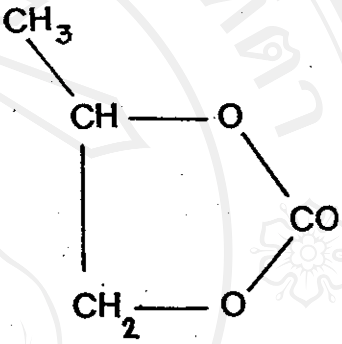
(3) copolymerisation of glycolide and propylene carbonate



glycolide



ethylene carbonate



propylene carbonate

Ethylene carbonate and propylene carbonate were chosen as the comonomers for this study:

(a) because they were both readily available, and

(b) because of their structural similarity to trimethylene carbonate, the comonomer used in 'Maxon'.

Table 4.1: Conditions used in homopolymer and copolymer synthesis.

Polymer	Copolymer	Monomer (1) (g)	Monomer (2) (g)	Initiator	Temperature (°C)	Time (mins)	Physical Appearance of Product	% Yield
PGA	–	G (1.2000)	–	SO	150	30	white powder	11
PEC	–	EC (2.0000)	–	SO	150	30	white powder	6
PPC	–	PC (2.0000)	–	SO	150	30	pale yellow powder	3
–	P(GA-co-EC)	G (1.2000)	EC (0.9104)	SO	150	30	fine white powder	20
–	P(GA-co-PC)	G (2.5000)	PC (2.2000)	SO+DEG	150	30	pale brown powder	21

ABBREVIATIONS :

G = glycolide
EC = ethylene carbonate
PC = propylene carbonate
PGA = poly(glycolic acid)
P(GA-co-EC) = poly(glycolic acid-co-ethylene carbonate)
P(GA-co-PC) = poly(glycolic acid-co-propylene carbonate)
SO = stannous octoate
DEG = diethylene glycol
PEC = poly(ethylene carbonate)
PPC = poly(propylene carbonate)

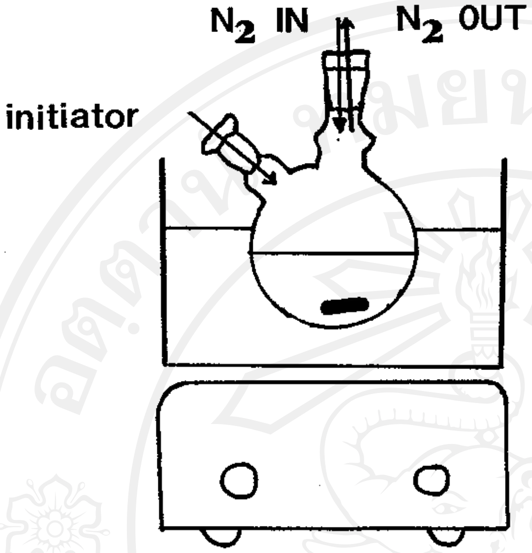


Fig. 4.3 : The apparatus used in the polymerisation and copolymerisation reactions.

4.4 Structural Characterisation of Reactants and Products

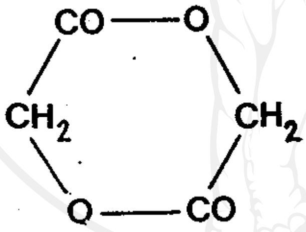
4.4.1 Infrared Spectroscopy

4.4.1.1 Glycolic Acid, Glycolide, and Poly(glycolic acid)

The chemical structures of the glycolic acid (starting material), glycolide (monomer), and the final poly(glycolic acid) (product) are compared below. Their respective infrared spectra are compared in Fig. 4.4 and interpreted in Table 4.2. The differences in their IR spectra reflect their differences in chemical structure and, in so doing, help to confirm their identities.

$$HO-CH_2-COOH$$

glycolic acid



glycolide

$$\left[O-CH_2-CO\right]_n$$

poly(glycolic acid)

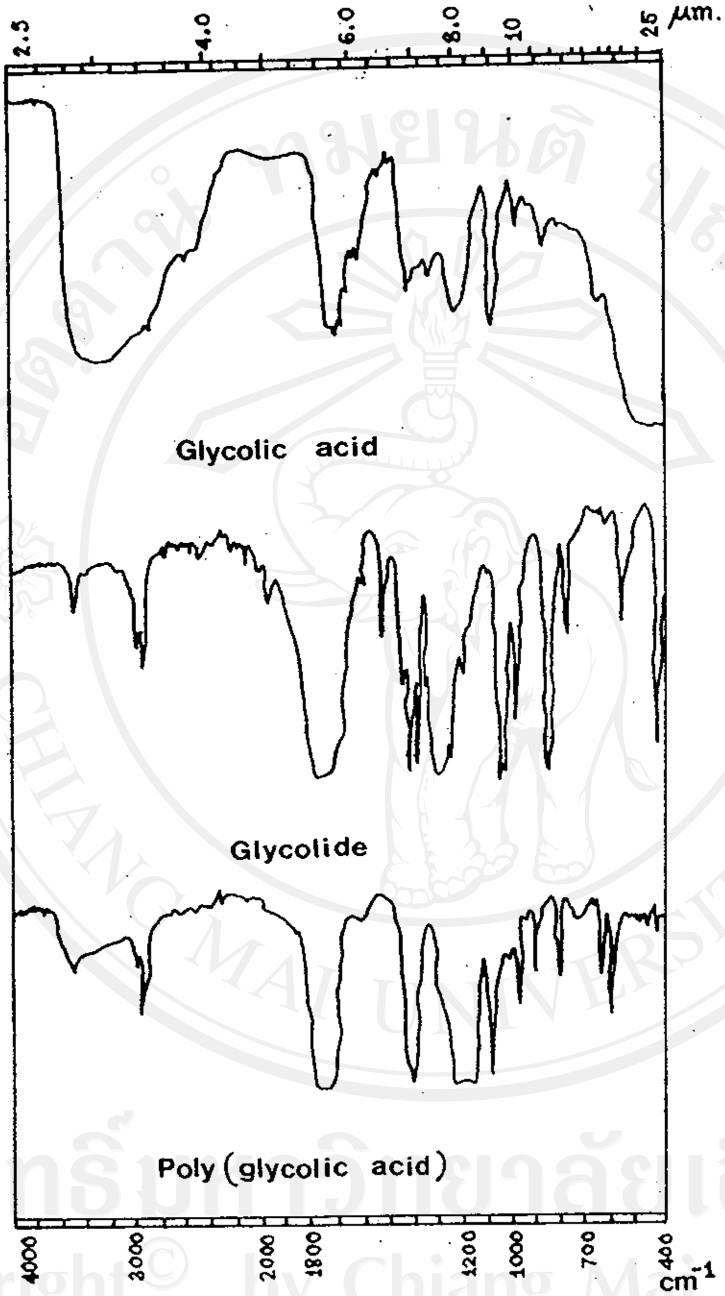


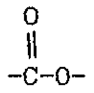
Fig. 4.4: IR spectra of glycolic acid, glycolide and the final poly(glycolic acid) product.

Table 4.2: Comparison of IR data of glycolic acid, glycolide and poly(glycolic acid) (PGA).

Vibrational Assignments	Glycolic Acid	Glycolide	PGA
	Wavenumber (cm^{-1})		
O-H str., s, b in OH and COOH	3600-2500		3600-3200
C-H str., m in CH_2	3000 (overlapped by the O-H stretching band)	3000-2960	3000-2980
C=O str., s	1760-1700	1800-1740	1800-1720
C-H bend, out-of-plane	1440 , 1350	1440 ,1400	1420,1320
C-O str., s	1260-1200(a) 1100-1080(b)	1320-1280(c) 1050(d)	1320-1260(c) 1100(d)
O-H bend, in-plane	1440 , 1350 (coupled with C-H bend, out-of-plane)		1420,1320
O-H bend, out-of-plane	1000-880		900-800

a = in COOH

b = in OH



c = in $-\overset{\overset{O}{\|}}{C}-O-$

d = in $-O-CH_2-$

str. = stretching

bend = bending

s = strong

w = weak

b = broad

m = medium

In Table 4.2, the most significant comparisons are those made in relation to :

(1) the O-H stretching band :

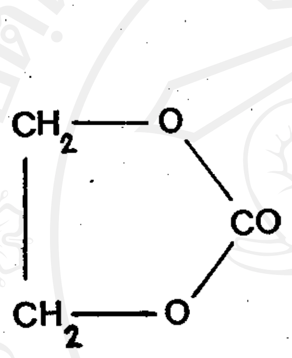
this strong broad band in glycolic acid is absent in glycolide due to the esterification of the OH and COOH groups in the cyclic diester; however, this band partially reappears in the polymer spectrum due to the presence of OH and/or COOH end-groups.

(2) the C=O stretching band :

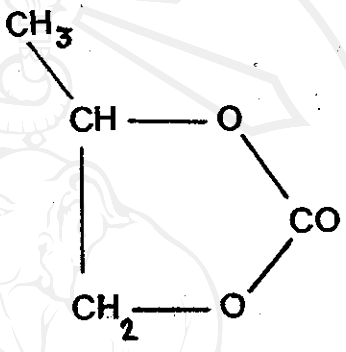
the shift in the position of this strong band from 1700-1760 cm^{-1} in glycolic acid to a slightly higher wavenumber of 1740-1800 cm^{-1} in glycolide reflects the effect of ring-strain in the latter, increasing the energy required for vibration; this ring-strain is released on polymerisation but is replaced instead by a certain amount of chain-strain arising from the restricted mobility of the polymer molecules.

4.4.1.2 Ethylene Carbonate and Propylene Carbonate

The chemical structures of the ethylene carbonate and propylene carbonate comonomers used in copolymerisation with glycolide are shown below.



ethylene carbonate



propylene carbonate

As would be expected from their similar chemical structures, their IR spectra, shown in Fig. 4.5, are also very similar. The main differences are those bands associated with the methyl substituent in propylene carbonate, as given in Table 4.3.

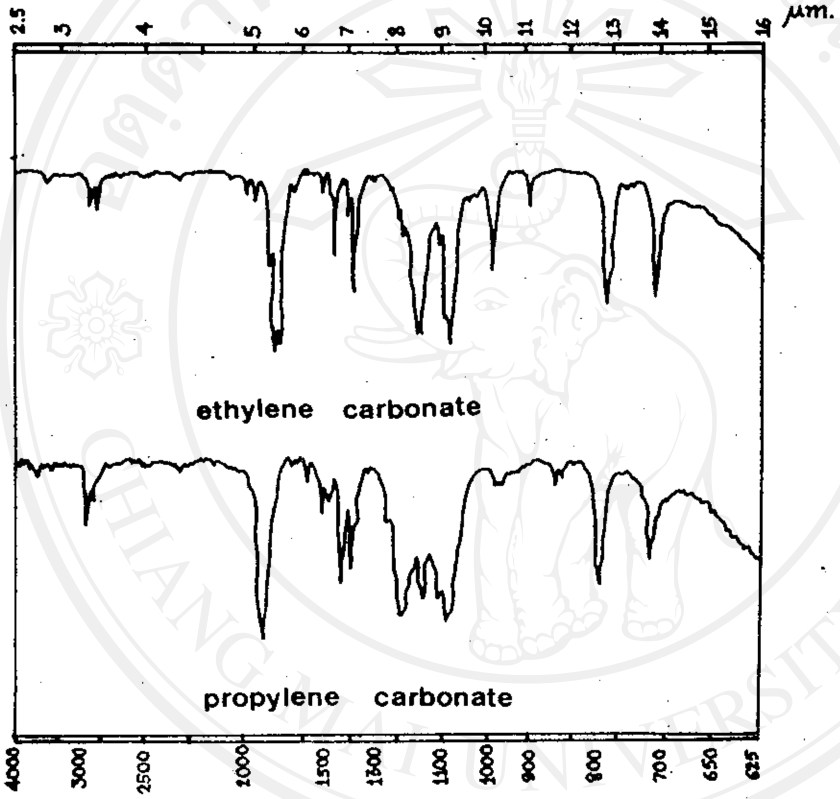


Fig. 4.5: IR spectra of ethylene carbonate and propylene carbonate.

Table 4.3: Comparison of IR data of ethylene carbonate and propylene carbonate.

Vibrational Assignments	Ethylene Carbonate	Propylene Carbonate
	Wavenumber (cm^{-1})	
C-H str., w	3000	3000
C=O str., s	1805	1800
C-H bend. in CH_2, m	1465	1465
C-H bend. in CH_3, m	–	1375,1450
C-O str., acyl, s	1150	1200
C-O str., alkyl, s	1080	1050
CH_2 rocking, m	720	720

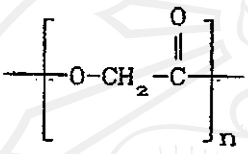
s = strong

m = medium

w = weak

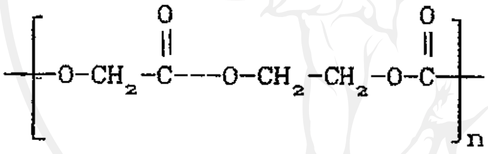
4.4.1.3 PGA, P(GA-co-EC) and P(GA-co-PC)

The chemical structures of the PGA, P(GA-co-EC) and P(GA-co-PC) products obtained in this work are given below. Their IR spectra are compared in Fig. 4.6 and interpreted in Table 4.4.



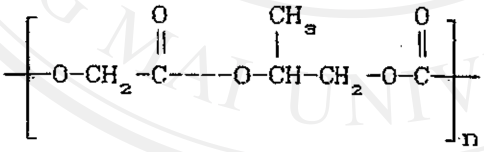
$$\left[-O-CH_2-\overset{\overset{O}{\|}}{C}- \right]_n$$

PGA



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

P(GA-co-EC)



$$\left[-O-CH_2-\overset{\overset{O}{\|}}{C}----O-\overset{\overset{CH_3}{|}}{CH}-CH_2-O-\overset{\overset{O}{\|}}{C}- \right]_n$$

P(GA-co-PC)

<u>Abbreviations :</u>

PGA = poly(glycolic acid)
P(GA-co-EC) = poly(glycolic acid - co - ethylene carbonate)
P(GA-co-PC) = poly(glycolic acid - co - propylene carbonate)

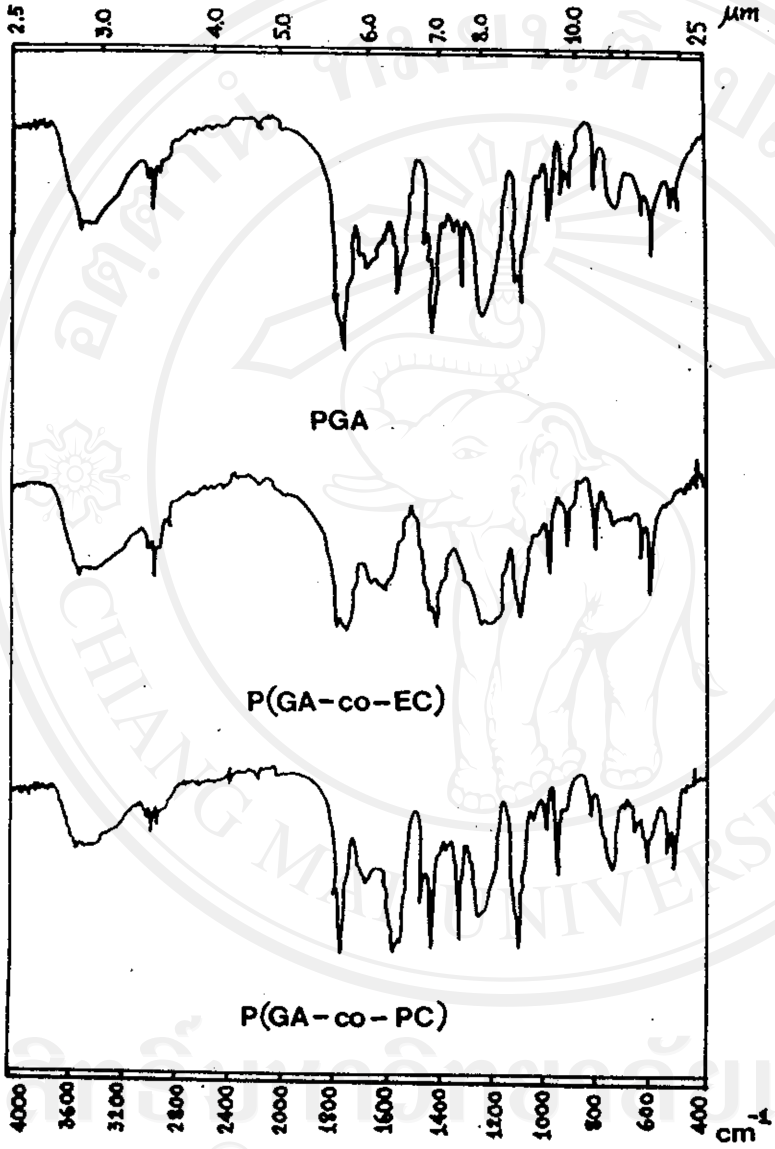
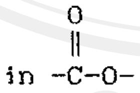
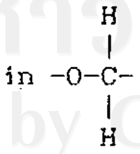


Fig. 4.6 : IR spectra of PGA, P(GA-co-EC) and P(GA-co-PC).

Table 4.4 : **Comparison of IR data of PGA, P(GA-co-EC) and P(GA-co-PC).**

Vibrational Assignments	PGA	P(GA-co-EC)	P(GA-co-PC)
	Wavenumber (cm^{-1})		
O-H str., m	3600-3200	3600-3200	3600-3200
C-H str., m in CH_2	3000-2950	3000-2950	3000-2950
C=O str., s	1800-1720	1800-1720	1800-1750
C-H bend , out-of-plane	1420	1420	1420
C-O str., s	1320-1260(a) 1100(b)	1320-1260(a) 1080(b)	1300(a) 1100(b)
O-H bend , out-of-plane	900-800	930-800	900-850

a = in 
$-\overset{\overset{\displaystyle O}{\|}}{C}-O-$

b = in 
$-O-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-$

From their IR spectra in Fig. 4.6, it is impossible to say exactly what type of copolymers the P(GC-co-EC) and P(GA-co-PC) are. However, following the example of 'Maxon', it seems most likely that they will be random copolymers. It is also possible, of course, that they may each contain homopolymeric fractions, i.e. PGA and either PEC or PPC.

A notable feature of the IR spectra is that they each exhibit a sizeable OH stretching band at 3200-3600 cm^{-1}. This is indicative of high OH end-group concentrations which, in turn, indicates relatively low molecular weights.

4.4.2 Dynamic Thermogravimetry (TG)

4.4.2.1 Analytical Conditions Used

- Initial sample weight : 80 mg (approx.)
- Heating rate : $4^{\circ}C\ .min^{-1}$
- Chart speed : $12\ ins.hr^{-1}$
- Atmosphere : N_2 (99.99 %)
- Gas flow-rate : $100\ ml.min^{-1}$

4.4.2.2 TG Curves for PGA, P(GA-co-EC) and P(GA-co-PC)

The dynamic thermogravimetric (TG) curves of the PGA, P(GA-co-EC) and P(GA-co-PC) products are shown in Fig. 4.7. From these curves, some qualitative comparisons can be made.

Firstly, the temperature ranges of decomposition appear to be quite similar at around 200-350°C. This suggests that copolymerisation does not seriously affect either the mechanism of decomposition or the upper limit of thermal stability. The latter is particularly important for melt spinning.

Secondly, the % mass losses are, however, quite different. The reasons for this are unclear, although possible explanations may include :

(a) variable amounts of cross-linking in the three samples;

(b) inhomogeneity of the two copolymers; e.g. they may contain homopolymeric fractions in what would effectively be polymer blends (compatibility unknown, but likely to be at least partially compatible).

The main conclusion to be drawn from this preliminary copolymerisation study is that a complete characterisation of copolymer composition and microstructure requires a much more detailed and systematic analysis than that described here. This should be the subject of a further study dedicated specifically to this purpose.

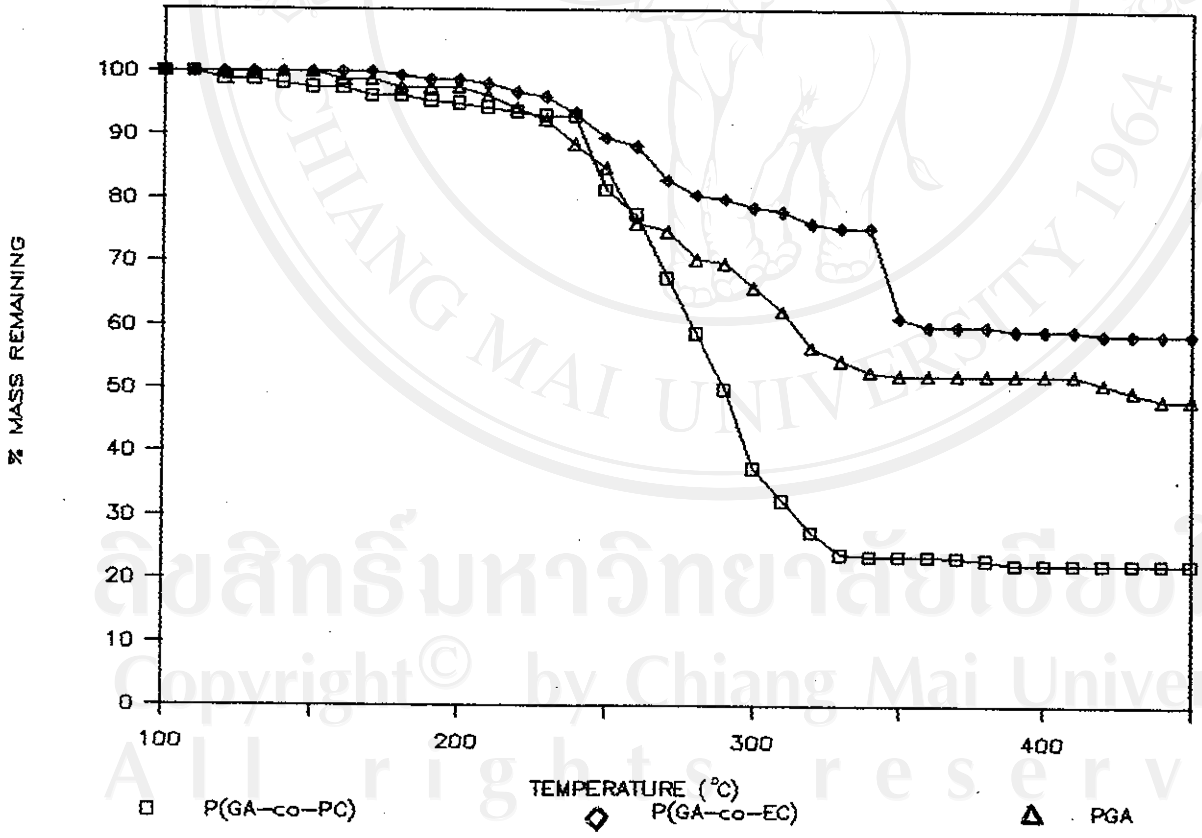


Fig. 4.7 : Dynamic TG curves of PGA, P(GA-co-EC) and P(GA-co-PC).