

CHAPTER V

RESULT AND DISCUSSION

5.1 Glycolyzed Product

5.1.1 Glycolyzed product before EG extraction

The sighted appearance of glycolyzed products are different if the PET/EG ratios and depolymerization time are various. At the high PET/EG ratios, the glycolyzed products obtained are more rigid than the ones obtained at low PET/EG ratios. This is proofed by using glass, to scratch on the surface of glycolyzed products. The glycolyzed products at high PET/EG ratios had shallow scratches, while the glycolyzed products at low PET/EG ratios had deep scratches.

Depolymerization of PET occurred fast at the high quantity of EG or at low PET/EG ratio.(discussion in 5.2) At low PET/EG ratios, the quantity of oligomers which occurred from PET scission were more than the quantity of oligomers at high PET/EG ratios. In contrast, the quantity of unreacted PET at the low PET/EG ratios were less than the quantity of unreacted PET at the high PET/EG ratios. The characteristics of PET is strong, due to PET is crystalline polymer. If the constituents of glycolyzed product consist a lot of unreacted PET, it implies that the characteristic of the glycolyzed products is hard. On the other hand, if the constituents of glycolyzed product consist a little of unreacted PET, it implies that the characteristic of glycolyzed products is soft.

The glycolyzed products at different depolymerization time have different characteristics. At the short time of depolymerization, the characteristics of glycolyzed product are more rigid than the glycolyzed product at the long depolymerization times. At the short time the quantity of unreacted PET was more than the quantity at the long depolymerization time.



The hydroxyl value of glycolyzed products from 190 to 250 °C had a little difference. The result show that the depolymerization rate and the quantity of unreacted PET in the glycolyzed products at 190 °C were closed to the ones at 250 °C. The characteristics of the glycolyzed products at different depolymerization temperature are the same. Figure 5.1 shows the glycolyzed product before EG extraction.



Figure 5.1 The glycolyzed product before EG extraction

5.1.2 Glycolyzed product after EG extraction

The visual appearance of glycolyzed products after EG extraction at different PET/EG ratios, depolymerization time and temperatures are the same. They are white powder. The glycolyzed products after EG extraction are shown in figure 5.2.



Figure 5.2 The glycolized product after EG extraction

5.2 Hydroxyl value of glycolized products

5.2.1 Dependence of hydroxyl value of glycolized product on the PET/EG ratios

Prior to chapter IV, the hydroxyl values of glycolized product before and after EG extraction were determined and showed in table 5.1. The plot of hydroxyl value of glycolized products before and after EG extraction and PET/EG ratios is shown in figure 5.3. The hydroxyl value of glycolized products before EG extraction rapidly increased when PET/EG ratios have increased. The same for hydroxyl value before EG extraction, the hydroxyl value after extraction increased too, but more slowly. The figure 5.4 shows the enlarged scale of hydroxyl values of glycolized products after EG extraction and moles of EG when the mole of PET is fixed at 1 mole. From figure 5.3 and 5.4 the trend of hydroxyl value increased when more EG was added in depolymerization. The hydroxyl values of glycolized products depend on the quantity of EG.

The figures 5.5, 5.6 and 5.7 show the relation of hydroxyl values of glycolized product after EG extraction and the depolymerization times at PET/EG ratios ,1:1.5,1:2.5

and 1:4. And the data of hydroxyl value are shown in table 5.2,5.3 and 5.4. The initial rate of depolymerization at various PET/EG ratios were calculated from the initial slope of figure 5.5,5.6 and 5.7 as shown in table 5.5. The code of glycolyzed product were explained in the table 5.7. 'GP' comes from glycolyzed product.

Table 5.1 Hydroxyl value of glycolyzed products before and after EG extraction at various PET/EG ratios, fixed depolymerization time at 4 hours.

PET/EG ratio	Mole of EG (fixed PET)	Code	Hydroxyl value (mg. of KOH/g.)	
			before	after
1:1.5	1.5	GP(1.5,4,190)	562.73	217.34
1: 2	2	GP(2 ,4,190)	692.74	236.22
1:2.5	2.5	GP(2.5,4,190)	791.00	278.93
1: 3	3	GP(3 ,4,190)	858.46	285.21
1:3.5	3.5	GP(3.5,4,190)	954.93	302.87
1: 4	4	GP(4 ,4,190)	1056.36	331.50

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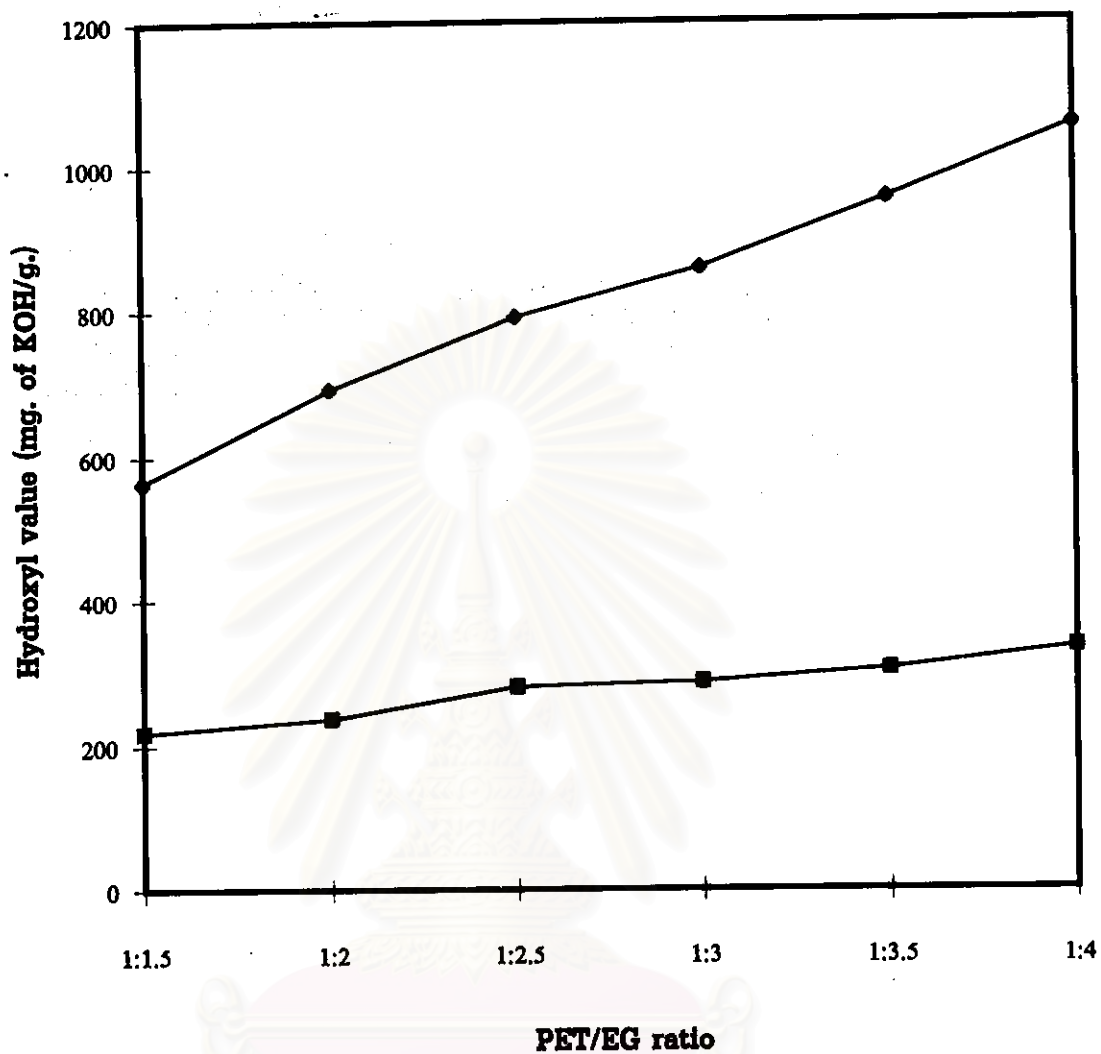


Figure 5.3 Hydroxyl value of glycolyzed products before and after EG extraction at various PET/EG ratios

—◆— Before extraction —■— After extraction

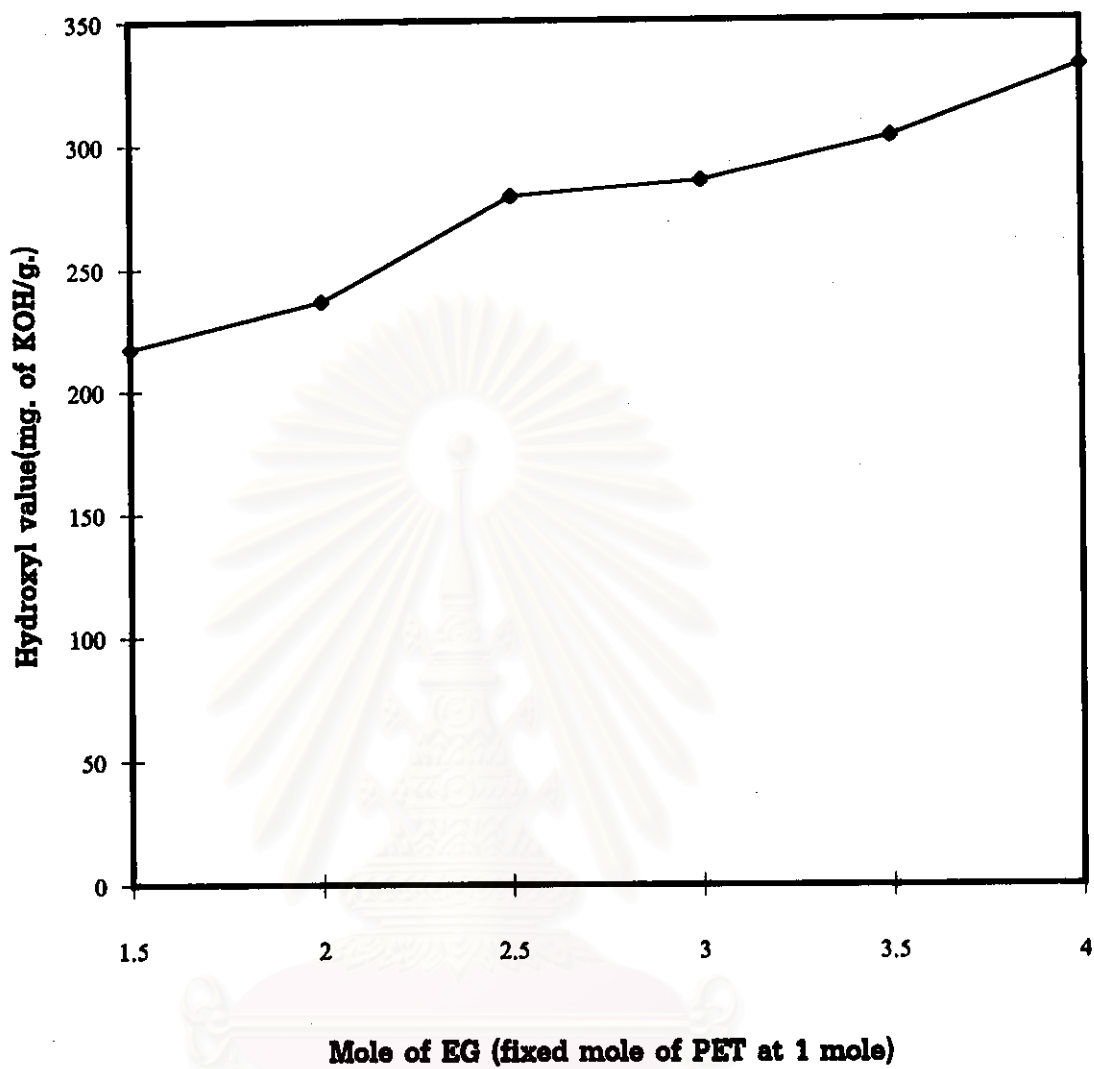


Figure 5.4 Hydroxyl value of the glycolized products after EG extraction versus mole of EG at fixed mole of PET at 1 mole

Table 5.2 Hydroxyl value of glycolyzed products after EG extraction at various depolymerization times, at PET/EG ratio 1:1.5.

Depolymerization times (hours)	Code	Hydroxyl value after EG extraction(mg. of KOH/g.)	Changing of hydroxyl value
0.5	GP(1.5,0.5,190)	62.50	-
1	GP(1.5, 1 ,190)	84.41	21.91
1.5	GP(1.5,1.5,190)	113.11	28.70
2	GP(1.5, 2 ,190)	135.18	22.07
3	GP(1.5, 3 ,190)	179.18	44.00
4	GP(1.5, 4 ,190)	217.34	38.16
5	GP(1.5, 5 ,190)	233.05	15.71
6	GP(1.5, 6 ,190)	251.74	18.69
7	GP(1.5, 7 ,190)	260.46	8.720
8	GP(1.5, 8 ,190)	271.39	10.93
9	GP(1.5, 9 ,190)	281.27	9.880

Table 5.3 Hydroxyl value of glycolyzed products after EG extraction at various depolymerization times, at PET/EG ratio 1:2.5.

Depolymerization times (hours)	Code	Hydroxyl value after EG extraction(mg. of KOH/g.)	Changing of hydroxyl value
0.5	GP(2.5,0.5,190)	96.13	-
1	GP(2.5, 1 ,190)	118.72	22.59
1.5	GP(2.5,1.5,190)	152.50	33.78
2	GP(2.5, 2 ,190)	185.26	32.76
3	GP(2.5, 3 ,190)	224.68	39.42
4	GP(2.5, 4 ,190)	278.93	54.25
5	GP(2.5, 5 ,190)	280.97	2.040
6	GP(2.5, 6 ,190)	287.75	6.780
7	GP(2.5, 7 ,190)	303.27	15.52
8	GP(2.5, 8 ,190)	316.68	13.40
9	GP(2.5, 9 ,190)	324.08	7.400

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Table 5.4 Hydroxyl value of glycolized products after EG extraction at various depolymerization times, at PET/EG ratio 1:4.

Depolymerization times (hours)	Code	Hydroxyl value after EG extraction(mg. of KOH/g.)	Changing of hydroxyl value
0.5	GP(4,0.5,190)	192.31	-
1	GP(4, 1 ,190)	215.60	23.29
1.5	GP(4,1.5,190)	248.31	32.71
2	GP(4, 2 ,190)	282.76	34.45
3	GP(4, 3 ,190)	303.90	21.14
4	GP(4, 4 ,190)	331.50	27.60
5	GP(4, 5 ,190)	346.72	15.22
6	GP(4, 6 ,190)	351.62	4.900
7	GP(4, 7 ,190)	355.18	3.560
8	GP(4, 8 ,190)	356.40	1.220
9	GP(4, 9 ,190)	355.83	0.570

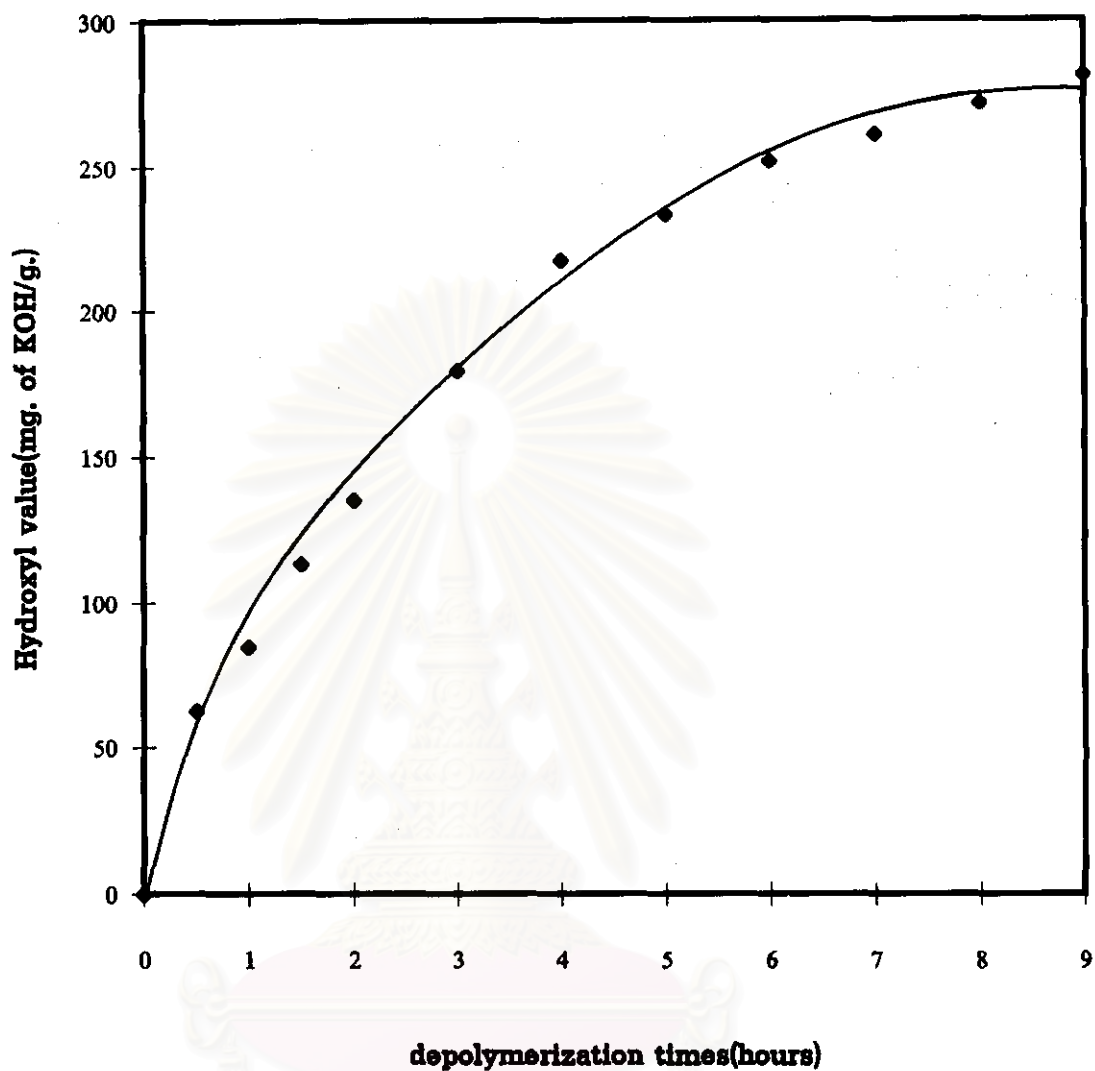


Figure 5.5 Hydroxyl value of glycolized products after EG extraction at various depolymerization times , at PET/EG ratio 1:1.5.

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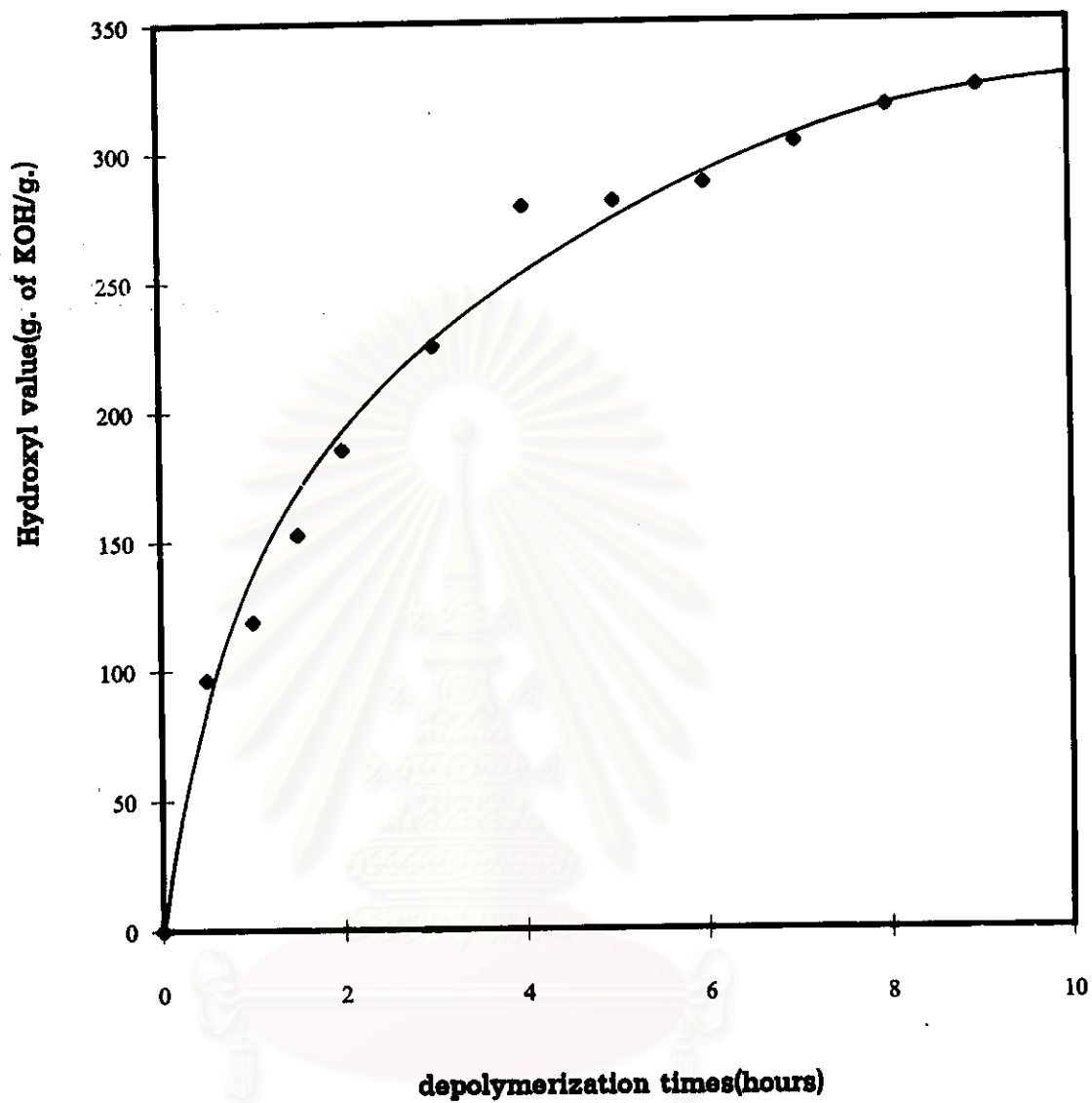


Figure 5.6 Hydroxyl value of glycolyzed products after EG extraction at various depolymerization times ,at PET/EG ratio 1:2.5

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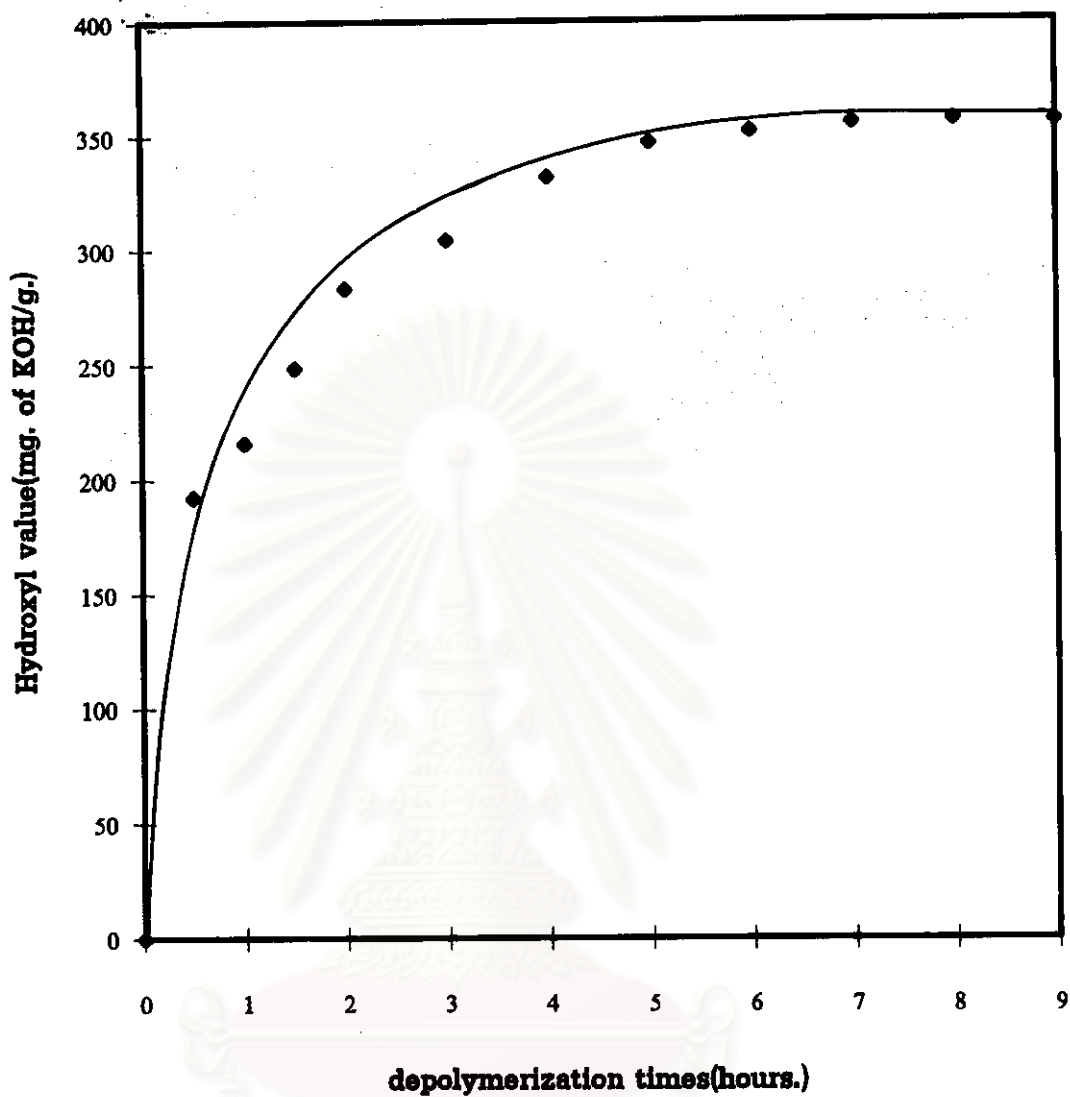


Figure 5.7 Hydroxyl value of glycolized products after EG extraction at various depolymerization times, at PET/EG ratio 1:4.

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Table 5.5 The initial rate of depolymerization of PET at the various PET/EG ratios.

PET/EG ratios	[EG]	[EG] ²	Initial rate (Hydroxyl value/hr.)
1:1.5	1.5	1.25	125.00
1:2.5	2.5	6.25	192.26
1: 4	4	16	384.82

where : [EG] is the mole of EG at fixed mole of PET at 1 mole

Initial rate of depolymerization of PET and the square of mole of EG were plotted in figure 5.8. From figure 5.8, the relation between two variables is linear. From the graph, we can conclude that the initial rates of depolymerization are varied by increasing of EG. From the mathematics theory, we could arrange the relation of initial rate and the square of mole of EG in the equation 5.1 and 5.2.

$$(5.1) \quad \text{initial rate} \propto [EG]^2$$

$$(5.2) \quad \text{initial rate} = 17.893[EG]^2 + 93.818$$

$$\text{where : } R^2 = 0.9924$$

The linear relation between initial rate and the square of mole of EG give R^2 approach 1. Equation 5.2 was calculated in the range of ratio of PET/EG between 1:1.5 to 1:4, so this equation is suitable for calculating the initial rate at the ratio of PET/EG nearly 1:1.5 to 1:4. The initial rates of depolymerization have been increased when the quantity of EG have been risen. PET scission occur quickly and the oligomer rapidly increase at high initial rate of depolymerization. The quantity of the oligomers has an effect on hydroxyl value of glycolyzed products because the oligomers have terminated - hydroxyl groups. Thus the hydroxyl values of glycolyzed product are risen when the quantity of EG increases. In other words , hydroxyl values depend on the quantity of EG.

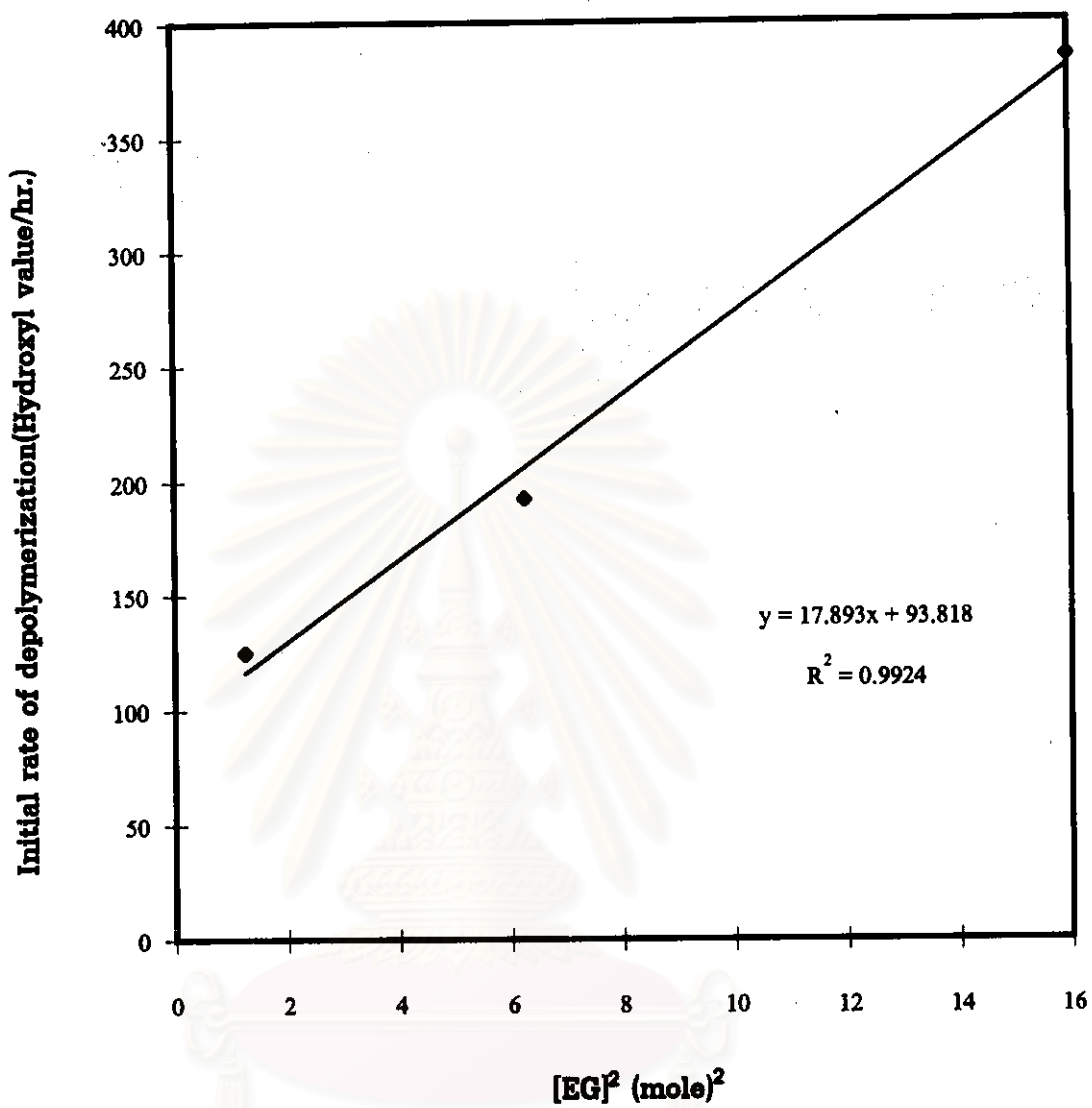


Figure 5.8 Initial rate of depolymerization of PET and the square of mole of EG



5.2.2 Dependence of hydroxyl value on depolymerization times

Table 5.6 The depolymerization rate at various time and PET/EG ratios of 1:1.5 1:2.5 and 1:4

Times(hrs.)	Depolymerization rate at various PET/EG ratio(Hydroxyl value/hr.)		
	1:1.5	1:2.5	1:4
0	125.00	192.26	384.62
0.5	89.38	118.00	150.00
1	60.94	80.96	81.25
1.5	45.00	52.44	54.16
2	39.46	49.82	32.50
3	32.50	47.20	17.33
4	23.21	25.56	12.19
5	18.57	22.72	11.54
6	16.25	17.61	6.67
7	15.00	16.48	3.33
8	10.83	11.36	0.3916
9	10	5.68	0.00086

The table 5.6 presents the depolymerization rates at various times at PET/EG ratios of 1:1.5, 1:2.5 and 1:4. Figure 5.9, 5.10 and 5.11 show the hydroxyl values and depolymerization rates at various times. Depolymerization rate or the rate of changing hydroxyl value at a fixed time was calculated from the slope of the graph of hydroxyl value and time.

From figure 5.9, when the time of depolymerization increased, the depolymerization rates have been decreased and the hydroxyl value of glycolized products have been obviously increased throughout 9 hours. When the time has passed 9 hours, the depolymerization rate still occurred. This implies that the depolymerization of PET does not reach the equilibrium at 9 hours, at PET/EG ratio of 1:1.5.

Table 5.7 Code of glycolized product at various times , various ratio of PET/EG , and temperature.

Code	Depolymerization time(hour)	PET/EG ratio	Temperature (°C)
GP(1.5,0.5,190)	0.5	1:1.5	190
GP(1.5, 1 ,190)	1	1:1.5	190
GP(1.5,1.5,190)	1.5	1:1.5	190
GP(1.5, 2 ,190)	2	1:1.5	190
GP(1.5, 3 ,190)	3	1:1.5	190
GP(1.5, 4 ,190)	4	1:1.5	190
GP(1.5, 5 ,190)	5	1:1.5	190
GP(1.5, 6 ,190)	6	1:1.5	190
GP(1.5, 7 ,190)	7	1:1.5	190
GP(1.5, 8 ,190)	8	1:1.5	190
GP(1.5, 9 ,190)	9	1:1.5	190

Table 5.7 Code of glycolyzed product at various times , various ratio of PET/EG , and temperature. (continue)

Code	Depolymerization time(hour)	PET/EG ratio	Temperature (°C)
GP(2.5,0.5,190)	0.5	1:2.5	190
GP(2.5, 1 ,190)	1	1:2.5	190
GP(2.5,1.5,190)	1.5	1:2.5	190
GP(2.5, 2 ,190)	2	1:2.5	190
GP(2.5, 3 ,190)	3	1:2.5	190
GP(2.5, 4 ,190)	4	1:2.5	190
GP(2.5, 5 ,190)	5	1:2.5	190
GP(2.5, 6 ,190)	6	1:2.5	190
GP(2.5, 7 ,190)	7	1:2.5	190
GP(2.5, 8 ,190)	8	1:2.5	190
GP(2.5, 9 ,190)	9	1:2.5	190

Table 5.7 Code of glycolized product at various times , various ratio of PET/EG , and temperature. (continue)

Code	Depolymerization time(hour)	PET/EG ratio	Temperature (°C)
GP(4,0.5,190)	0.5	1:4	190
GP(4, 1 ,190)	1	1:4	190
GP(4,1.5,190)	1.5	1:4	190
GP(4, 2 ,190)	2	1:4	190
GP(4, 3 ,190)	3	1:4	190
GP(4, 4 ,190)	4	1:4	190
GP(4, 5 ,190)	5	1:4	190
GP(4, 6 ,190)	6	1:4	190
GP(4, 7 ,190)	7	1:4	190
GP(4, 8 ,190)	8	1:4	190
GP(4, 9 ,190)	9	1:4	190

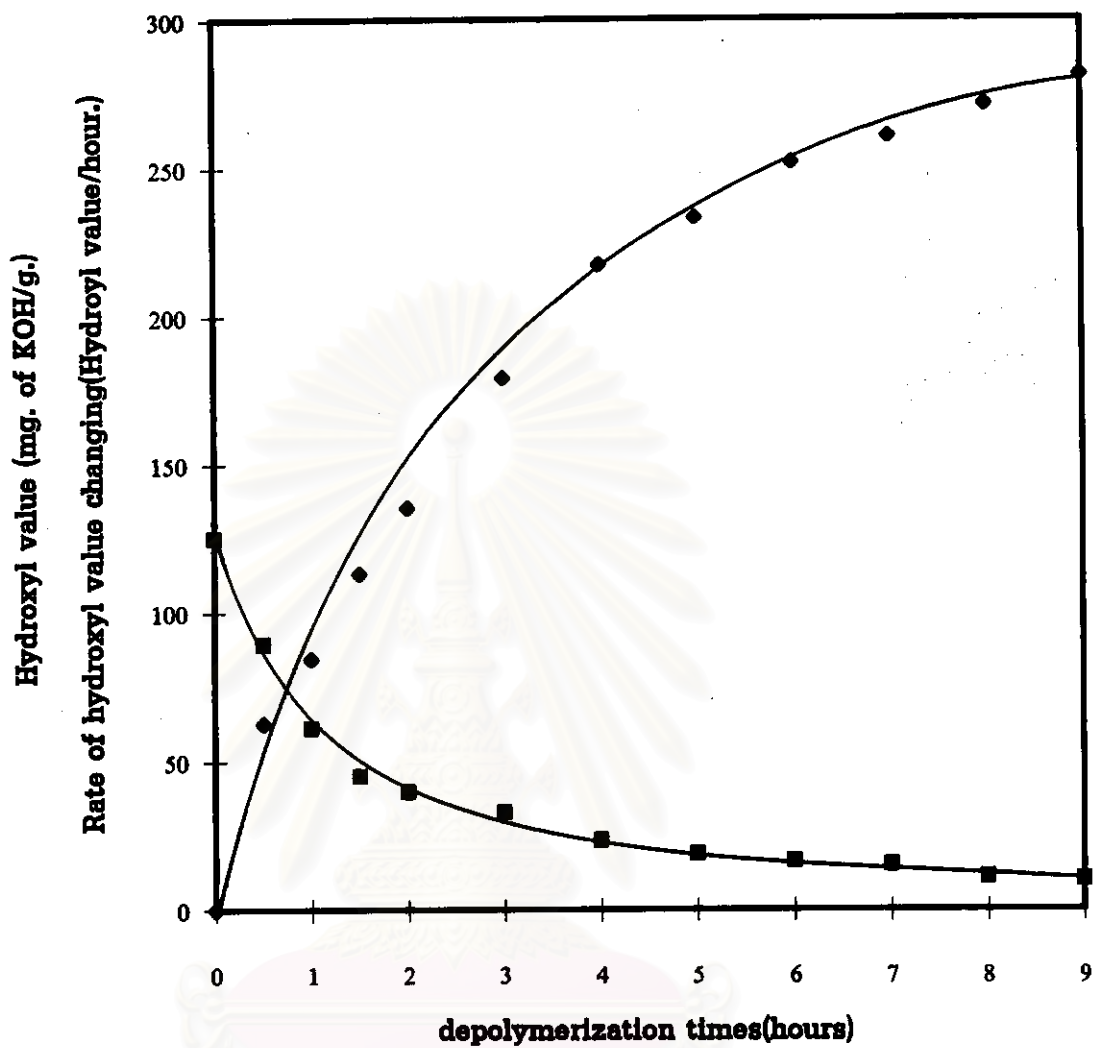


Figure 5.9 Hydroxyl value of glycolized products after EG extraction and the depolymerization rate at various at PET/EG ratio at 1:1.5

● Hydroxyl value(g. of KOH/g.) ■ Rate of hydroxyl value changing(Hydroxyl value/hour)

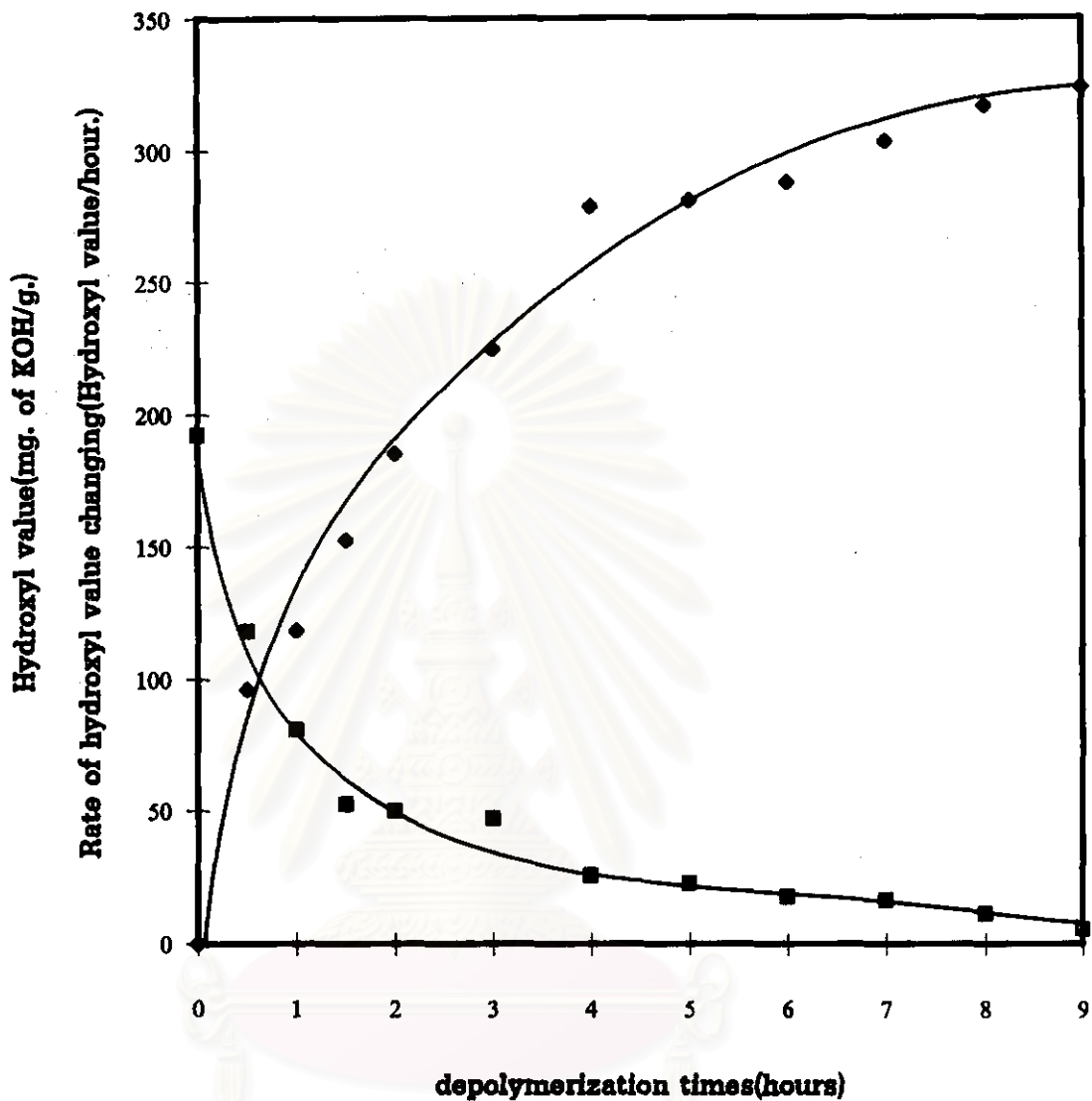


Figure 5.10 Hydroxyl value of glycolized products after EG extraction and the depolymerization rate at the various times at PET/EG ratio 1:2.5

◆ Hydroxyl value(g. of KOH/g.) ■ Rate of hydroxyl value changing(Hydroxyl value/hour)

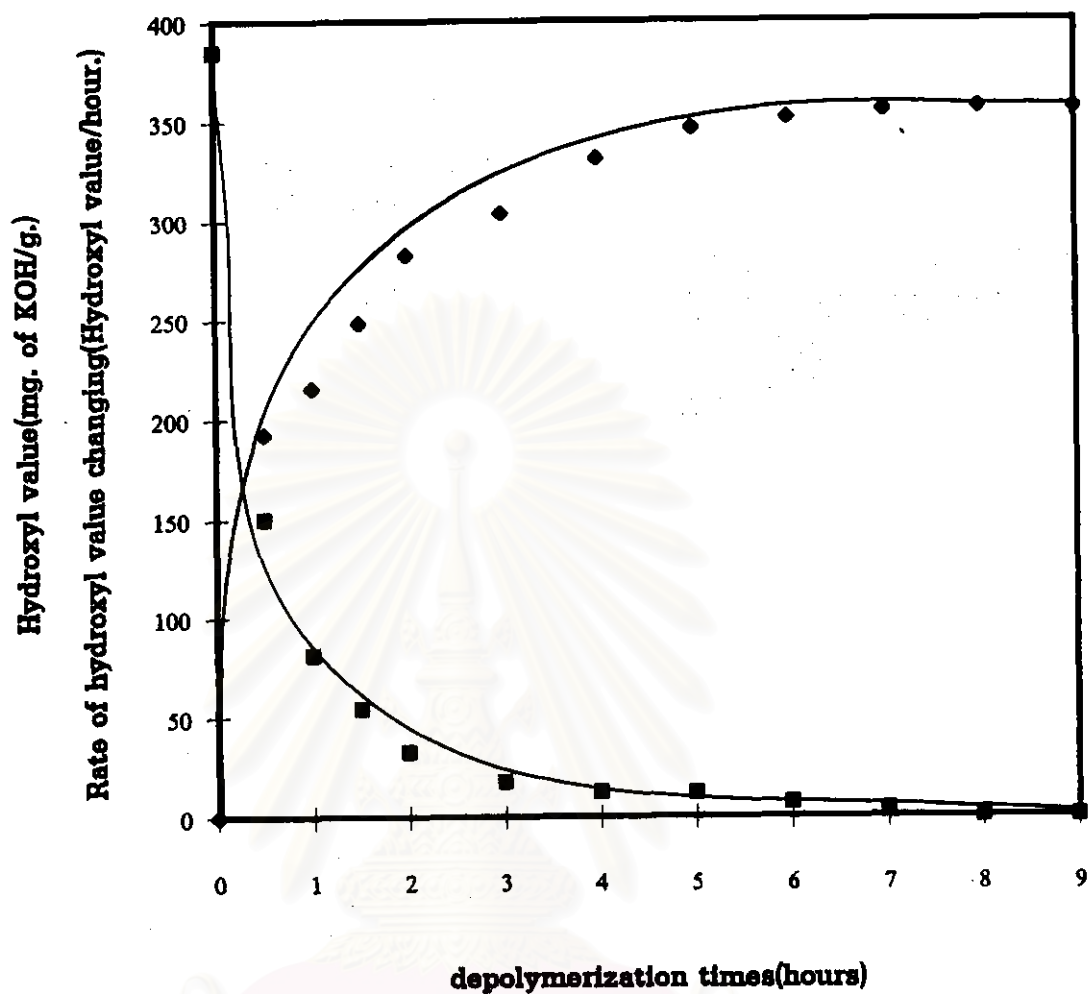


Figure 5.11 Hydroxyl value of glycolyzed products after EG extraction and the depolymerization rate at various times at PET/EG ratio 1:4

◆ Hydroxyl value(g. of KOH/g.) ■ Rate of hydroxyl value changing (Hydroxyl value/hour)

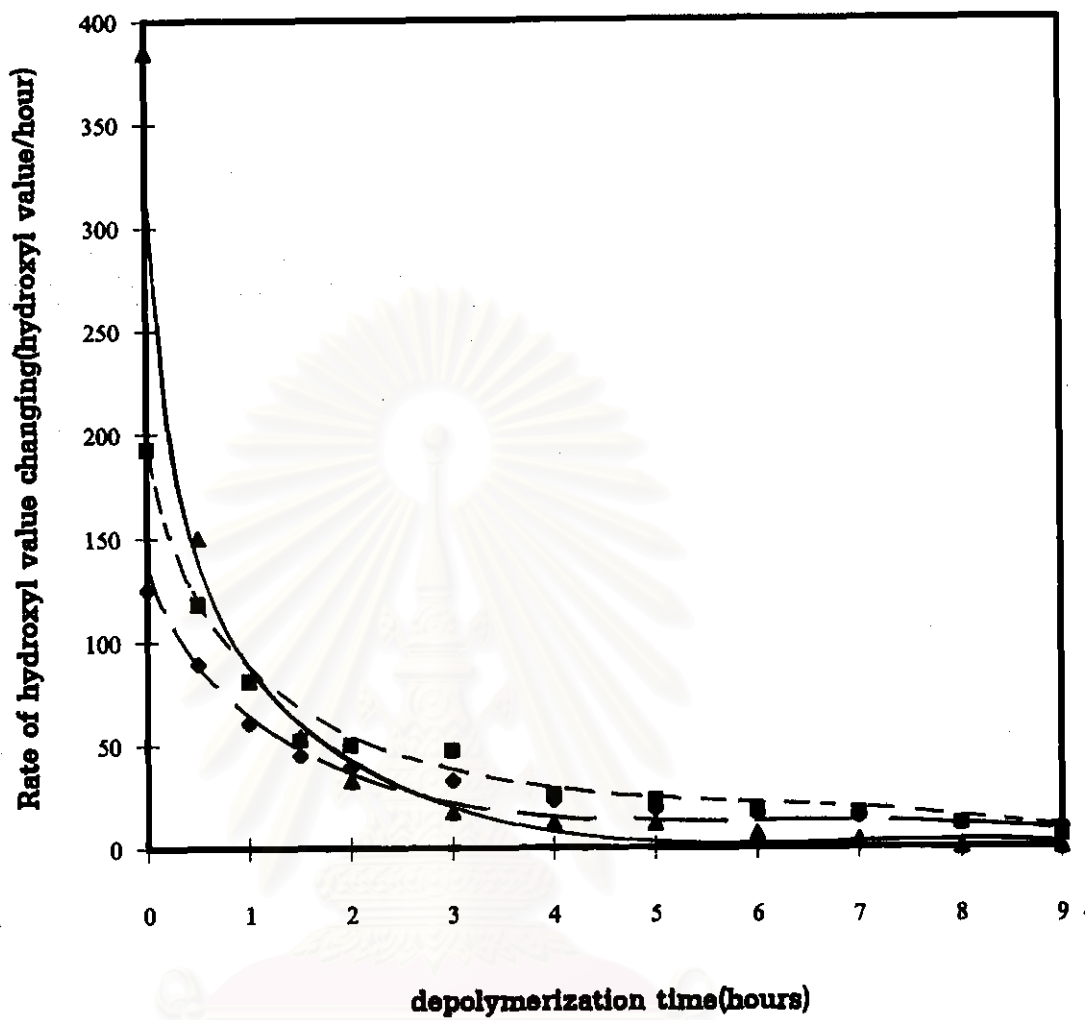


Figure 5.12 The rate of hydroxyl value changing at the various times and the various PET/EG ratio

◆ 1:1.5 ■ 1:2.5 ▲ 1:4

From figure 5.10, when the time of depolymerization increased, the depolymerization rates have been decreased and the hydroxyl value of the glycolyzed products have been obviously increased at the beginning of depolymerization process. When the time has passed about 4 hours, the hydroxyl value of glycolyzed products have still increased, but not very much. For 9 hours of depolymerization, the depolymerization rates have still happened. This implies that the depolymerization of PET does not reach the equilibrium at PET/EG ratio of 1:2.5, at 9 hours.

From 5.11, the same as figure 5.9 and 5.10, the time increased as the depolymerization rates have been decreased. At the beginning of depolymerization process, the hydroxyl values have obviously increased, when the times have passed about 2 hours, the hydroxyl values have slowly increased. At 8 hours, the depolymerization rate approached zero, the hydroxyl value is more or less consistent. It probably say that the depolymerization of PET reaches equilibrium at 8 hours of depolymerization, at PET/EG ratio 1:4.

From figure 5.9, 5.10 and 5.11, the hydroxyl value of glycolyzed product after EG extraction are increased when the time of depolymerization increases. Until the reaction reaches equilibrium, the hydroxyl values do not change. To examine the depolymerization rate in figure 5.12, at the half hour, the depolymerization rate are obviously different at various PET/EG ratios. After the time has passed 1 hour, depolymerization rate at various PET/EG ratios have been slightly different.

The scission of PET happens so quickly and randomly at the first half hour, the length of the molecule of oligomers which occurs from scission of PET is different if the PET/EG ratios are different. At PET/EG ratio of 1:4, the length of oligomers is shorter than the ones at 1:1.5 and 1:2.5 because the initial rate of depolymerization at PET/EG ratio of 1:4 is higher than the ones at 1:1.5 and 1:2.5, so the scission of PET rapidly occurs. After one hour, the scission of oligomers occurs and depolymerization rate at various PET/EG ratios are nearly. This implies that the quantity of EG slightly affects the scission of oligomer, it probably say that the short molecules have more chance to be the product at

the equilibrium than the long molecules. So the depolymerization at ratio of PET/EG of 1:4 reaches equilibrium faster than at the ratios of 1:1.5 and 1:2.5.

5.2.3 Dependence of hydroxyl value on temperature

Table 5.8 Hydroxyl value of glycolized products before and after EG extraction and temperature of depolymerization

Temperature(°C)	Hydroxyl value (mg. of KOH/g.)	
	before EG extraction	after EG extraction
190	562.73	217.34
210	566.15	221.14
230	573.64	224.46
250	584.73	227.49

Table 5.8 and figure 5.13 show the data and the graph of hydroxyl value after EG extraction at various temperatures. When the temperature of depolymerization increased, the hydroxyl value after EG extraction slowly increased. This result has confirmed the conclusion of Chen and the others(1991). They said that temperature had an effect on depolymerization rate and the rate of depolymerization was high at the high temperature. At high temperature, the rate of scission of PET is higher than the one at low temperature because the molecules of EG have the high energy to attack the molecule of PET at the high temperature.

5.3 Chain extender

In this work 4 types of chain extenders were used separately in polyurethane manufacture : EG, GP(1.5,4,190),GP(4,8,190),GP(4,8,190) without EG. Three of them came from depolymerization of PET. The polyurethane with EG was used as the reference. In

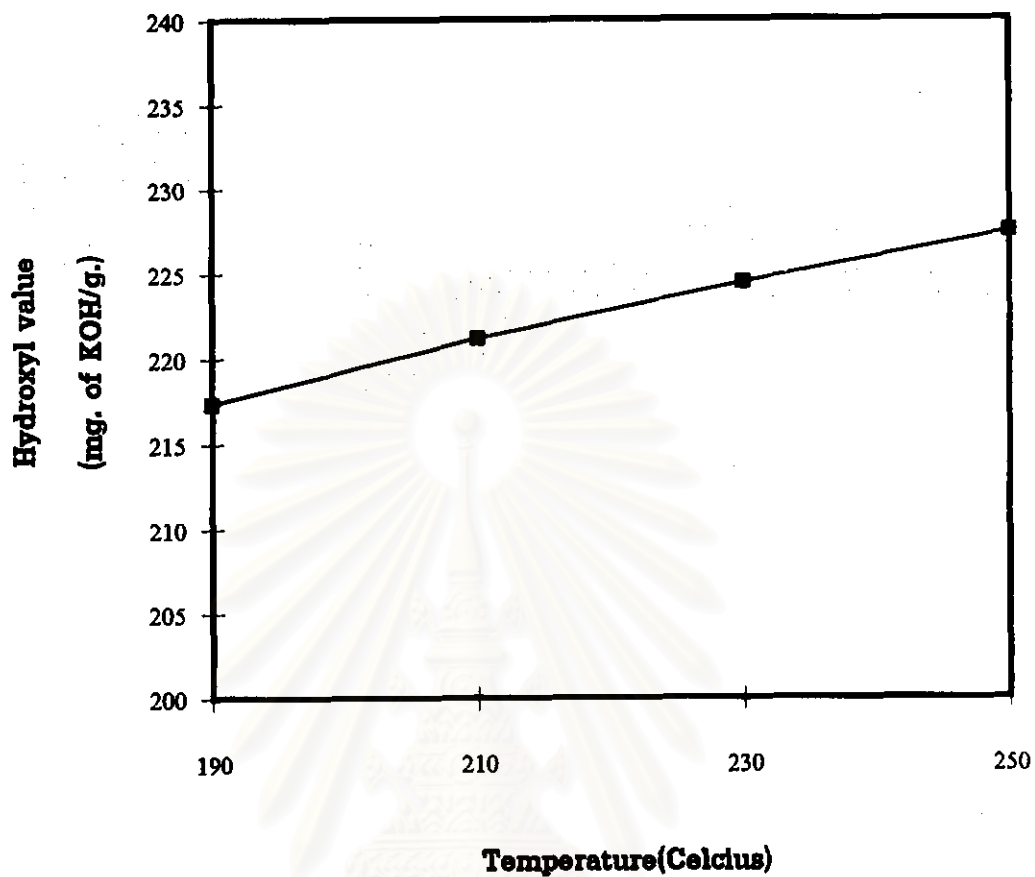


Figure 5.13 The hydroxyl value of glycolyzed products after EG extraction versus the temperature (Celcius), at PET/EG ratio 1:1.5, 4 hours.

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this part, the functional group of the glycolized products from depolymerization of PET is discussed and is compared the average molecular weight of GP(1.5,4,190) without EG and GP(4,8,190) without EG.

5.3.1 Identification of functional group

PET bottles are different from PET resin because manufacturing of PET bottles, some additive were added to increase properties of the bottles. Figure 5.14 shows the structure formula of PET and the figure 5.15 shows the infrared spectroscopy of PET bottle that had lots of additive.

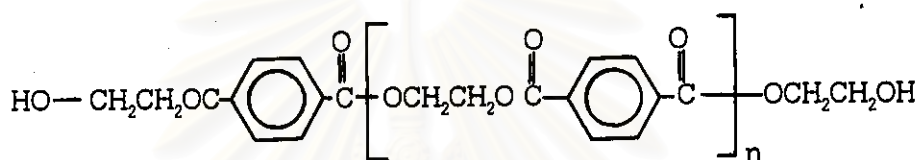


Figure 5.14 The structure formula of PET

From figure 5.15, chain of molecule of PET consists of the important functional groups such as, ester group, aromatic rings and terminated hydroxyl group. From the infrared spectroscopy of PET bottles in figure 5.15, some peaks at the wavenumber lower than 2000 cm^{-1} are not clear. For this result some of the functional groups cannot be identified. In this figure, there are three peaks which have been clearly identified. The one is the peak of O-H bond which occurred at the wavenumber between $3250\text{-}3500\text{ cm}^{-1}$. The others are the C-H bond of aliphatic molecule and aromatic ring, C-H bond of aliphatic has happened at the wavenumber between $2800\text{-}3000\text{ cm}^{-1}$. and C-H bond of aromatic ring has happened the wavenumber between $3000\text{-}3110\text{ cm}^{-1}$. The peak of ester group cannot be identified because there are a lot of contaminated peaks at the wavenumber lower than 2000 cm^{-1} .

Although PET bottles have lots of additives, the infrared spectroscopy of final product is exactly the same as BHET which was the final product of the work of Chen and the others(1991). Figure 5.16 illustrates the infrared spectroscopy of the final product

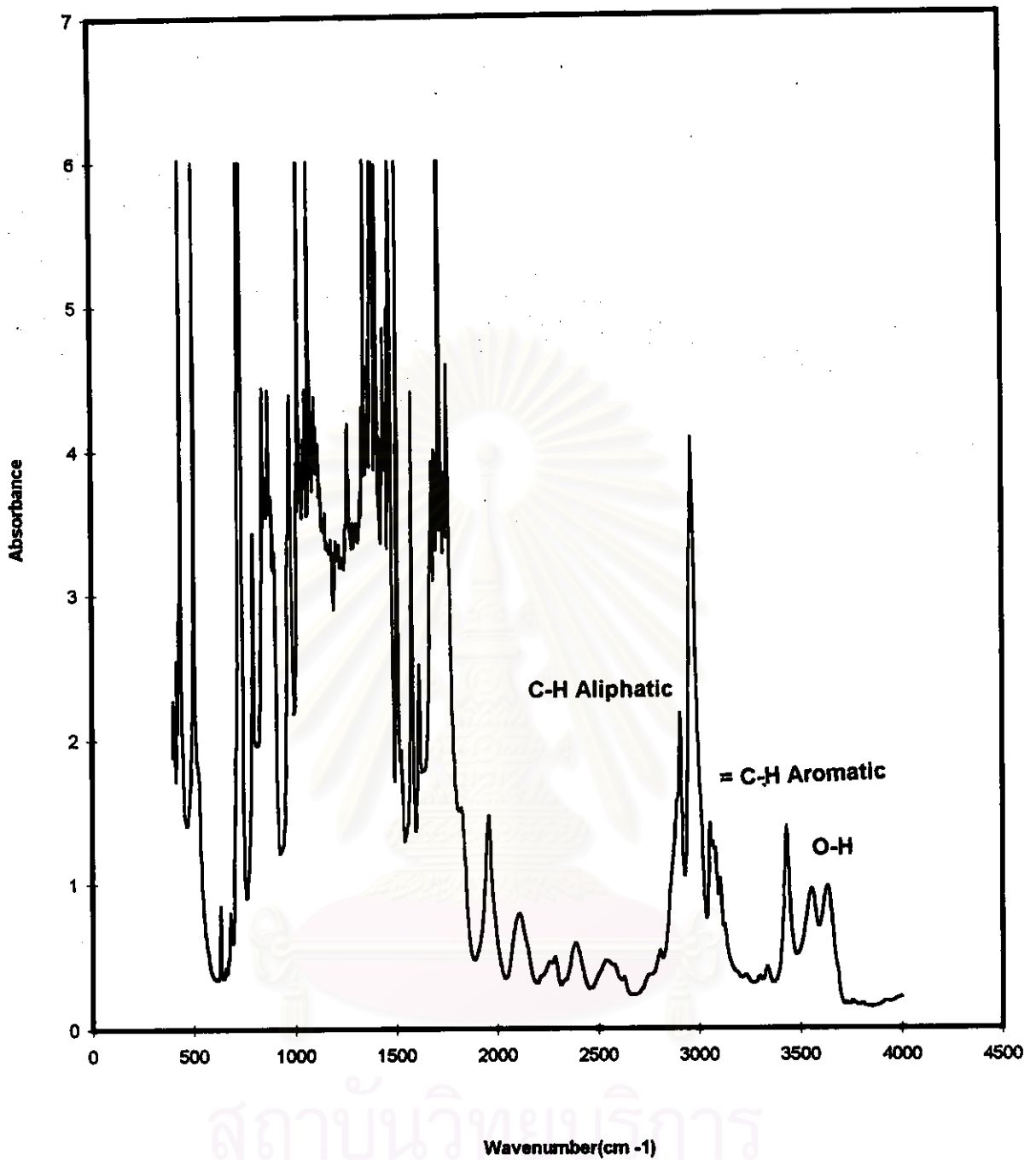


Figure 5.15 Infrared spectroscopy of PET from soft-drink bottles and functional group identification

based-on PET bottles and figure 5.17 illustrates the infrared spectroscopy of BHET (Chen and the others,1991).

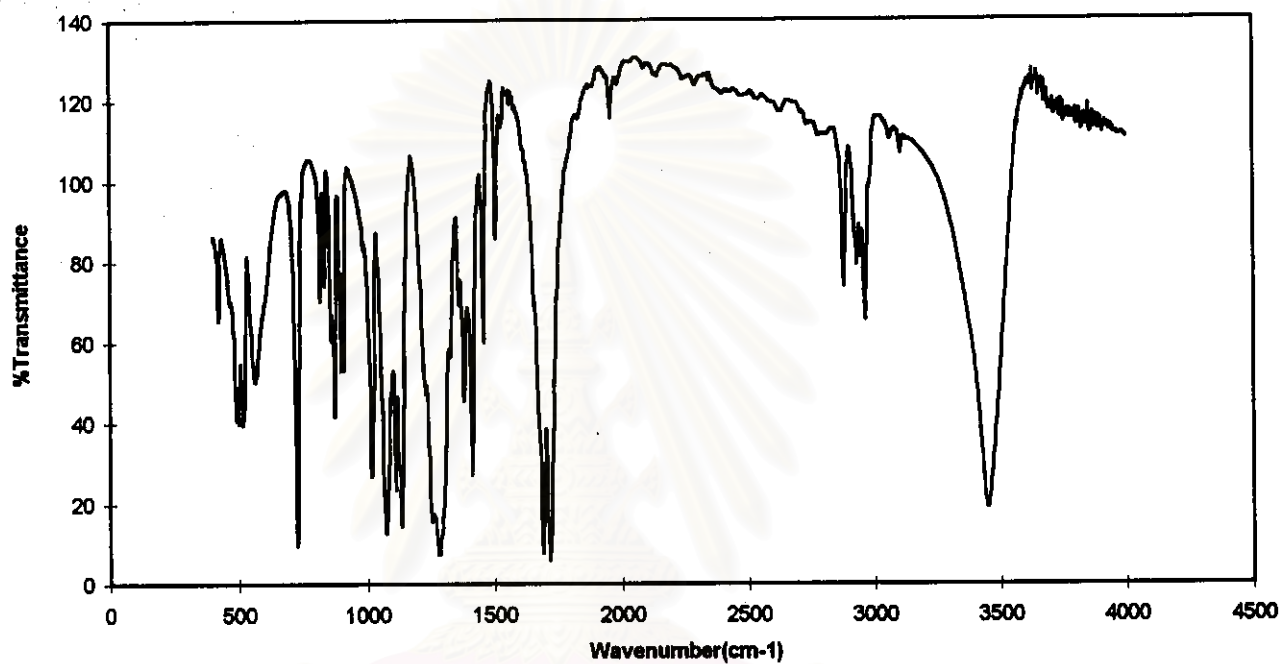


Figure 5.16 The infrared spectroscopy of final product based-on PET bottle.

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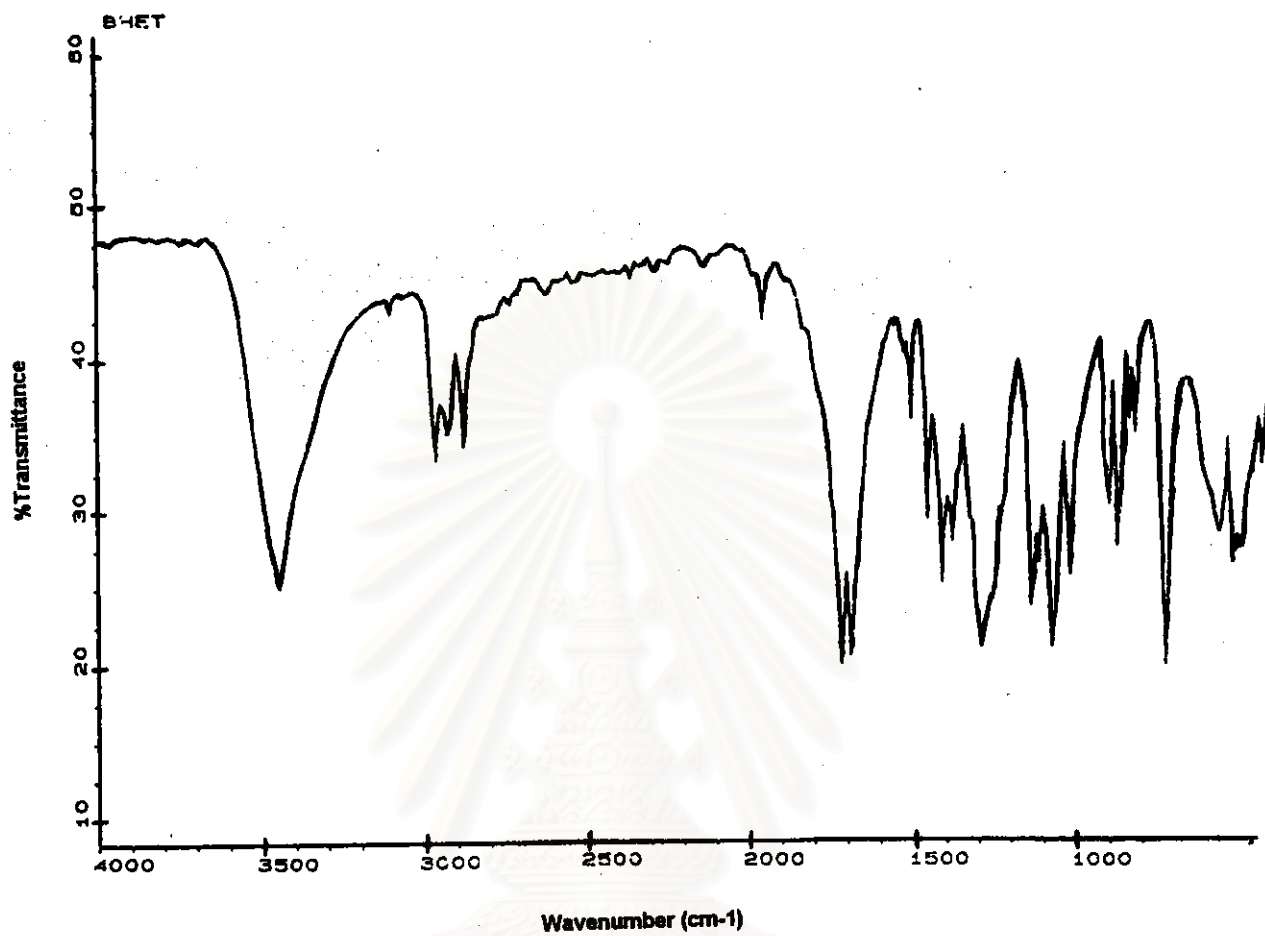


Figure 5.17 The infrared spectroscopy of BHET (Chen and the others,1991)

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From figure 5.16 and figure 5.17, it can be suggested conclude that the final products based-on PET bottles is BHET. Figure 5.18 shows the structure formula of BHET and figure 5.19 shows the infrared spectroscopy of BHET from PET bottles and the identification of the functional groups.

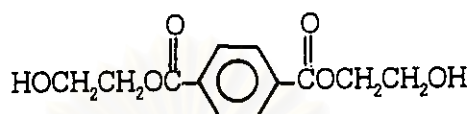


Figure 5.18 The structure formula of BHET

The molecule of BHET consists of ester group, aromatic rings and hydroxyl group. Ester group consists of C-O bonds and C=O bonds. There are two peaks of C-O bonds which have occurred at the wave number between $1000-1300\text{ cm}^{-1}$. In general ester group, C=O peak happens at the wavenumber at 1735 cm^{-1} , but C=O peak in BHET was disturbed by nearly aromatic rings, the peak of C=O bonds have occurred at the wavenumber lower than 1735 cm^{-1} . The peak of O-H groups has occurred at the wavenumber between $3250-3500\text{ cm}^{-1}$. In aromatic rings, it consists of C=C bonds and C-H bond, C=C bonds have absorbed the wavenumber at 1600 cm^{-1} and 1475 cm^{-1} . C-H bonds in the aromatic rings have absorb the wavenumber less than 3000 cm^{-1} . Some C-H bonds are not fixed at the same plane of C=C bonds which have absorbed the wavenumber between $690-900\text{ cm}^{-1}$. and C-H bonds in the aliphatic have absorbed the wavenumber between $2800-3000\text{ cm}^{-1}$.

Figure 5.20 and 5.21 illustrate the infrared spectroscopy of GP(1.5,4,190) without EG and GP(4,8,190) without EG, respectively the peaks of functional group have occurred at the same wavenumber of BHET, but the percent of transmittance are different. The peaks of GP(4,8,190) without EG have the percent of transmittance nearly the same as the peaks of BHET. GP(4,8,190) without EG is the products at equilibrium of depolymerization of PET. The constituents of GP(4,8,190) without EG maybe consist of only BHET and dimer.

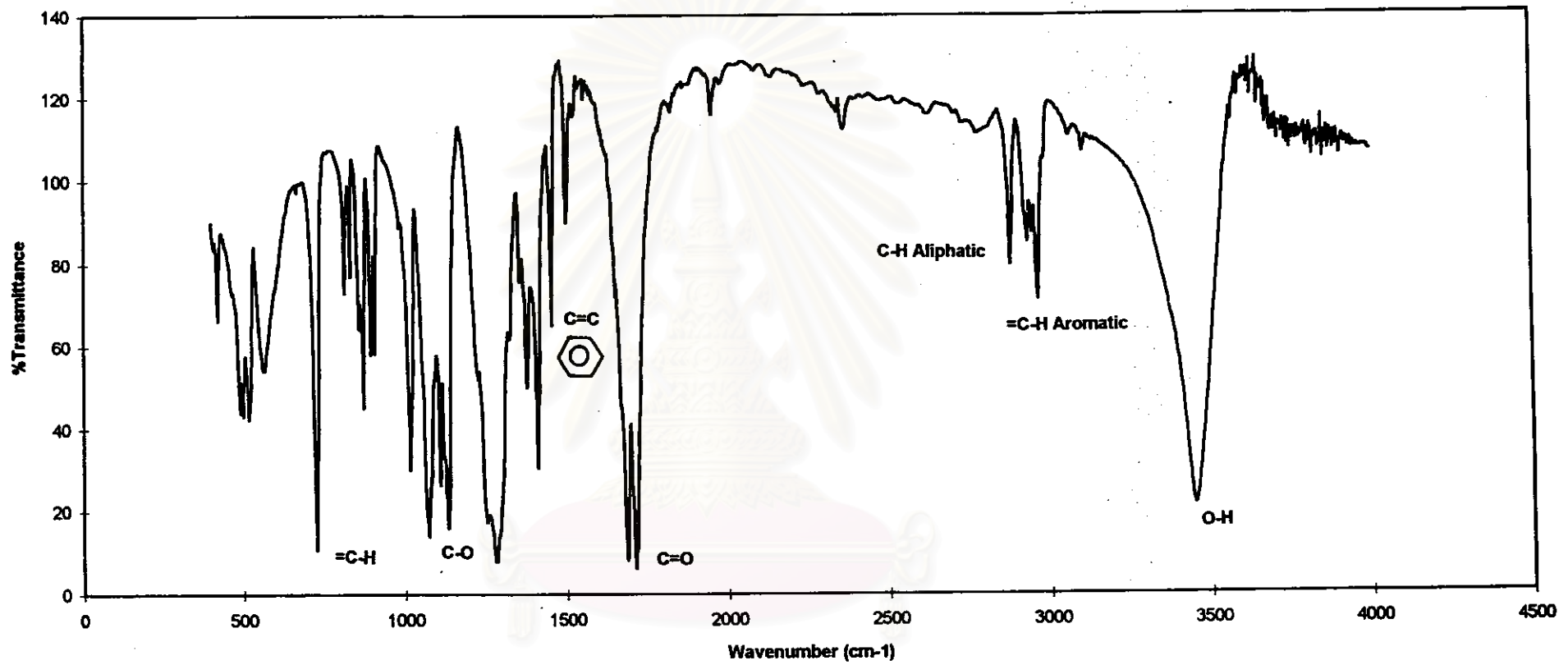


Figure 5.19 Infrared spectroscopy of BHET based on PET bottles and identification of functional groups

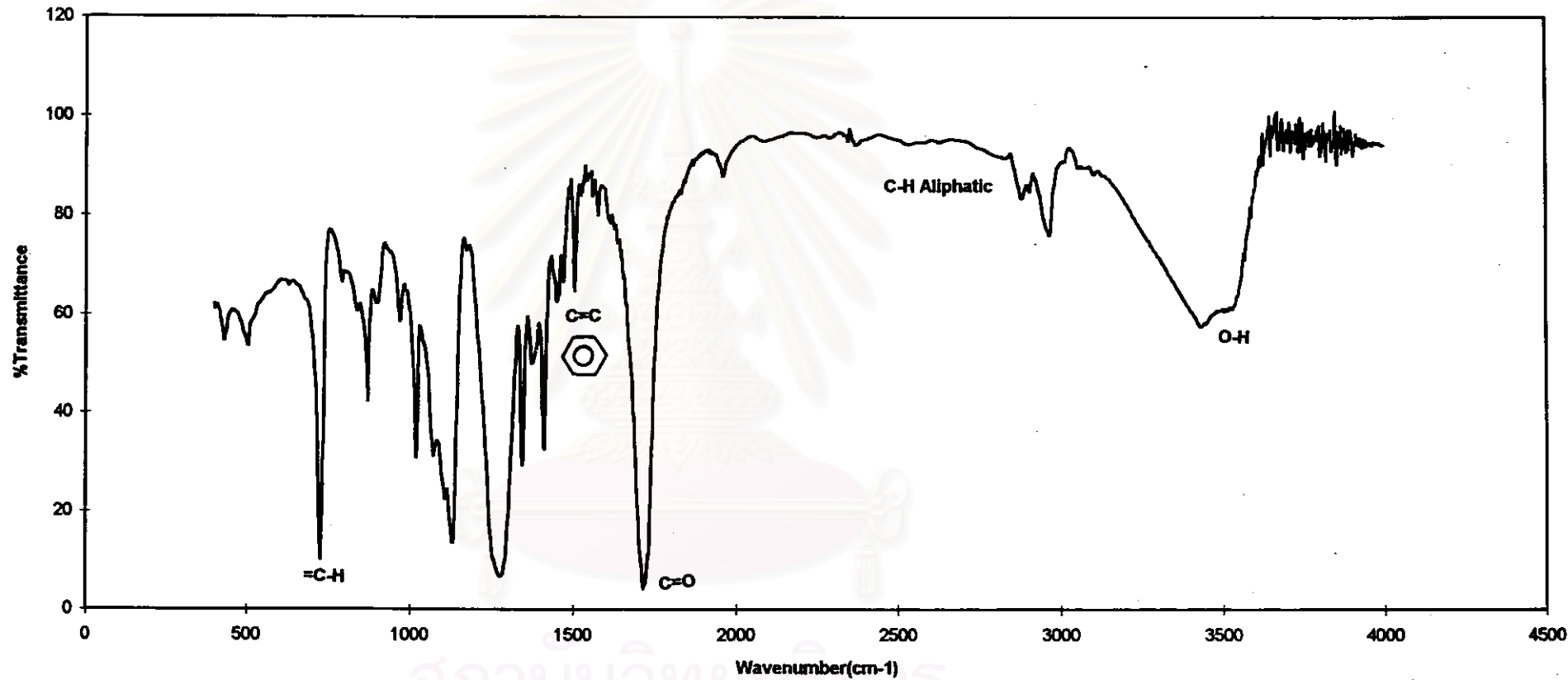


Figure 5.20 Infrared spectroscopy of GP(1.5,4,190) without EG and identification of functional groups

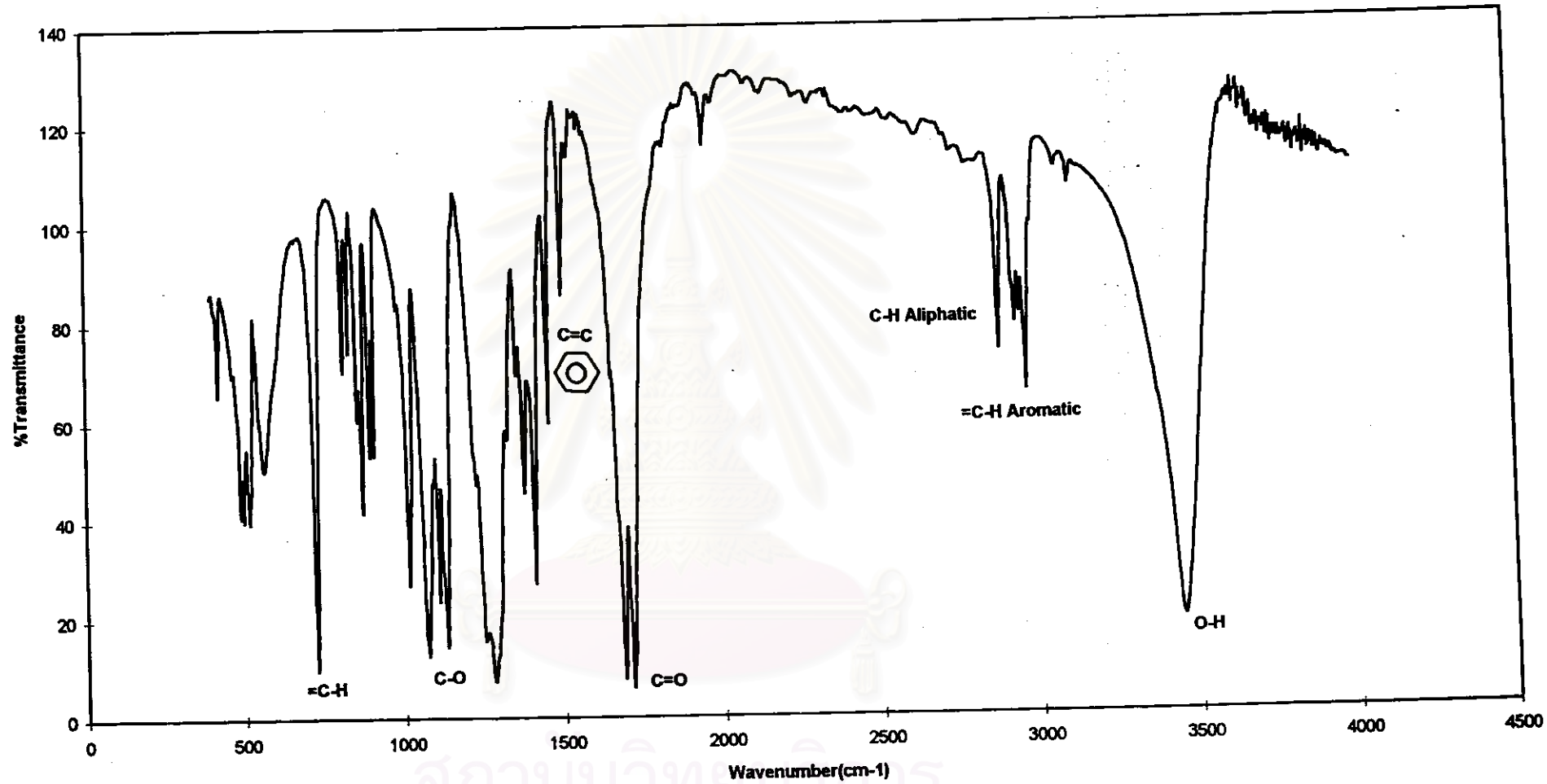


Figure 5.21 Infrared spectroscopy of GP(4,8,190) without EG and identification of functional groups

GP(1.5,4,190) without EG is glycolized products of which the reaction did not approach equilibrium. The scission of oligomers in GP(1.5,4,190) occurred at the time less than GP(4,8,190) without EG, the length of molecule of GP(1.5,8,180) without EG is longer than the length of GP(4,8,190) without EG. From 5.2.1, the hydroxyl values of GP(1.5,4,190) without EG have been less than the GP(4,8,190) without EG, this result is confirmed by the peak of O-H bonds. The percent of transmittance of GP(1.5,4,190) without EG is about 60 % and the percent of transmittance of GP(4,8,190) without EG is about 20%. The transmittance of GP(1.5,4,190) without EG is more than GP(4,8,190) without EG. In the fact of absorption, the high absorption occurs when the product has high concentration of functional groups. When the products have high absorption, this means that they have low transmittance. So GP(4,8,190) without EG has the concentration of hydroxyl group more than GP(1.5,4,190) without EG.

5.2.3 Average molecular weight from the relative viscosity

Table 5.9 The relative viscosity, intrinsic viscosity and average molecular weight

Sample	t_0 (sec.)	t (sec.)	η_r	$\eta_{at\ 25^\circ C}$ (dl./g.)	C (g./dl.)	\bar{M}_v (g./gmole)
PET	129.78	166.97	1.2884	0.5248	0.4996	10511.57
GP(1.5,4,190) without EG	129.78	133.75	1.0858	0.1663	0.5002	1744.72
GP(4,8,190) without EG	129.78	131.32	1.0133	0.0264	0.5036	596.19

where :

t_0 is average solvent flow time (sec.)

t is average solution flow time (sec.)

η_r is relative viscosity

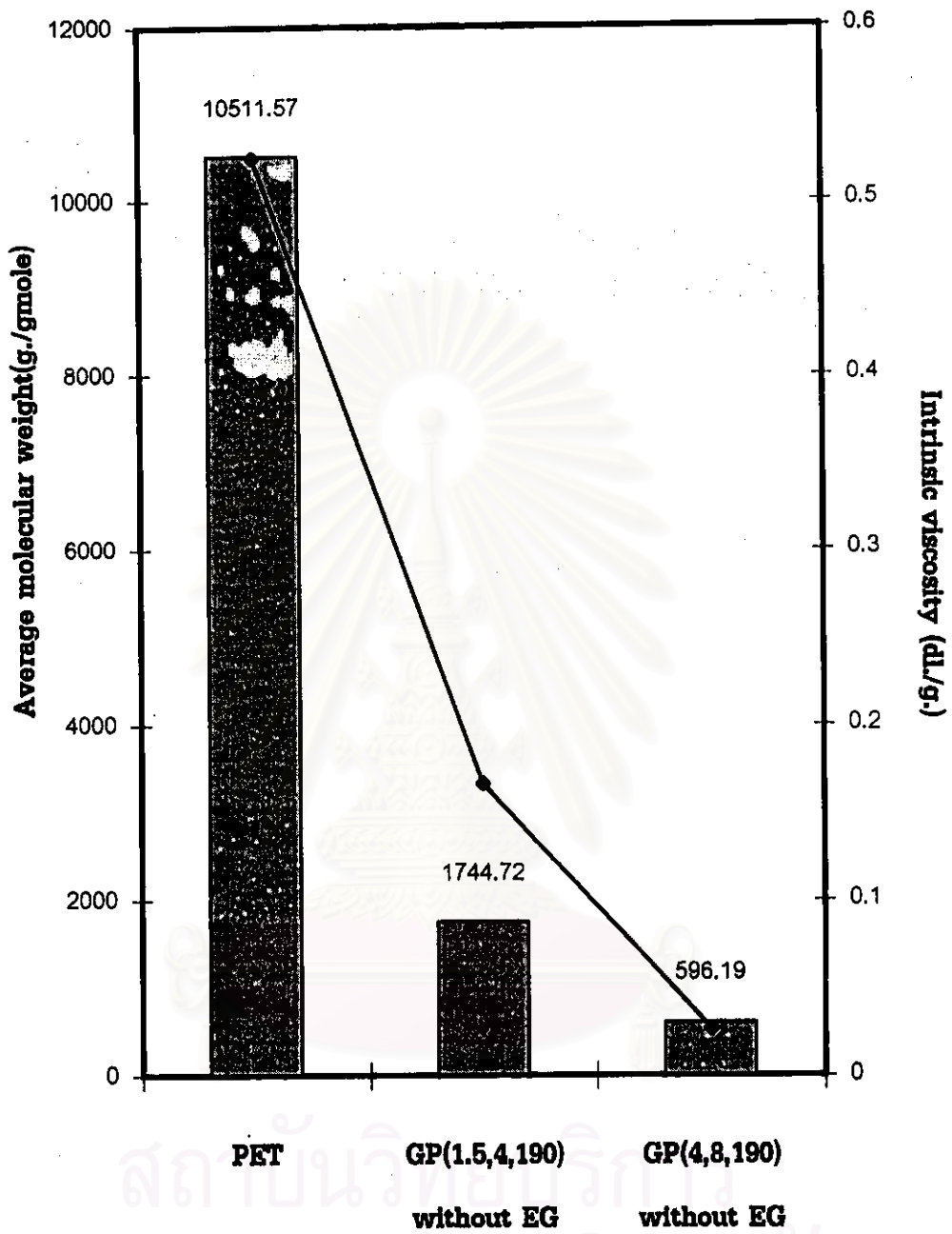


Figure 5.22 The average molecular weight(g./gmole) and the intrinsic viscosity (dl./g.)



$\eta_{\text{at } 25^\circ \text{C}}$ is intrinsic viscosity of the sample in 60:40 (w/w) phenol/1,1,2,2 tetrachloroethane solution at 25 °C (dl./g.)

C is concentration of solution (g./dl.)

\overline{M}_v is average molecular weight (g./gmole)

From table 5.9 and figure 5.22 , the typical intrinsic viscosity of PET, GP(1.5,4,190) without EG, GP(4,8,190) without EG in 60:40 (w/w) phenol /1,1,2,2-tetrachloroethane solution at 25 °C are about 0.5248 ,0.1663 ,0.0264 dl./g.,respectively, which correspond to the number-average molecular weight of 10511.57,1744.72 and 596.19 g./gmole,respectively. PET has the highest average molecular weight. GP(1.5,4,190) without EG has the molecular weight higher than GP(4,8,190) without EG. PET has depolymerized in excess EG at PET/EG ratio of 1:1.5 when the time has passed to 4 hours , the equilibrium has not been reached, the length of molecule of GP(1.5,4,190) without EG has been longer than the length of molecule of GP(4,8,190) without EG , which are the product at equilibrium.

Table 5.10 Code of polyurethane with chain-extender at various molar ratio of polyol : MDI : chain-extender

Chain-exreuder	Molar ratio of Polyol : MDI : chain-extender	Code
Ethylene glycol	1:2:1	PUE1
	1:3:2	PUE2
	1:4:3	PUE3
	1:5:4	PUE4
	1:6:5	PUE5
GP(1.5,4,190)	1:2:1	PUG41
	1:3:2	PUG42
	1:4:3	PUG43
	1:5:4	PUG44
	1:6:5	PUG45

Table 5.10 Code of polyurethane with chain-extender at various molar ratio of polyol : MDI : chain-extender (continue)

Chain-extender	Molar ratio of Polyol : MDI : chain-extender	Code
GP(4,8,190)	1:2:1	PUG81
	1:3:2	PUG82
	1:4:3	PUG83
	1:5:4	PUG84
	1:6:5	PUG85
GP(4,8,190) without EG	1:2:1	PUGN81
	1:3:2	PUGN82
	1:4:3	PUGN83
	1:5:4	PUGN84
	1:6:5	PUGN85

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5.4 Polyurethane with chain-extender

5.4.1 Hardness

Tables 5.11 ,5.12 ,5.13 and 5.14 show the hardness of polyurethane with different chain-extenders at the various molar ratios of polyol : MDI : chain-extender. The code of polyurethane were explained in table 5.10. PU means polyurethane, E means from ethylene glycol, G means from glycolyzed product and GN means glycolyzed product without ethylene glycol. Polyurethane consists of two segments; one is the short-chain diols ,along with MDI form the hard segment in polyurethane. The hard segment provides reinforcement and hardness. The other one is the long chain diols and MDI form the soft-segment which acts as the flexible soft-segments.

In this work, polyol was used to form the soft segment with MDI while EG, GP(1.5,4,190), GP(4,8,190) , GP(4,8,190) without EG were used as the chain extenders to form the hard segment in polyurethane.

Table 5.11 The hardness of polyurethane with EG at the various molar ratio, NCO/OH ratio at 1.

Molar ratio Polyol:MDI:EG	% EG (% by weight)	Code	Hardness(Shore A)
1:2:1	2.39	PUE1	16.56
1:3:2	4.22	PUE2	28.56
1:4:3	5.68	PUE3	30.31
1:5:4	6.87	PUE4	32.37
1:6:5	7.85	PUE5	33.87

Table 5.12 The hardness of polyurethane with GP(1.5,4,190) at the various molar ratio,
NCO/OH ratio at 1.

Molar ratio Polyol:MDI:GP(1.5,4,190)	%GP(1.5,4,190) (% by weight)	Code	Hardness(Shore A)
1:2:1	7.24	PUG41	32.00
1:3:2	12.36	PUG42	34.00
1:4:3	16.16	PUG43	34.13
1:5:4	19.08	PUG44	35.88
1:6:5	20.83	PUG45	-

Table 5.13 The hardness of polyurethane with GP(4,8,190) at the various molar ratio,
NCO/OH ratio at 1.

Molar ratio Polyol:MDI:GP(4,8,190)	%GP(4,8,190) (% by weight)	Code	Hardness(Shore A)
1:2:1	2.86	PUG81	22.25
1:3:2	5.04	PUG82	30.87
1:4:3	6.77	PUG83	33.06
1:5:4	8.16	PUG84	34.31
1:6:5	9.32	PUG85	35.43

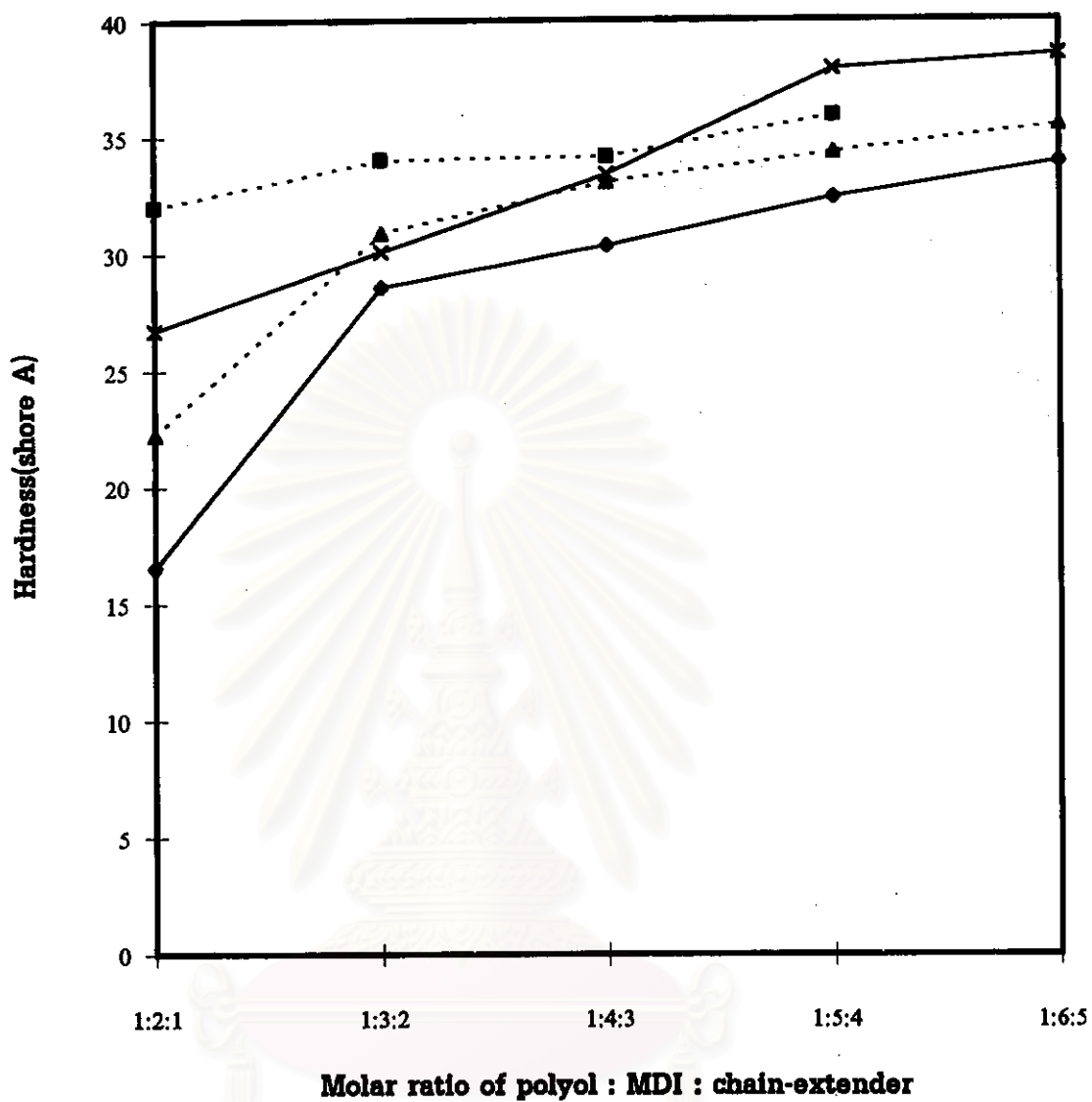


Figure 5.23 The hardness of polyurethane with chain extender at the various molar ratios

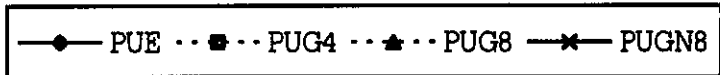


Table 5.14 The hardness of polyurethane with GP(4,8,190) without EG at the various molar ratio, NCO/OH ratio at 1.

Molar ratio Polyol:MDI:GP(4,8,190) without EG	%GP(4,8,190) without EG (% by weight)	Code	Hardness(Shore A)
1:2:1	8.19	PUGN81	24.69
1:3:2	13.88	PUGN82	30.06
1:4:3	18.05	PUGN83	33.38
1:5:4	21.25	PUGN84	37.88
1:6:5	23.77	PUGN85	38.50

From figure 5.23, the hardness of polyurethane increases which increasing the molar ratio of the chain-extender in polyurethane. Comparing the hardness of polyurethane with EG and polyurethane with glycolized product, figure 5.23 shows that the polyurethane with glycolized products have higher hardness value than the polyurethane with EG at the same molar ratio. The length of EG is shorter than the length of glycolized products, the appearance of crystalline segment in polyurethane with EG maybe more than the appearance of crystalline segment in polyurethane with glycolized products. This is because the short molecule forms the crystalline segment easier than the long molecule.

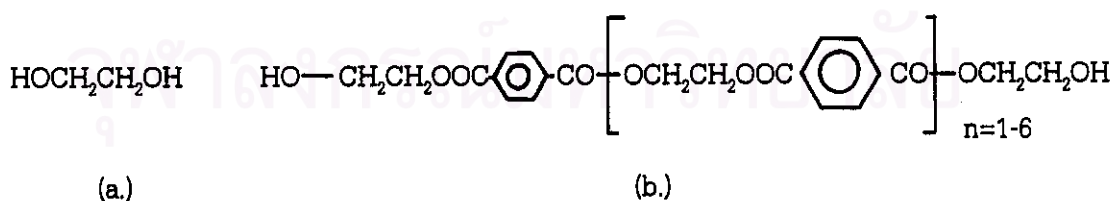


Figure 5.24 The structure formula of EG and oligomers

Polyurethane with EG have lots of hard segments which made the polyurethane to be brittle, so the hardness value of polyurethane with EG was lower than the hardness value of polyurethane with glycolized products.

5.4.2 Tensile properties

Table 5.15 The tensile properties of polyurethane with EG at various molar ratio.

Molar ratio of polyol:MDI:EG	%EG (% by weight)	Code	Tensile properties		
			E.modulus (N./mm. ²)	Max. stress at break (N./mm. ²)	%Elongation at break
1:2:1	2.39	PUE1	1.3094	1.5446	231.2
1:3:2	4.22	PUE2	1.1747	2.7886	241.8
1:4:3	5.68	PUE3	2.7575	3.0078	130.7
1:5:4	6.87	PUE4	8.5372	6.3736	102.2

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Table 5.16 The tensile properties of polyurethane with GP(1.5,4,190) at various molar ratio.

Molar ratio of polyol:MDI:EG	%EG (% by weight)	Code	Tensile properties		
			E.modulus (N./mm. ²)	Max. stress at break (N./mm. ²)	%Elongation at break
1:2:1	7.24	PUG1	1.8190	1.5022	149.4
1:3:2	12.36	PUG2	1.4603	1.7703	178.6
1:4:3	16.16	PUG3	4.3430	4.7770	135.2
1:5:4	19.08	PUG4	18.0700	7.5810	118.0

Table 5.17 The tensile properties of polyurethane with GP(4,8,190) at various molar ratio.

Molar ratio of polyol:MDI:EG	%EG (% by weight)	Code	Tensile properties		
			E.modulus (N./mm. ²)	Max. stress at break (N./mm. ²)	%Elongation at break
1:2:1	2.86	PUG41	3.2116	2.704	155.80
1:3:2	5.04	PUG42	2.6520	2.976	152.80
1:4:3	6.77	PUG43	4.1440	5.296	114.04
1:5:4	8.16	PUG44	14.45	6.765	110.4

Table 5.18 The tensile properties of polyurethane with GP(4,8,190) without EG at various molar ratio.

Molar ratio of polyol:MDI:EG	%EG (% by weight)	Code	Tensile properties		
			E.modulus (N./mm. ²)	Max. stress at break (N./mm. ²)	%Elongation at break
1:2:1	8.19	PUG41	1.0190	1.5485	217.1
1:3:2	13.88	PUG42	1.9590	2.6558	207.4
1:4:3	18.05	PUG43	4.4140	5.9310	183.8
1:5:4	21.25	PUG44	32.910	12.7331	152.4

From table 5.15 and 5.16, figure 5.25 and 5.26, it can be seen that the maximum percent elongation at break have been at the molar ratio of 1:3:2, after that the percent elongation at break decrease when increasing the molar ratios. In contrast, the modulus of elasticity and maximum stress at break increased when increasing the molar ratio of the components.

From table 5.17 and 5.18, figure 5.27 and 5.28 , the percent of elongation at break has been decreased and the modulus of elasticity and the maximum stress at break have been increased. when the molar ratio of the components of polyurethane increases.

The percent elongation at break of polyurethane with four kinds of chain-extendors is compared in figure 5.29 . At molar ratio of 1:2:1 ,1:3:2 , percent elongation at break of PUE > PUGN8 > PUG4 > PUG8 and at molar ratio of 1:4:3 and 1:5:4 , percent elongation at break of PUGN8 > PUG4 > PUG8 > PUE. Increasing the molar ratio of MDI:chain-extender or ratio of MDI and chain-extender decreases percent elongation of polyurethane. This is

because there were lots of hard-segment when increased molar ratio of MDI and chain extender. The hard-segment concern hardness, modulus of elasticity and maximum stress at break of polyurethane, but they were not flexible. Consequently, the flexibility of polyurethane decreases when increasing the ratio of MDI and chain-extender, the flexibility of polyurethane are shown by the percent elongation at break.

At the high molar ratio, the polyurethane with chain-extender containing of EG, i.e., EG, GP(1.5,4,190), GP(4,8,190) gives the low percent of elongation while the polyurethane with GP(4,8,190) without EG gives high percent of elongation.

The comparative modulus of elasticity and maximum stress at break of polyurethane with four kinds of chain-extender is shown in figure 5.30 and 5.31, respectively at the molar ratio less than 1:4:3, the modulus of elasticity and maximum stress at break are not much different, but at the molar ratio 1:5:4, the modulus of elasticity and maximum stress at break are obviously different, PUGN8 > PUG4 > PUG8 > PUE.



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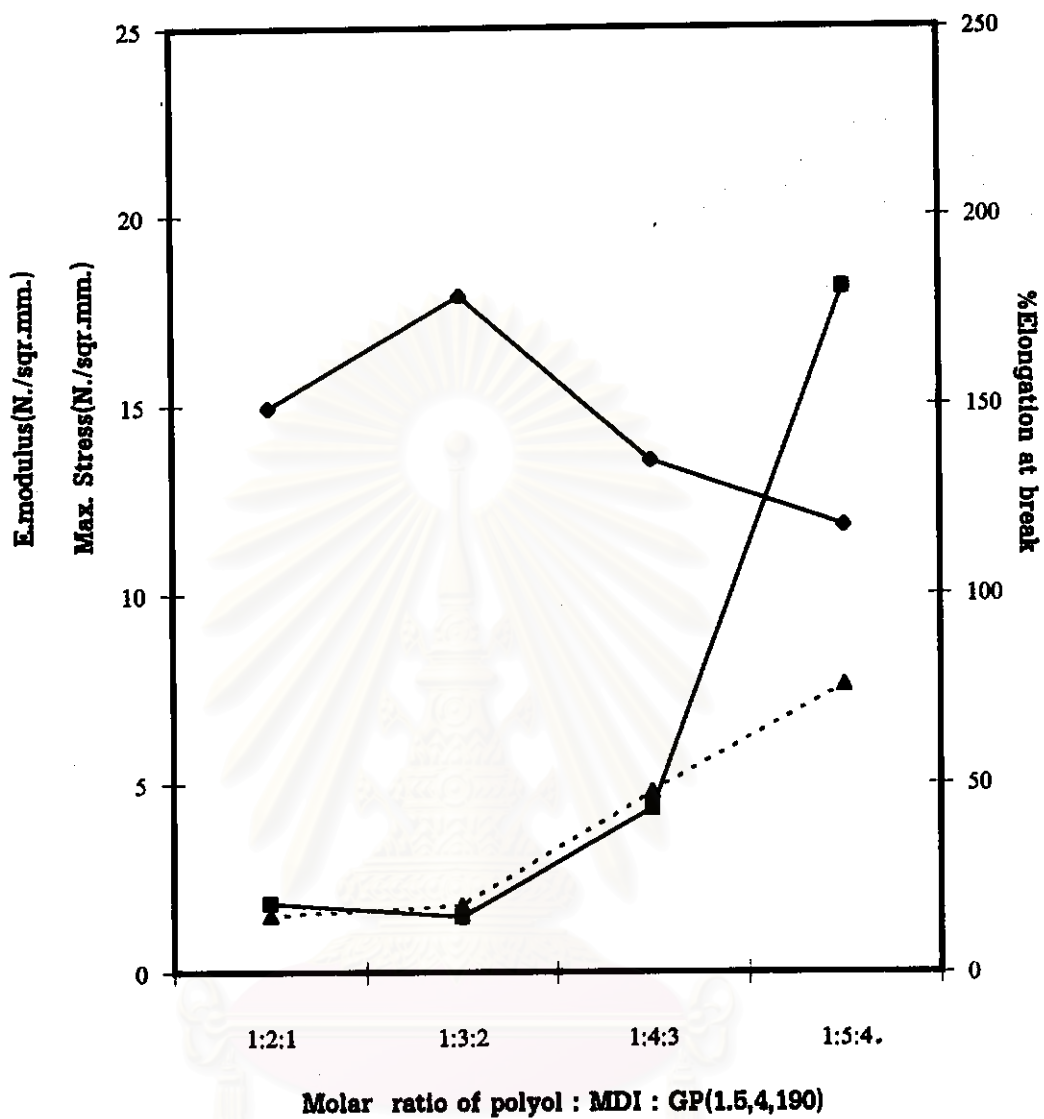
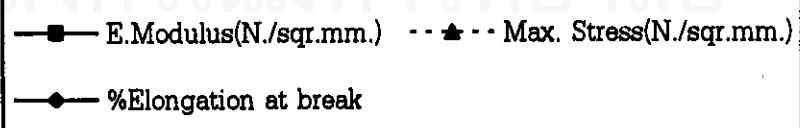


Figure 5.25 The tensile properties of polyurethane with GP(1.5,4,190) at various ratio, NCO/OH at 1.



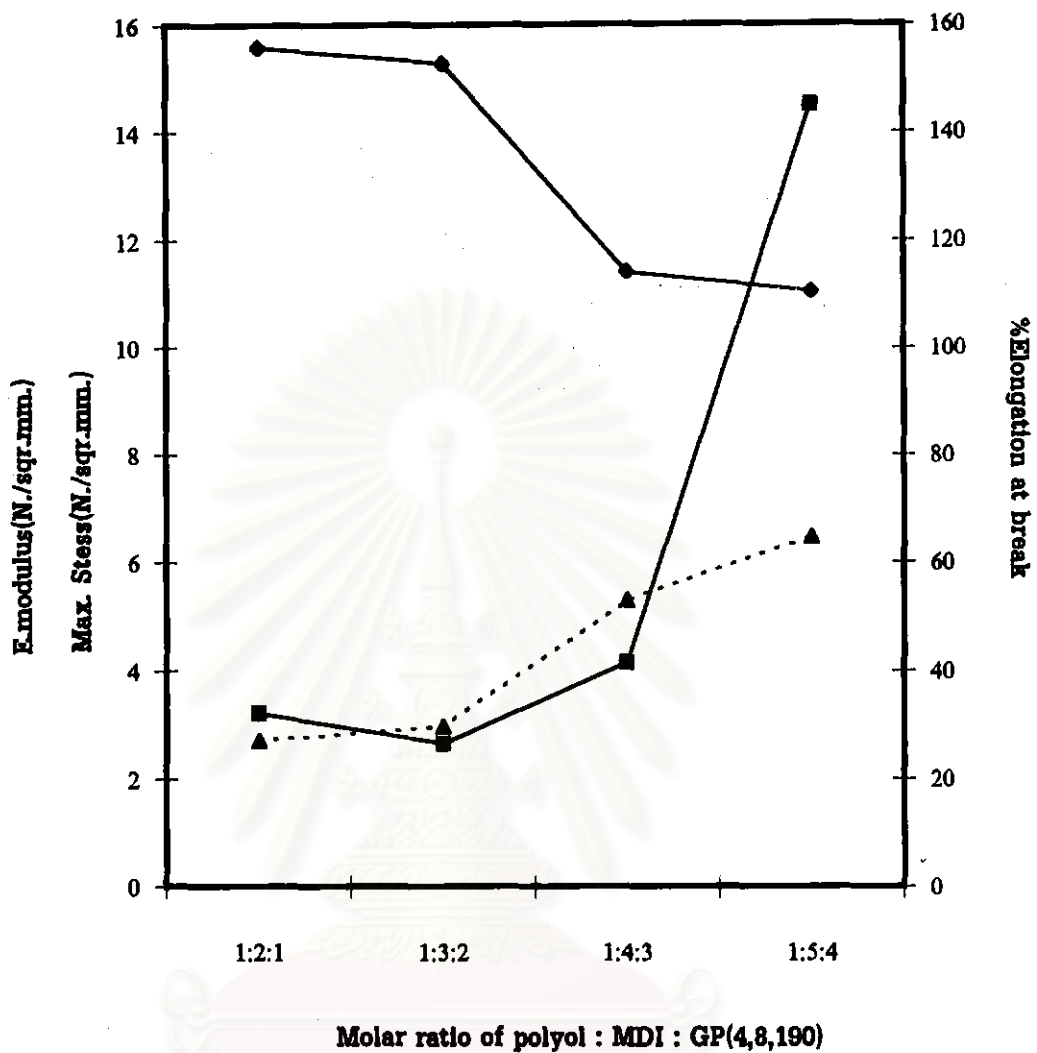
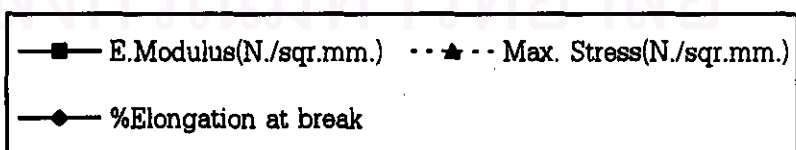
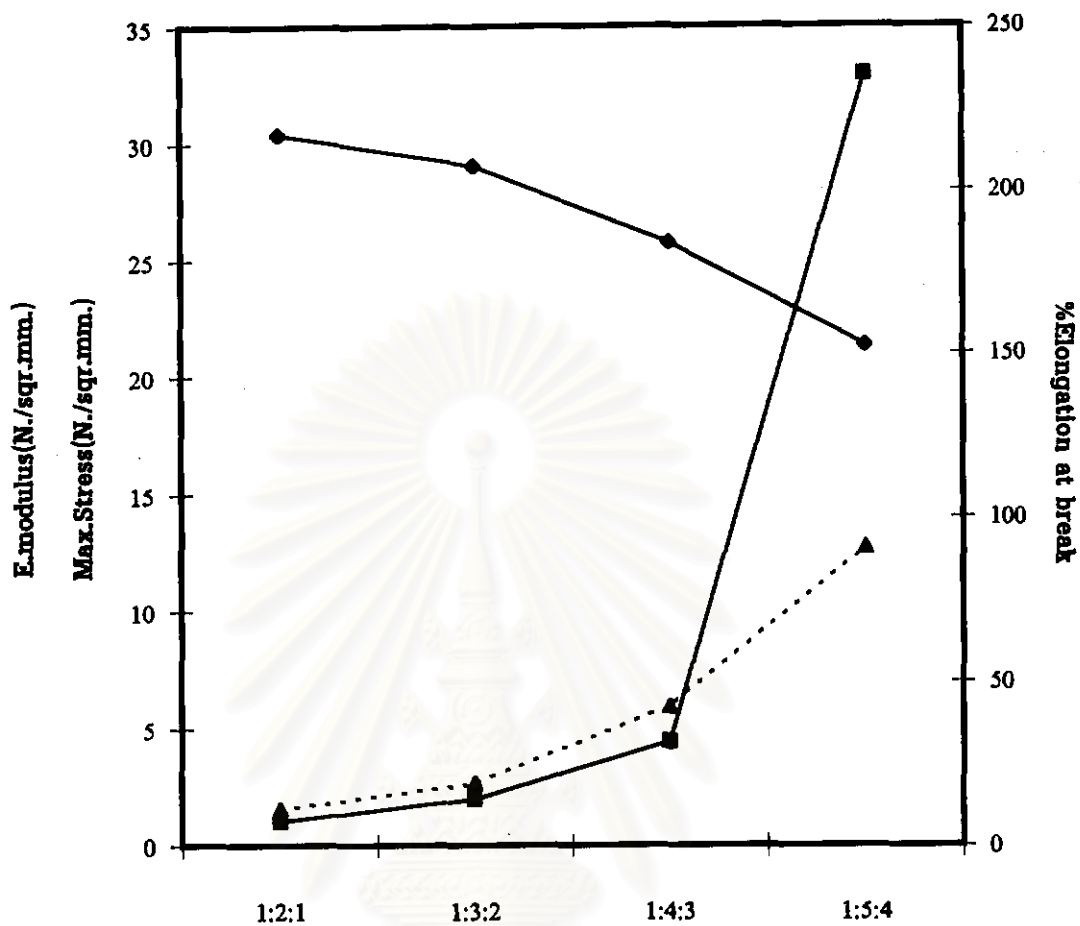


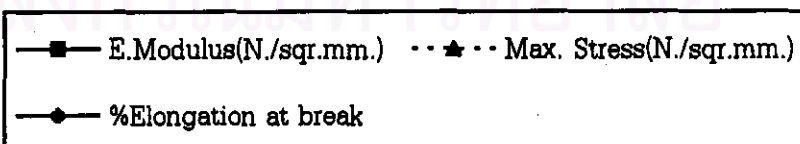
Figure 5.26 The tensile properties of polyurethane with GP(4,8,190) at various molar ratio, NCO/OH at 1.





Molar ratio of polyol : MDI : GP(4,8,190) without EG

Figure 5.27 The tensile properties of polyurethane with GP(4,8,190) without EG at various ratio, NCO/OH at 1.



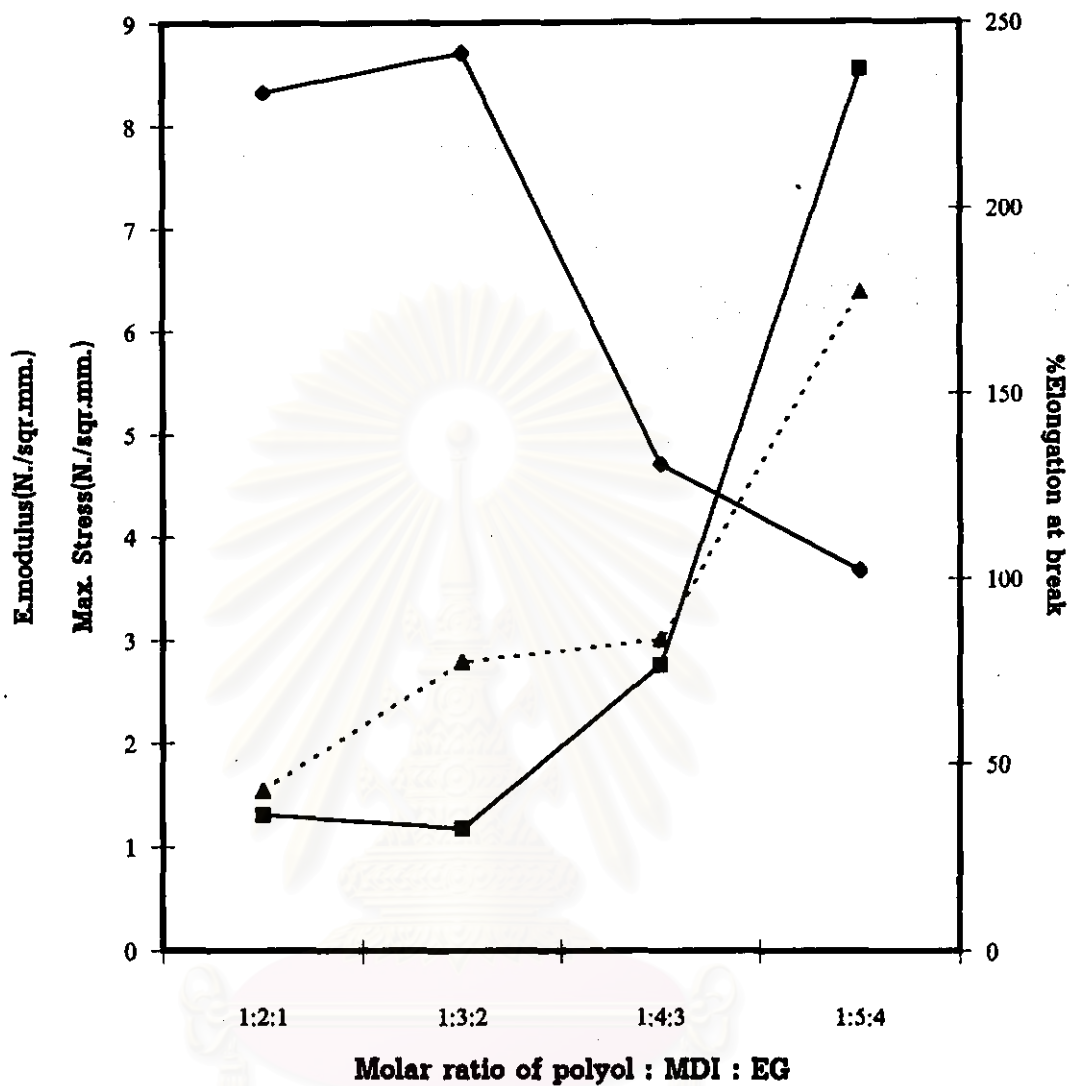
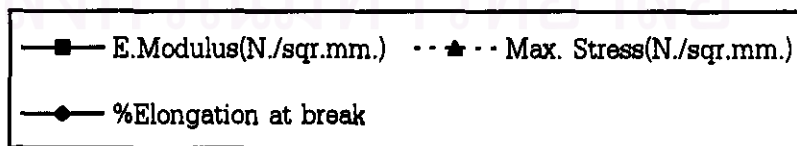


Figure 5.28 The tensile properties of polyurethane with EG at various molar ratio, NCO/OH at 1.



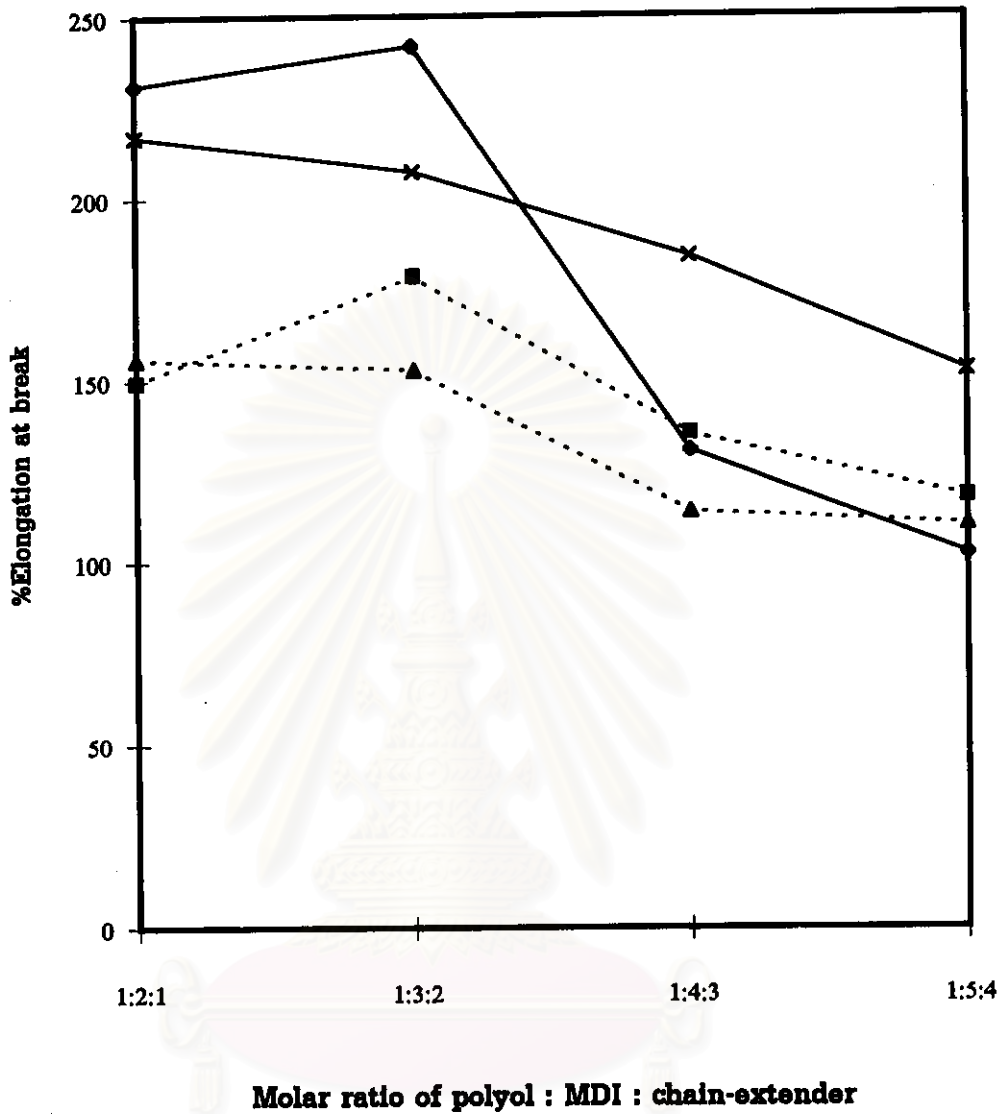
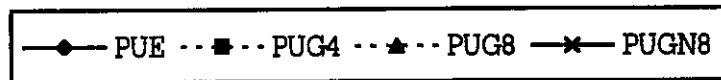


Figure 5.29 %Elongation at break of polyurethane with four types of chain extender



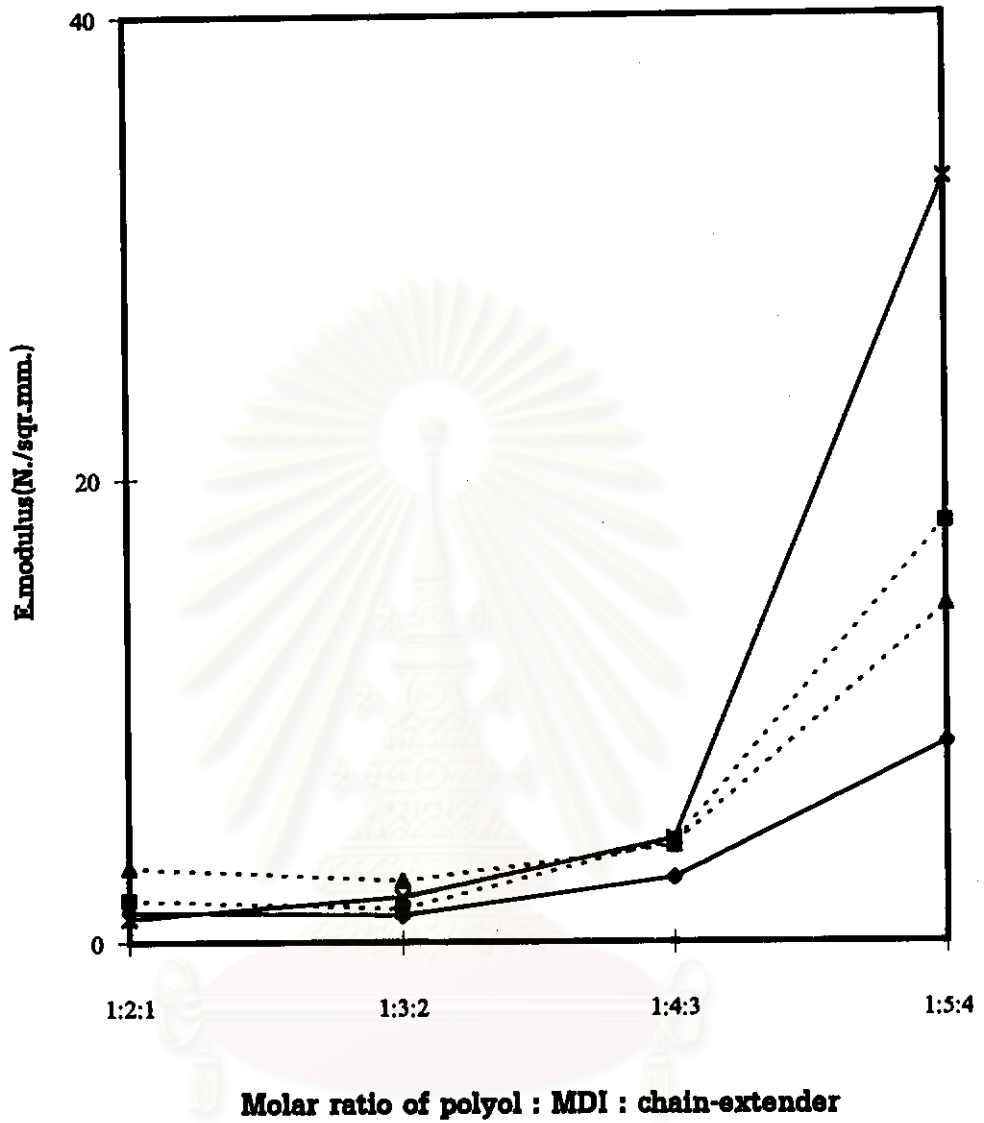
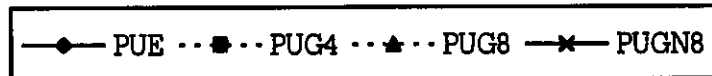


Figure 5.30 Modulus of elasticity of polyurethane with four types of chain-extender



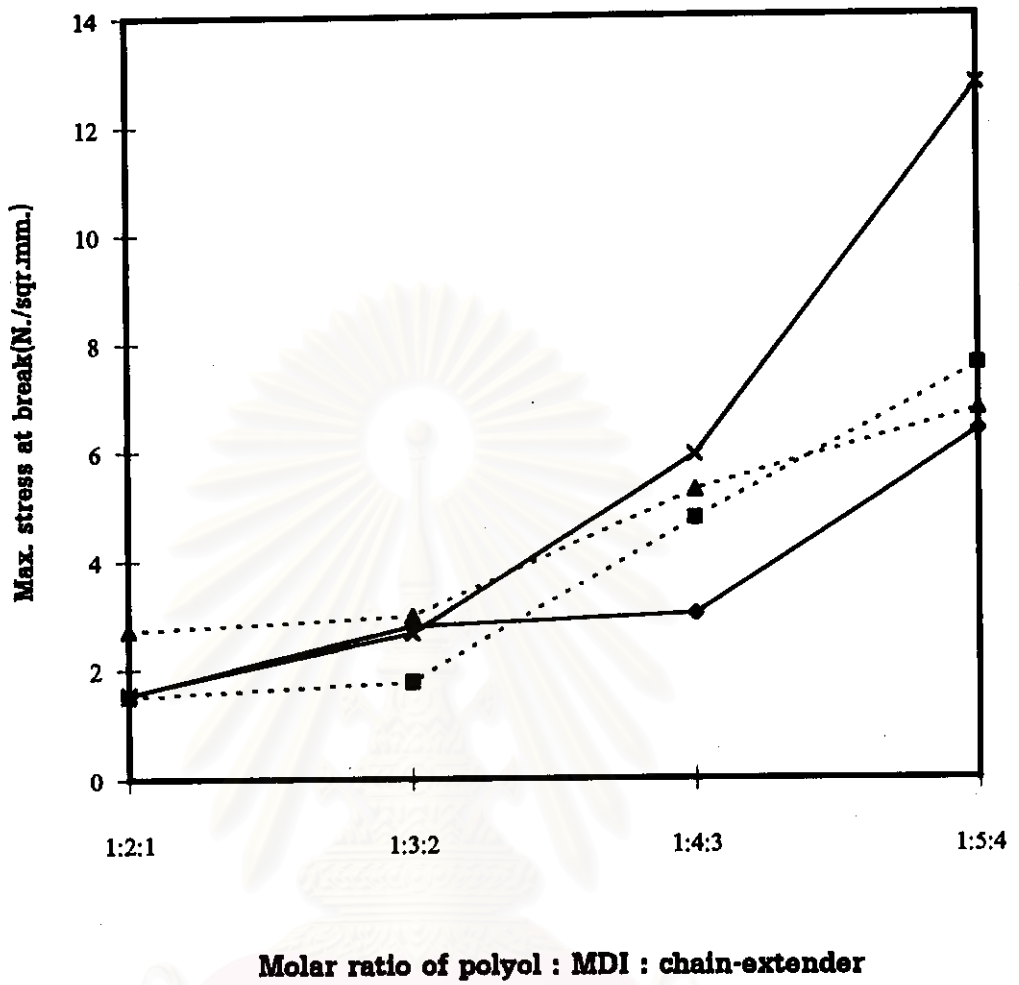


Figure 5.31 Maximum stress at break of polyurethane with four types chain extender

