

# Chain Extenders for Polyesters. VI. Properties of the Polyesters Chain-Extended by 2,2'-Bis(4H-3,1-Benzoxazin-4-one)

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## Synopsis

Some properties of polymers derived by treating poly(ethylene terephthalate) (PET) with such hydroxyl-addition-type chain extenders as 2,2'-bis(4H-3,1-benzoxazin-4-one) (BNZ) were investigated. Compared with ordinary PET, the chain-extended PET has a slightly lower melting point and nearly equal molecular size distribution, which indicate that BNZ reacts to form linear chain-extended polymers without branching. Oxalyl bis(anthranilate) unit copolymerized in the polyester chain showed little influence on thermal and hydrolytic stabilities. In addition, benzoxazinone groups remaining unreacted can act as a heat stabilizer to prevent the decrease in the molecular weight by the chain-extending reaction in the solid phase. But they showed adverse effect on the hydrolytic stability by promoting hydrolysis of the polymer as much as the carboxyl groups.

## INTRODUCTION

Seeking a practically applicable method to produce the high-molecular-weight polyesters which can give fibers, films, or plastics having high tenacity or toughness, we have been investigating the "addition-type chain extenders," which are reactive with the polymer terminal groups by addition reaction to couple the polymer chains.

As reported in previous paper,<sup>1,2</sup> we found that some bis(cyclic-iminoesters) were effective as hydroxyl-reactive addition-type chain extenders. Especially 2,2'-bis(4H-3,1-benzoxazin-4-one) (BNZ) was so highly effective as to give PET having intrinsic viscosity ( $[\eta]$ ) of above 1.0 within a few minutes of heating under atmospheric nitrogen starting from an usual PET.

To evaluate the practical applicability of this chain extender, we have to investigate the influence of the BNZ units copolymerized in the polymer chain or remaining unreacted in the polymer phase on physical and chemical properties of the chain-extended polyesters.

In the present paper, we would like to report the results from such investigation.

## EXPERIMENTAL

### Materials

BNZ was prepared as previously reported by the reaction of oxalyl chloride and isoic anhydride in pyridine<sup>3</sup> followed by recrystallization from nitrobenzene.

PET having various  $[\eta]$  and carboxyl content (CV) were prepared by changing reaction conditions such as a temperature and a pressure under the typical polycondensation method from bis( $\beta$ -hydroxyethyl terephthalate) using  $\text{Sb}_2\text{O}_3$  (0.03 mol %) as a catalyst.

PET copolymerized with oxalyl bis(anthranilite) (model co-PET) was prepared as PET described above from bis( $\beta$ -hydroxyethyl terephthalate) and a prescribed amount of BNZ.

The chain-extending reaction was carried out as follows. To the molten polymer prepared as above, a prescribed amount of BNZ was added at 280°C under a nitrogen flow and stirred for 5 min.

All of the polymers were pulverized to about 10–20 mesh and provided for analysis.

### Analytical Procedure

$[\eta]$  was measured in *o*-chlorophenol at 35°C.

CV (eq/10<sup>6</sup> g polymer) was measured as follows. Polymer chips (100 mg) were dissolved in 10 mL 60/40 (w/w) phenol–tetrachloroethane at 140°C. After cooling, the solution was titrated with 0.1N sodium hydroxide in benzyl alcohol using tetrabromophenolphthalein blue as an indicator.

Benzoxazinone content (iV eq/10<sup>6</sup> g polymer) was determined by extrapolation from a calibration curve prepared in advance on the basis of (BV–CV), where CV was the carboxyl content measured as above and BV was measured as follows. Polymer chips (100 mg) were dissolved in 10 mL of benzyl alcohol containing about 20 ppm of water under stirring for 2 min at 210°C. After cooling, the solution was titrated with 0.1N sodium hydroxide solution in benzyl alcohol using phenol red as an indicator.

Melting points ( $T_m$ ) of the polymers which had been crystallized by heating at 140°C for 1 h were measured by DSC at a temperature raising rate of 10°C/min.

Molecular size distribution (polydispersity index) was determined by gel permeation chromatography (GPC) using a Toyo Soda HCL802UR equipped

TABLE I  
Properties of the Chain-Extended PET and Model Co-PET

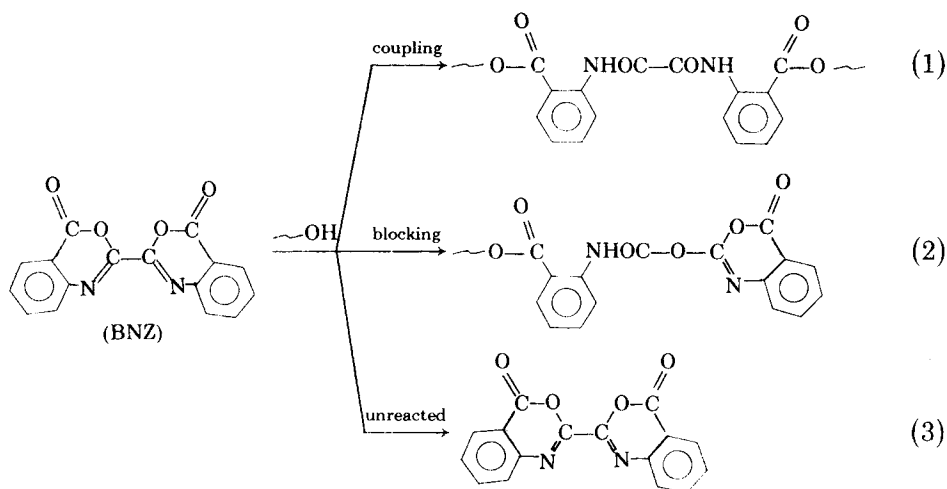
Added amount of BNZ (mol %/PET)	Properties of the polymer			
	$[\eta]$	CV (eq/10 <sup>6</sup> g)	iV (eq/10 <sup>6</sup> g)	$T_m$ (°C) <sup>a</sup>
Chain-extended PET				
1.0	0.96 (0.57)	17 14	38 —	248 255) <sup>a</sup>
0.6	0.72 (0.51)	12 10	5 —	252 256) <sup>a</sup>
0.5	0.82 (0.67)	37 34	19 —	251 255) <sup>a</sup>
Model co-PET				
0.5	0.61	17	—	254
1.5	0.57	9	—	252

<sup>a</sup>Properties of the initial PET.

with four crosslinked polystyrene columns of Toyo Soda TSK-GEL G5000H6, G4000H8, G3000H8, and G2000H8 in series. Chloroform was used as a solvent. A sample was prepared as follows. PET (20 mg) and 1,1,1,3,3,3-hexafluoro-2-propanol (10 mL) were brought into a test tube. The solution was stirred until PET was dissolved, and then 10 mL of chloroform was added. The solution thus prepared was applied to the GPC measurement.

## RESULTS AND DISCUSSION

The reaction of BNZ with polyesters can be classified into the following three types.



The effects of each BNZ unit remaining reacted or unreacted in the resultant polymer on the physical and chemical properties of the resultant polymer were investigated.

### Physical Properties

Table I shows  $[\eta]$ , CV,  $iV$ , and  $T_m$  of the BNZ-treated PET and model co-PET. In all cases of the BNZ-treated PET, a little melting point depressions are observed. In Figure 1  $T_m$  is plotted vs  $[\eta]$  for these polymers and other ordinary PET.  $T_m$  of the ordinary PET seems to show that  $T_m$  slightly decreases with increase in  $[\eta]$ . Therefore, the melting point depression by the reaction of BNZ with PET might be caused almost by the increase in  $[\eta]$ , and only a slight deviation of the plot of the BNZ-treated PET or model co-PET from the extrapolated line of the ordinary PET, as can be seen in the Figure 1, is caused by the copolymerization of BNZ unit.

Typical GPC curves for the BNZ-treated PET and the initial ordinary PET are shown in Figure 2. Small peaks on the low-molecular-weight side are caused by the cyclic oligomers of PET. Average molecular weight ( $M_w$  = the weight-averaged and  $M_n$  = the number-averaged) and polydispersity indices ( $M_w/M_n$ ) for several examples of both the BNZ-treated PET and the untreated ordinary PET excluding the cyclic oligomers were calculated from the GPC curves. As shown in Table II and Figure 3, the resultant  $M_w$  and  $M_n$

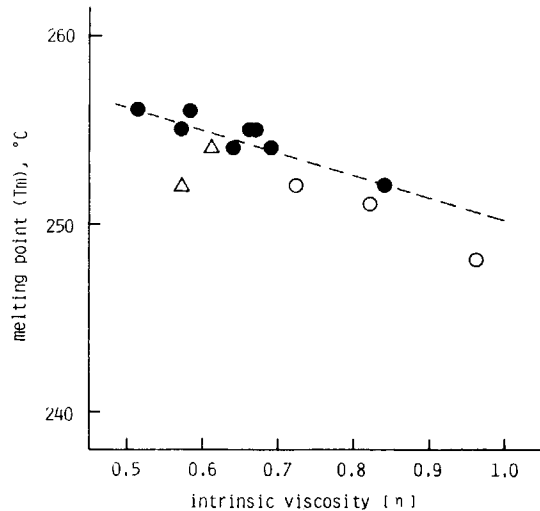


Fig. 1. Relationship between  $T_m$  and  $[\eta]$  of the BNZ-treated PET (○), model co-PET (Δ), and ordinary PET (●).

formed two separate parallel straight lines, respectively, and polydispersity indices ( $M_w/M_n$ ) fell on an almost constant value, regardless of the treated and the untreated.

These results indicate that the BNZ-treated PET has the same molecular size distribution, and therefore the same degree of linearity as the ordinary

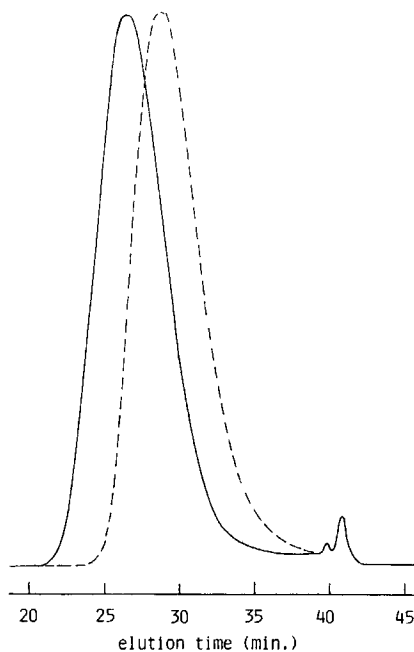


Fig. 2. GPC charts of the BNZ treated PET  $\{[\eta] = 0.96$  (—) and its initial polymer  $\{[\eta] = 0.57$  (---).

TABLE II  
 GPC Measurement of the BNZ Treated and the Ordinary PET

[ $\eta$ ] of the sample	Molecular weight		Polydispersity index ( $M_w/M_n$ )
	$M_w$	$M_n$	
BNZ-treated PET			
0.72	55,800	25,100	2.22
0.82	73,000	33,500	2.18
0.96	93,200	40,300	2.31
Ordinary PET			
0.66	48,600	22,700	2.14
0.69	54,900	24,600	2.23
0.84	76,600	34,200	2.24
Branched PET <sup>a</sup>			
0.55	51,200	15,000	3.41

<sup>a</sup> Pentaerithritol-copolymerized PET (0.3 mol %).

PET. For reference, we prepared an example of branched PET (0.3 mol % pentaerithritol-copolymerized PET) and measured  $M_w$ ,  $M_n$ , and  $M_w/M_n$ , to confirm a considerable deviation of such values of the branched PET from those of the corresponding ordinary PET, as also shown in Table II and Figure 3. It is easily understood that the straight lines in Figure 3 correspond to the Mark-Houwink equation for PET excluding the cyclic oligomers.

$$[\eta] = 5.1 \times 10^{-4} M_w^{0.66} \quad (4)$$

$$[\eta] = 8.7 \times 10^{-4} M_n^{0.66} \quad (5)$$

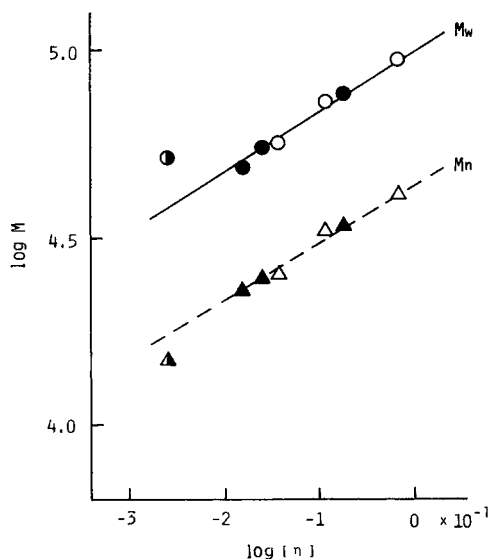


Fig. 3. Relationship between  $M_w$  (—),  $M_n$  (---), and [ $\eta$ ] of the BNZ-treated PET (○, △), the ordinary PET (●, ▲), and the branched PET (●, ▲).

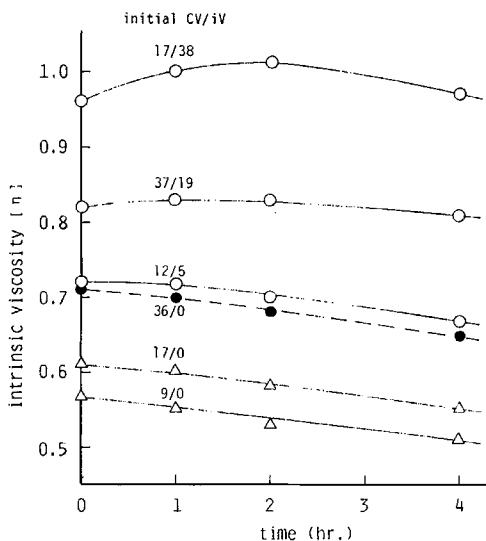


Fig. 4. Thermal stabilities of the BNZ treated PET (○), model co-PET (△), and the ordinary PET (●) at 230°C in air circulation.

### Chemical Properties

In the BNZ-treated PET there might remain unreacted benzoxazinone groups derived from blocked [eq. (2)] or unreacted [eq. (3)] BNZ, which could react with hydroxyl groups of PET at higher temperatures to act as a heat stabilizer. To confirm this, changes in  $[\eta]$  of the BNZ-treated PET when heated at 230°C in air circulation have been investigated. As shown in Figure 4,  $[\eta]$  of the PET having rather high *iV* is retained better than those of the ordinary PET and the model co-PET. This means that the unreacted benzoxazinone groups can react to couple the polymer chains even in the solid phase and act as a heat stabilizer. The results of the ordinary PET, the model co-PET, and the BNZ-treated PET having rather low *iV* indicate that the oxalyl bis(anthranilate) unit has nearly the same thermal stability as the ethylene terephthalate unit in the tested condition.

It is well known that PET having a low CV showed improved chemical stabilities, especially improved hydrolytic stability. As reported in the previous paper,<sup>2</sup> hydroxyl-addition-type chain extenders such as BNZ can give PET having a higher  $[\eta]$  and lower CV from PET having a low CV, regardless of its  $[\eta]$ . Therefore, BNZ is useful to produce PET of low CV. To evaluate the influence of BNZ unit remaining in the BNZ treated PET, in Figure 5 is plotted the change in  $[\eta]$  of various PET chips when they were heated in water at 130°C in a sealed glass tube. The results indicate that the ordinary PET and the model co-PET having a lower CV are more stable, but the BNZ-treated PET having a low CV but a high *iV* is not so stable. To understand these results more precisely, in Figure 6 are plotted the number of scission (*D*) by hydrolysis in 15 h vs. CV of the initial PET.

*D* was calculated as follows:

$$\text{number of scission } (D \text{ eq}/10^6 \text{ g}) = \frac{1}{2}(N_d - N_0) \quad (6)$$

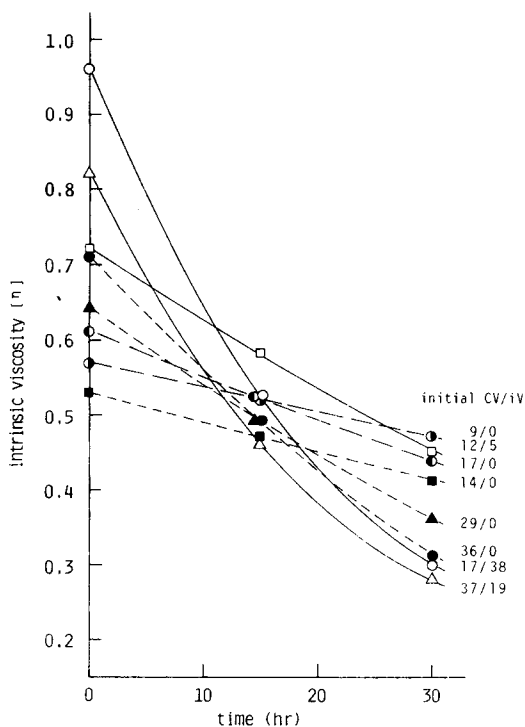


Fig. 5. Hydrolysis of the BNZ-treated PET (—), model co-PET (---), and the ordinary PET (· · ·) at 130°C in water.

where  $N_0$  and  $N_d$  mean the numbers of the total terminal groups of the initial polymer and the degraded polymer, respectively.  $N_0$  and  $N_d$  can be calculated from  $[\eta]$  using the following Mark-Houwink equation:

$$[\eta] = KM^a = K \left( \frac{2 \times 10^6}{N} \right)^a \quad (7)$$

where  $M$  is the number average molecular weight, and  $K$  and  $a$  are such empirical constants as  $2.75 \times 10^{-4}$  and 0.77, respectively.<sup>4</sup> Plots for the ordinary PET and the model co-PET fall on the same line. This means that oxalyl bis(anthranilate) unit copolymerized in the polyester chains shows little influence on the hydrolytic stability of the resultant polymer. To evaluate the effect of the unreacted benzoxazinone groups,  $D$  vs.  $(CV + iV)$  regarding to the BNZ-treated PET are also plotted. These plots fall nearly on the same line. This means that the benzoxazinone groups promote the hydrolysis of the polymer as much as the carboxyl groups.

### CONCLUSION

The PET treated with BNZ has a slightly lower melting point but almost the same molecular size distribution as compared with the ordinary PET. The oxalyl bis(anthranilate) unit copolymerized in the polyester chain has little influence on such chemical stabilities as thermal and hydrolytic stabilities.

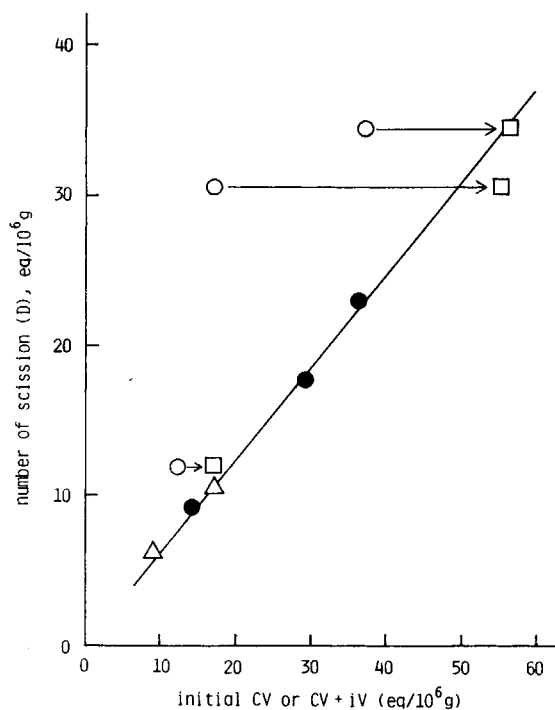


Fig. 6. Relationship between the initial CV [BNZ-treated PET (○), model co-PET (Δ), ordinary PET (●) or (CV + iV) (□)] and the number of scission ( $D$ ) by hydrolysis at 130°C in water for 15 h.

The benzoxazinone groups remained unreacted in polyester can act as a heat stabilizer by further reacting with hydroxyl terminals to prevent decrease in the molecular weight. But they adversely affect the hydrolytic stability as much as the carboxyl groups.

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