

## Preparation of PET Using Homogeneous Catalysts. II. Effect of BHPP, NPG and PD in Sb<sub>2</sub>O<sub>3</sub> Glycol Solution Catalysts

Tae Won Son\*, Hae Shik Son, Won Ki Kim, Dong Won Lee, Kwang Il Kim, and Jae Hun Jeong<sup>1</sup>

School of Textiles, Yeungnam University, Kyungsan, Korea

<sup>1</sup>Tongkook Synthetic Fibers Co., Ltd. Kumi. Korea

(Received June 19, 2000 ; Revised August 17, 2000 ; Accepted August 21, 2000)

**Abstract :** In the polycondensation reaction of polyethyleneterephthalate(PET), Sb<sub>2</sub>O<sub>3</sub> can react effectively as a catalyst, if physically transformed. Sb<sub>2</sub>O<sub>3</sub> powder is transformed into liquid solution by dissolving in ethylene glycol(EG). Homogeneous catalyst is made by mixing this liquid solution with glycols having different solubility. The efficient reaction of PET polymerization is expected by using homogeneous catalyst. PET was synthesized using homogeneous catalysts of 4 wt.% Sb<sub>2</sub>O<sub>3</sub> solution dissolved in glycol[EG, 2,2-bis(4-(2-hydroxyethoxy)phenol)propane(BHPP), neopentyl glycol(NPG), and 1,3-propanediol(PD)]. PET using EG-BHPP(Sb<sub>2</sub>O<sub>3</sub>) catalysts shows the highest I.V. within a reaction time of 120 min. In the p-d analysis, PET using EG-BHPP(Sb<sub>2</sub>O<sub>3</sub>) catalysts has the fastest propagation rate and slowest degradation rate. EG-BHPP(Sb<sub>2</sub>O<sub>3</sub>) catalysts are more efficient than EG(Sb<sub>2</sub>O<sub>3</sub>) catalysts and Sb<sub>2</sub>O<sub>3</sub> powder catalysts.

### Introduction

Sb<sub>2</sub>O<sub>3</sub> catalyst is usually used in PET polymerization but it has some problems in the process. Sb<sub>2</sub>O<sub>3</sub> doesn't dissolve at the reaction temperature because it has a high melting point( $T_m$ ) of 665°C as a white powder. And it has limited solubility in ethylene glycol(EG). Therefore, it is a difficult reagent to handle and remains as a residue after the reaction. In the PET polymerization, various catalysts are usually added which include not only Sb<sub>2</sub>O<sub>3</sub> powder or Sb<sub>2</sub>O<sub>3</sub> dissolved in EG, but metallic catalysts filled with Ge, Sn, Mg, Zn and Ti except Sb[1-5]. The catalytic compounds of Ti or Sn type have prominent activity of catalyst, but replacing Sb<sub>2</sub>O<sub>3</sub> with other catalysts has not occurred because the products have several defects in their properties. As a different approach, some researchers have conducted studies to improve the activity of catalyst by varying its state to act in the molecular dimension. Son *et al.* studied the use of liquid-phase catalysts in the PET polymerization[6,7].

In this study, an efficient polymerization method was studied by using homogeneous catalysts created by dissolving BHPP, PD, NPG in 4 wt %. Sb<sub>2</sub>O<sub>3</sub> ethylene glycol solution in order to improve reactivity of reaction materials.

### Experimental

#### Materials and Reagents

BHET oligomer with an inherent viscosity(I.V.) of 0.103 dl/g and carboxyl end group of 292 eq./10<sup>6</sup> g was

used after drying. The EG was treated by a drying process at 70°C to eliminate moisture before use. Sb<sub>2</sub>O<sub>3</sub> powder with average particular size 12.73  $\mu$ m was used without purification in this study. BHPP was supplied by Takemoto Oil & Fat Co. without any treatment. NPG and PD were supplied by Aldrich Chem. Co..

#### Polycondensation Reaction

Polymerization was carried out as follows. Finely ground BHET oligomer was placed in polymerization bath and heated to 260°C to dissolve the reaction materials. A catalyst of 400 ppm was added and then polymerization bath was made to a vacuum of 20 torr with mechanical stirring. And then, the mixture was heated to 280°C, the melting point, and kept in vacuum of less than 2 torr, varying the reaction time of 30, 60, 90, 120, 150 and 180 min..

#### Inherent Viscosity(I.V.)

The I.V. was measured with 60/40 phenol/1,1,2,2-tetrachloroethane at 30°C using Cannon-Ubbelohde dilution viscometers. I.V. was calculated only for the 0.5% concentration using the Solomon-Ciuta equation[8]. The number average molecular weight( $M_n$ ) was calculated by intrinsic viscosity( $[\eta]$ ) using the Berkowitz equation[9] ;

$$[\eta] = [2(\eta_{sp} - \ln \eta_{rel})]^{0.5}/C$$
$$M_n = 3.29 \times 10^4 [\eta]^{1.54}$$

#### Carboxyl end group determination

The carboxyl end group content was determined for the PET samples that were dried at 105°C for 2 hours, dissolved in boiling benzyl alcohol(0.2 g/5 ml) at 215°C(110 sec.), quenched to 135°C, and then diluted with 10 ml of

\*To whom correspondence should be addressed:  
twson@yu.ac.kr

chloroform. The PET samples were titrated by microburette(100  $\mu$ l) with 0.1 N NaOH benzyl alcohol solution with 2-3 drops of phenol red(0.1% benzyl alcohol solution) as an indicator[10].

$\text{COOH eq./}10^6 \text{ g} = [(\text{net } \mu\text{l of NaOH benzyl alcohol})(\text{N of NaOH benzyl alcohol}) \times f] / \text{wt. PET(g)}$

Where, net  $\mu$ l NaOH benzyl alcohol for titration is the total titer value for the sample titration minus blank titer value. And  $f$  is 0.1 N NaOH benzyl alcohol factor.

### Thermal Analysis

Thermal analysis of PET samples was performed to analyze the thermal factors such as  $T_g$ ,  $T_c$  and  $T_m$  in the range of 20°C and 300°C at the heating and cooling rate of 10°C/min., using differential scanning calorimeter (DSC 2010, TA Instruments).

### NMR measurements

$^1\text{H-NMR}$  spectrum was performed by 301.13 MHz ARS-300 Bruker NMR Instruments in deuterated chloroform ( $\text{CDCl}_3$ ) and trifluoroacetic acid(TFA)(10%) at 27°C[11].

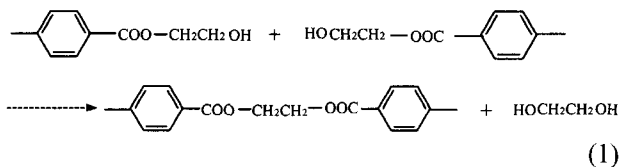
### GPC measurements

GPC analysis of each PET sample was carried out by GPC equipments that was furnished 150R viscometer and external RI(Waters HT 3,4,5 column ; Viscotek Model 250 Conc. Det.). PET samples were dissolved in chloroform( $\text{CHCl}_3$ ) and hexafluoroisopropanol(HFIP). GPC-grade *m*-cresol was used as a mobile phase at 100°C[12].

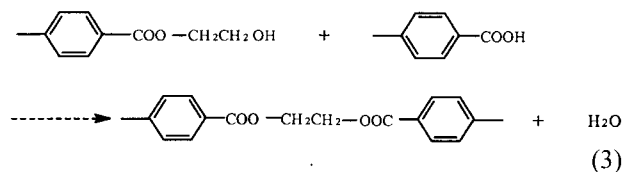
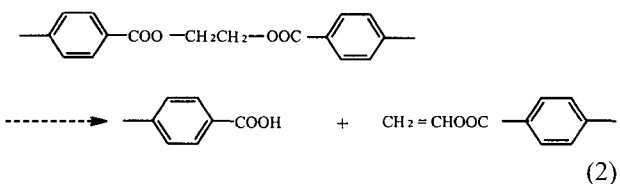
## Results and Discussion

### Effects of Homogeneous Catalysts

Generally, in the initial stage of PET polymerization, thermal degradation occurs negligibly, the degree of polymerization appears to increase linearly, and EG forms as a by-product.



But, thermal degradation begins when the reaction reaches equilibrium, and the degree of polymerization appears to be reducing in contrast to the initial reaction[13].



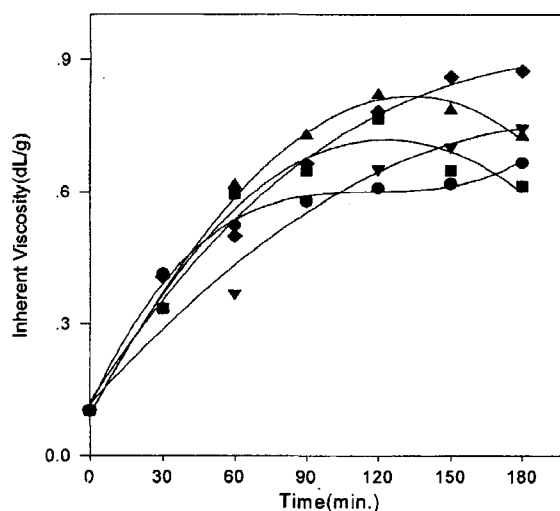
The reaction(3) occurs as a result of reaction(2). We can conclude that water formation and thermal degradation occurs at the same point of time. In the case of polycondensation process of BHET oligomer, the reaction rate depends significantly on the reaction conditions, including composition and catalysts.

Evolutions of I.V. with reaction time are shown in Figure 1. In general, all the samples showed a decreasing tendency because of the effects of thermal degradation at the reaction time of ca. 120 min.. PET using EG-BHPP ( $\text{Sb}_2\text{O}_3$  4%) catalyst showed the fastest reaction rate and high degree of polymerization in the initial reaction. Evidence to support this is seen in Table 3. This suggests that a catalyst reacted quickly with ester group of BHET oligomer to yield high degree of polymerization.

### Application of p-d analysis

Normally, reaction kinetics could be predicted by the analysis of reactive composition at different times during the polymerization in the PET condensation reaction. The polymerized PET sample had different numbers of mole ( $n$ ) by the polycondensation reaction as well as the degradation reaction.

The polycondensation reaction of PET is classified into the propagation reaction rate( $p$ ) according to the



**Figure 1.** Plot of the inherent viscosity(I.V.) vs. reaction time. ● : PET 1( $\text{Sb}_2\text{O}_3$  powder catalyst), ■ : PET 2(EG( $\text{Sb}_2\text{O}_3$  4%) catalyst), ▲ : PET 3(EG-BHPP( $\text{Sb}_2\text{O}_3$  4%) catalyst), ▼ : PET 4(EG-NPG( $\text{Sb}_2\text{O}_3$  4%) catalyst), ◆ : PET 5(EG-PD( $\text{Sb}_2\text{O}_3$  4%) catalyst).

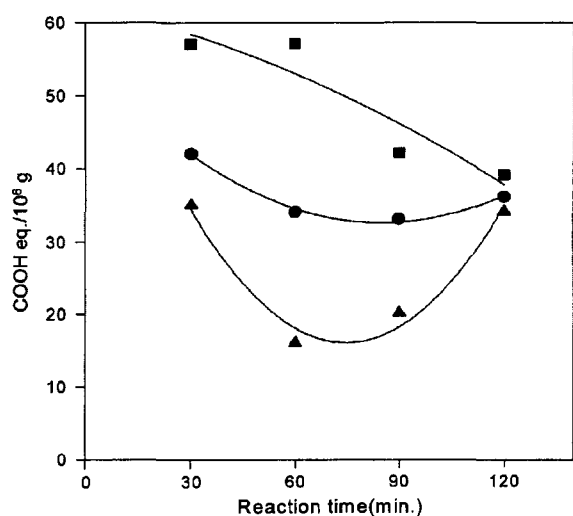
increased degree of polymerization in the reaction(1) and the degradation reaction rate( $d$ ) according to the formation of vinyl ester end group and carboxylic acid in the reaction(2). The  $n$  value for  $p$  and  $d$  is calculated by the equation (4).

$$n = 1/(1 + pt) + dt \quad (4)$$

Where,  $n$  is the number of mole,  $p$  is propagation reaction rate,  $d$  is degradation reaction rate, and  $t$  is reaction time. The  $n$  value was obtained through the molecular

**Table 1.** Values of the propagation rate( $p$ ) and degradation rate ( $d$ ) of polycondensation of PET using homogeneous catalysts

PETNO.	Catalyst system	$p$ (mol · h)	$d$ ( $\times 10^{-3}$ mol/h)
1	Sb <sub>2</sub> O <sub>3</sub> powder	23.32	5.2
2	EG(Sb <sub>2</sub> O <sub>3</sub> 4%)	29.91	5.3
3	EG-BHPP(Sb <sub>2</sub> O <sub>3</sub> 4%)	35.12	3.6
4	EG-NPG(Sb <sub>2</sub> O <sub>3</sub> 4%)	24.25	5.2
5	EG-PD(Sb <sub>2</sub> O <sub>3</sub> 4%)	32.63	3.8



**Figure 2.** Carboxyl group content of PET using different catalysts with reaction time.

● : PET 1(Sb<sub>2</sub>O<sub>3</sub> powder catalyst), ■ : PET 2(EG(Sb<sub>2</sub>O<sub>3</sub> 4%) catalyst), ▲ : PET 3(EG-BHPP(Sb<sub>2</sub>O<sub>3</sub> 4%) catalyst).

weight of the formed polymer against the structure unit of PET. Accordingly,  $n$  at arbitrary  $t$  may be calculated from the equation[14,15].

$$n = 192/(\text{molecular weight of formed polymer}) \quad (5)$$

The values of  $p$  and  $d$  for  $n$  value are summarized in Table 1. A high degree of polymerization can be obtained using EG-BHPP(Sb<sub>2</sub>O<sub>3</sub> 4%) catalyst in a short time, but  $d$  value is lower than using EG-NPG(Sb<sub>2</sub>O<sub>3</sub> 4%) and EG-PD(Sb<sub>2</sub>O<sub>3</sub> 4%) catalysts. The  $d$  value when using EG-BHPP(Sb<sub>2</sub>O<sub>3</sub> 4%) was the lowest among the polymerized PET at  $3.6 \times 10^{-3}$  mol/h.

The content of carboxyl group was plotted versus the reaction time using different catalysts in Figure 2. Carboxyl end group content of PET polycondensation using EG-BHPP(Sb<sub>2</sub>O<sub>3</sub> 4%) catalyst represented 16 eq./10<sup>6</sup> g at 60 min, and after that it slowly increased. It is likely that the degree of polymerization of PET using EG-BHPP(Sb<sub>2</sub>O<sub>3</sub> 4%) catalyst has the fastest reaction rate at around 60 min. and rarely has side reaction, indicating, the degree of reaction was superior.

### Solubility Parameter

The solubility parameter was calculated by using the Hoftyzer and Krevelen equation[16]. The solubility parameter components may be predicted from the group contributions, using the following equations;

$$\delta_d = \sum F_{di}/V \quad \delta_p = \sqrt{\sum F_{di}^2}/V \quad \delta_h = \sqrt{\sum E_{hi}/V}$$

$$\delta = \sqrt{(\delta_d^2 + \delta_p^2 + \delta_h^2)}$$

where,  $V$  is molar volume( $\text{cm}^3/\text{mol}$ ),  $\delta_d$  is dispersion forces component,  $\delta_p$  is polar component,  $\delta_h$  is hydrogen bonding component, and  $\delta$  is solubility parameter( $\text{J}^{1/2}/\text{cm}^{3/2}$ ).

The values of solubility parameter of both PET and BHET oligomer(DP=5.17) were calculated, to be 22.69  $\text{J}^{1/2}/\text{cm}^{3/2}$  and 23.8  $\text{J}^{1/2}/\text{cm}^{3/2}$ , respectively. In terms of the structure of glycol, the values of solubility parameter increased in the order of BHPP < NPG < PD < EG(see Table), and it was noted that the solubility parameter of check BHET oligomer was very similar to that of BHPP.

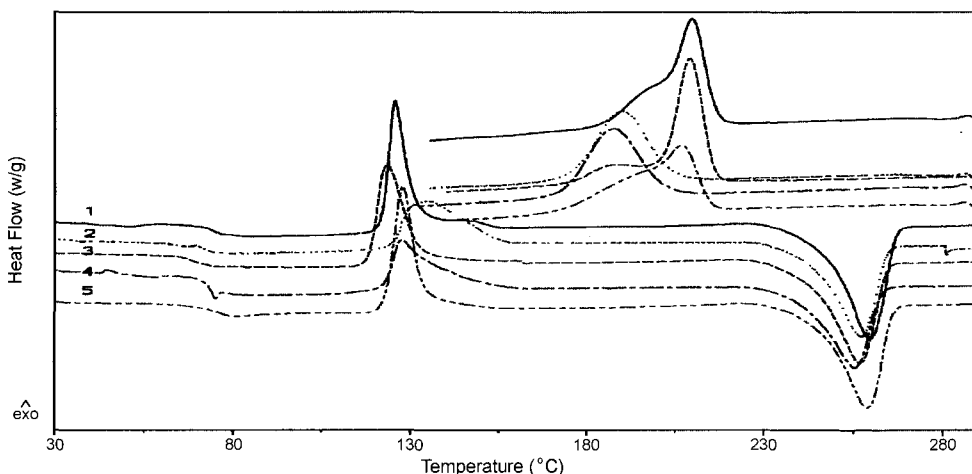
**Table 2.** Solubility parameters of different glycols and PET polymerizaion

Glycols	$V^a$	$\delta_d$	$\delta_p$	$\delta_h$	$\delta^b$	Catalyst system <sup>c</sup>	Reaction time(min.) <sup>d</sup>	$p$ (/mol · h)	$d$ ( $\times 10^{-3}$ mol/h)
EG	55.70	17.23	17.95	26.79	36.50	EG(Sb <sub>2</sub> O <sub>3</sub> 4%)	89	29.91	5.3
BHPP	301.8	16.6	4.30	12.34	21.12	EG-BHPP(Sb <sub>2</sub> O <sub>3</sub> 4%)	83	35.12	3.6
NPG	97.70	17.70	10.23	20.23	28.76	EG-NPG(Sb <sub>2</sub> O <sub>3</sub> 4%)	120	24.25	5.2
PD	72.26	17.02	13.83	23.52	32.16	EG-PD(Sb <sub>2</sub> O <sub>3</sub> 4%)	89	32.63	3.8

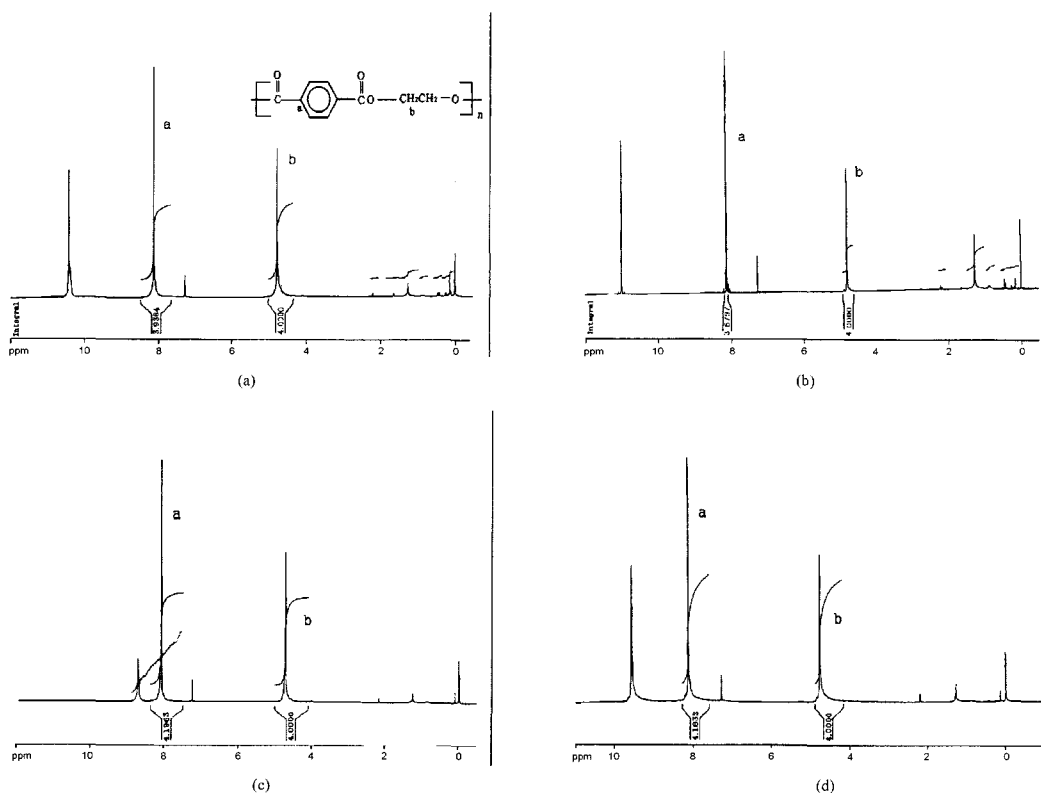
a : $V$ (molar volume) ( $\text{cm}^3/\text{mol}$ ), b : $\delta$ (solubility parameter ( $\text{J}^{1/2}/\text{cm}^{3/2}$ )), c :Catalyst content of 400 ppm, d :Reaction time to obtain I.V. of 0.65 dl/g.

PET using BHPP which has the fastest propagation rate requires the least reaction time of 83 min. in order to get I.V. of 0.65 dl/g. It is also in accord with the result of the

p-d analysis in which PET using EG-BHPP( $Sb_2O_3$ ) catalyst has the fastest propagation rate and slowest degradation rate. It might be considered that the similarity of



**Figure 3.** DSC thermograms of PET samples from different liquid-phase catalysts.  
 1) PET 1( $Sb_2O_3$  4%) catalyst at 150 min (I.V. : 0.619 dl/g), 2) PET 2(EG( $Sb_2O_3$  4%) catalyst at 90 min (I.V. : 0.647 dl/g), 3) PET 3(EG-BHPP( $Sb_2O_3$  4%) catalyst at 60 min (I.V. : 0.615 dl/g), 4) PET 4(EG-NPG( $Sb_2O_3$  4%) catalyst at 120 min (I.V. : 0.652 dl/g), 5) PET 5(EG-PD( $Sb_2O_3$  4%) catalyst at 90 min (I.V. : 0.664 dl/g).



**Figure 4.**  $^1H$ -NMR spectrum of PET sample.  
 a) PET( $Sb_2O_3$  powder catalyst), b) PET(EG-BHPP( $Sb_2O_3$  4%) catalyst), c) PET(EG-NPG( $Sb_2O_3$  4%) catalyst), d) PET(EG-PD( $Sb_2O_3$  4%) catalyst).

**Table 3.** The molecular weight distribution from polycondensation reaction of PET sample

PET NO.	Catalyst system	Reaction time (min.)	I.V. (dl/g)	$M_n$	$M_v$	$M_w$	$M_z$	Polydispersity ( $M_w/M_n$ )
1	Sb <sub>2</sub> O <sub>3</sub> powder	150	0.619	18,500	29,300	32,100	47,300	1.735
2	EG(Sb <sub>2</sub> O <sub>3</sub> 4%)	90	0.647	25,000	37,700	44,900	68,800	1.796
3	EG-BHPP(Sb <sub>2</sub> O <sub>3</sub> 4%)	90	0.729	23,300	37,600	40,800	62,200	1.751
4	EG-NPG(Sb <sub>2</sub> O <sub>3</sub> 4%)	120	0.652	24,000	36,300	38,200	55,300	1.633
5	EG-PD(Sb <sub>2</sub> O <sub>3</sub> 4%)	90	0.664	18,200	27,400	31,600	47,200	1.736

solubility parameter between BHET oligomer and BHPP dissolved catalyst facilitates easy dispersion in solution.

### Thermal properties

Figure 3 is the DSC diagram of PET sample using different homogeneous catalysts. The  $T_m$  of PET samples using EG-BHPP(Sb<sub>2</sub>O<sub>3</sub> 4%) and EG-NPG(Sb<sub>2</sub>O<sub>3</sub> 4%) catalysts were 255°C and 254°C respectively. However  $T_m$  of PET using Sb<sub>2</sub>O<sub>3</sub> powder, EG(Sb<sub>2</sub>O<sub>3</sub> 4%) and EG-PD(Sb<sub>2</sub>O<sub>3</sub> 4%) catalysts were similar values of 257-259°C.

$T_m$  of regular PET chip is 257°C. PET using EG-BHPP (Sb<sub>2</sub>O<sub>3</sub> 4%) and EG-NPG(Sb<sub>2</sub>O<sub>3</sub> 4%) catalysts had a lower  $T_m$  by about 2-3°C, and the rest were similar in  $T_m$ [17]. It seems reasonable to conclude that the different homogeneous solution catalysts do not affect the thermal properties.

### NMR analysis

The <sup>1</sup>H-NMR spectra of the PET are shown in Figure 4. For chemical shift of PET using Sb<sub>2</sub>O<sub>3</sub> powder catalyst, aromatic ring (=CH-) signals are found at 8.11 ppm, and aliphatic group(-CH<sub>2</sub>-) at 4.78 ppm. For PET using EG-BHPP(Sb<sub>2</sub>O<sub>3</sub> 4%) catalyst, aromatic ring (=CH-) signals are found at 8.12 ppm, and aliphatic group(-CH<sub>2</sub>-) at 4.78 ppm. For PET using EG-NPG(Sb<sub>2</sub>O<sub>3</sub> 4%) catalyst, aromatic ring (=CH-) signals are found at 8.07 ppm, and aliphatic group(-CH<sub>2</sub>-) at 4.71 ppm. For PET using EG-PD(Sb<sub>2</sub>O<sub>3</sub> 4%) catalyst, aromatic ring (=CH-) signals are found at 8.10 ppm, and aliphatic group(-CH<sub>2</sub>-) at 4.84 ppm. The integral of aromatic group (=CH-) was shown as 3.93, 3.67, 4.19 and 4.18 ppm compared to the standard value 4.00 of aliphatic group(-CH<sub>2</sub>-). Given these results, it was found that the ratio of =CH- : -CH<sub>2</sub>- of each PET sample using Sb<sub>2</sub>O<sub>3</sub> powder, EG-NPG (Sb<sub>2</sub>O<sub>3</sub> 4%) and EG-PP(Sb<sub>2</sub>O<sub>3</sub> 4%) was a proportion of nearly 1:1, but PET sample using EG-BHPP(Sb<sub>2</sub>O<sub>3</sub> 4%) catalyst showed a ratio of 1:1.109. This is most likely due to the presence of ethylene glycol units of BHPP. The spectra of the PET using different catalysts are found to be identical.

### Molecular Weight and Molecular Weight Distribution

The molecular weight of the samples were estimated by

GPC and summarized in Table 3. The number average molecular weight( $M_n$ ) are in the range of 18,200~25,000. We obtained the higher molecular weight when using Sb<sub>2</sub>O<sub>3</sub> liquid catalysts. BHPP used catalyst gives rise to yield the highest I.V. and higher molecular weight, as expected by p-d analysis. On the whole, all the samples have the similar MWD. MWD was found to be in the narrow range of 1.633~1.796, suggesting that the polymerization method is effective. PET sample using EG-NPG (Sb<sub>2</sub>O<sub>3</sub> 4%) catalyst had the lowest polydispersity( $M_w/M_n$ ) as 1.633. These results suggest that the PET polymeric chains were produced by the combination of the molecules of relatively uniform molecular weights.

### Conclusion

In PET polymerization, it was found that PET using EG-BHPP(Sb<sub>2</sub>O<sub>3</sub> 4%) catalyst among homogeneous catalysts exhibited a high degree of polymerization within a short reaction time and highest I.V.. The PET samples using EG-BHPP(Sb<sub>2</sub>O<sub>3</sub> 4%) has the fastest propagation rate and slowest degradation rate. In the carboxyl end group determination, the reaction rate of the PET sample using EG-BHPP(Sb<sub>2</sub>O<sub>3</sub> 4%) catalyst made rapid progress at 60 min., suggesting that products which exist in a stabilized state have the least side reaction during the polymerization. Different homogeneous catalysts don't affect the thermal properties and chemical structure. It can be concluded that EG-BHPP(Sb<sub>2</sub>O<sub>3</sub> 4%) catalyst is more efficient than EG(Sb<sub>2</sub>O<sub>3</sub> 4%) catalyst and Sb<sub>2</sub>O<sub>3</sub> powder catalyst.

### Acknowledgement

The authors wish to acknowledge the financial support for the study titled characterization and application of functional polyester copolymers in the Program Year 1998 from the Korea Research Foundation.

### References

1. T. W. Son, H. S. Son, W. K. Kim, K. I. Kim, and D. H. Chun, *Korea Polymer Journal*, 7, 156 (1999).
2. C. Y. Kim and H. N. Cho, *Polymer Science and Tech-*

- nology(Korea)*, **3**, 77 (1992).
3. L. S. Park and J. H. Yoon, *Polymer(Korea)*, **18**, 693 (1994).
  4. H. F. Mark, D. F. Othmer, C. G. Overberger, and G. T. Seaborg, "Encyclopedia of Chemical Technology", 3th ed., P 96, *John Wiley & Sons, Inc.*, (1978).
  5. S. S. Park, S. S. Im, and D. K. Kim, *Polymer(Korea)*, **17**, 324 (1993).
  6. H. S. Son, S. K. Lim, K. H. Park, T. W. Son, and W. S. Yoon, *Polymer(Korea)*, **22**, 23 (1998).
  7. H. S. Son, S. K. Lim, T. W. Son, K. Koo, and Y. Lim, *Polymer(Korea)*, **22**, 352 (1998).
  8. O. F. Solomon and I. Z. Ciuta, *J. Appl. Polym. Sci.*, **6**, 683 (1962).
  9. S. A. Berkowitz, *J. Appl. Polym. Sci.*, **29**, 4353 (1984).
  10. H. A. Phol, *Anal. Chem.*, **26**, 1614 (1954).
  11. S. Spera and R. Po, *Polymer*, **37**, 730 (1996).
  12. W. S. Ha, S. K. Oh, and J. H. Youg, *J. Korean Fiber Sci.*, **27**, 66 (1990).
  13. H. Zimmerman and E. Lebnitz, *faserforsch Textiltech-nik*, **16**, 282 (1965).
  14. K. Tomita, *Polymer*, **14**, 50 (1973).
  15. S. S. Park, S. S. Im, D. K. Kim, and J. R. Huh, *Polymer (Korea)*, **17**, 588 (1993).
  16. D. W. Van Krevelen, "Properties of Polymers", 3rd ed., p. 212, Elsevier Sci. Publishing Company Inc., 1990.
  17. B. G. Min, S. C. Lee, K. H. Yoon, and T. W. Son, *J. Korean Fiber Soc.*, **34**, 668 (1997).