

# Chain Extenders for Polyesters. IV. Properties of the Polyesters Chain-Extended by 2,2'-Bis(2-oxazoline)

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## Synopsis

Some properties of the polyesters treated with such an addition-type chain extender as 2,2'-bis(2-oxazoline) (BOZ) have been investigated. The molecular size distribution and the melting point of the resultant polyesters indicate that BOZ reacts to form linear chain-extended polymers without branching. As for their thermal stabilities, unreacted oxazoline remained in the polymer can act as a heat stabilizer by further reacting with carboxyl terminals of the polymers and by preventing decrease in the molecular weight even in the solid state. On the other hand, BOZ unit incorporated in the polyester chain was relatively thermally unstable compared with the ordinary polyester chain, especially under the polyester melt condition. The polyester treated with BOZ has a rather low carboxyl content, and considerable improvement in the hydrolytic stability has been observed. But unreacted oxazoline groups adversely affected the hydrolytic stability, although the effect was about eight times as small as that of carboxyl groups.

## INTRODUCTION

Poly(ethylene terephthalate) (PET) has been well known to be one of the most commercially important polymers, which is used as synthetic fibers, biaxially oriented films, blow-molded bottles, and plastics. In most of its applications, PET with improved mechanical and chemical properties is always needed. The most desirable implementation is to use PET of high molecular weight and low carboxyl content (CV). In a conventional melt polycondensation, however, it has been difficult to obtain the PET having intrinsic viscosity ( $[\eta]$ ) of above 0.9 and CV of below 15 eq/10<sup>6</sup> g.

To overcome the difficulty, we have sought for so-called "addition-type chain extender," which is reactive with the polymer chain ends through addition reactions without generating any by products.

In the previous papers,<sup>1,2</sup> we reported new effective addition-type carboxyl-reactive chain extenders such bis(cyclic-imino-ethers) as 2,2'-bis(2-oxazoline) (BOZ), 2,2'-bis(5,6-dihydro-4H-1,3-oxazine), and *N,N'*-hexamethylenebis(2-carbamoyl-2-oxazoline), which resulted in obtaining PET with  $[\eta]$  above 1.0 and CV below 5 eq/10<sup>6</sup> g. These chain extenders react within a few minutes under PET melt conditions at an atmospheric pressure, so that in practice they can be easily applied during the ordinary melt processing such as spinning, extruding, and injection molding. But the use of such a chain extender unavoidably leads to the introduction of foreign linkages other than ester, and some properties of the resulting polymer should be influenced by them.

In the present paper, we would like to report our investigations on such influences.

## EXPERIMENTAL

### Materials

BOZ was prepared as previously reported.<sup>3</sup> PET having various  $[\eta]$  and CV were prepared by changing reaction conditions such as temperature, pressure, or time from dimethyl terephthalate and ethylene glycol by the ordinary polycondensation method using  $\text{Sb}_2\text{O}_3$  (0.03 mol %) and  $\text{Mn}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.04 mol %) as catalysts and  $(\text{CH}_3\text{O})_3\text{P} = \text{O}$  (0.05 mol %) as a stabilizer.

### CHAIN-EXTENDING REACTION

To a 500-mL three-necked, round-bottom flask, equipped with a mechanical stirrer, a nitrogen inlet, and an outlet tube, 100 g of dried PET pellets were added, and the system was evacuated and purged with nitrogen. Under a flow of nitrogen the flask was placed in a salt bath heated at 280°C. After all polymer pellets were melted, the prescribed amount of BOZ was added under stirring. After a predetermined period of the reaction, resulting polymer was pulverized to about 10–20 mesh and provided for analyses.

### ANALYTICAL PROCEDURE

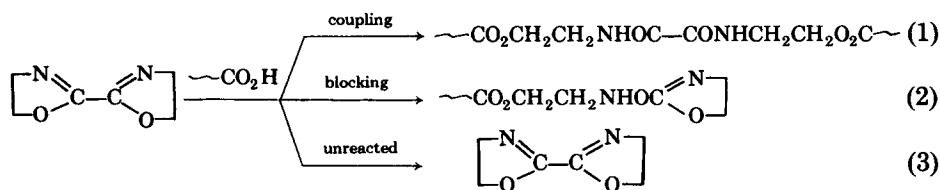
$[\eta]$  was measured in *o*-chlorophenol at 35°C. CV (eq/10<sup>6</sup> g polymer) was measured by Conix method.<sup>4</sup> Oxazoline content (LV) was measured as follows. Polymer chips (100 mg) were brought into a test tube. Ten milliliters of 0.003*N* solution of *p*-toluenesulfonic acid in 60/40 (W/W) phenol–tetrachloroethane was added, and the test tube was held for 15 min at 140°C. After cooling, 10 mL of chloroform was added and titrated using a 0.1*N* solution of sodium hydroxide in benzyl alcohol. Two drops of 0.3% solution of tropaeolin OO in ethanol were used as an indicator. A blank measurement was also made and taken into account for calculation. The exact value was determined from calibration curve which was given from the polymer having known oxazoline content.

Melting points ( $T_m$ ) of the polymers which were 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 was determined by gel permeation chromatography (GPC) using a Toyo Soda HLC802UR equipped 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: 20 mg of PET and 10 mL of 1,1,1,3,3,3-hexafluoro-2-propanol were brought into a test tube. The solution was stirred until the 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 BOZ with the polyesters can be classified into the following three types.



Detailed studies were made to see the effect of the incorporated BOZ on the physical and chemical properties of the resultant polymers.

## PHYSICAL PROPERTIES

### *Melting Point*

Table I shows the effects of the BOZ treatment (for 5 min at 280°C) on such properties as  $[\eta]$ , CV, and  $T_m$  using PET samples of various  $[\eta]$  and CV. In any case, increase in  $[\eta]$ , decrease in CV, and a slight depression in  $T_m$  were observed on the treatment. The relations between the added amount of BOZ and the change in  $[\eta]$  and CV of the treated PET were already discussed in our previous paper.<sup>2</sup>

As shown in Figure 1, we plotted  $T_m$  vs.  $[\eta]$  of both the initial PET and the BOZ-treated PET, to find them to form a straight line regardless of the treated and the untreated. This means the  $T_m$  depression accompanying the BOZ treatment should be not mainly due to the introduction of the foreign linkage in the PET chain but due to the increase in  $[\eta]$ . Therefore, it may be concluded that the chain-extending treatment by BOZ does not have a serious effect on the  $T_m$  of the treated PET at least under the treating conditions we are considering to apply.

### *Molecular Size Distribution*

A typical GPC curve for the ordinary PET prepared by melt polycondensation is 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 in-

TABLE I  
Effects of the BOZ Treatment of PET on  $[\eta]$ , CV, and  $T_m$

Added amount of BOZ (wt %)	$[\eta]$ /CV		$T_m$ (°C)	
	Initial PET	BOZ-treated PET <sup>a</sup>	Initial PET	BOZ-treated PET <sup>a</sup>
0.3	0.51/21	0.58/2	256	255
0.4	0.58/38	0.76/4	256	252
0.2	0.64/32	0.81/22	254	252
0.3	0.69/26	0.88/3	254	251
0.5	0.66/46	1.06/4	255	248
0.1	0.84/29	0.97/17	252	250

<sup>a</sup>Treated for 5 min at 280°C.

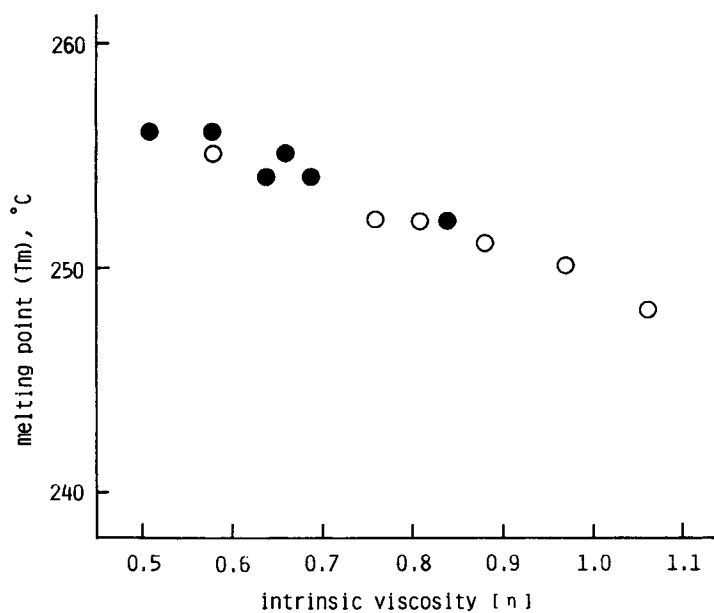


Fig. 1. Relationship between  $T_m$  and  $[\eta]$  of the BOZ-treated PET (○) and the initial PET (●).



Fig. 2. A typical GPC chart for PET prepared by melt polymerization.

TABLE II  
GPC measurement of the BOZ treated and the ordinary PET

[ $\eta$ ] of the sample	Molecular weight		Polydispersity index ( $M_w/M_n$ )
	$M_w$	$M_n$	
BOZ-treated PET			
0.58 (0.51 <sup>a</sup> )	42800	20000	2.14
0.88 (0.69)	85500	38300	2.23
1.06 (0.66)	106700	46500	2.29
Ordinary PET			
0.66	48600	22700	2.14
0.69	54900	24600	2.23
0.84	76600	34200	2.24
Branched PET <sup>b</sup>			
0.55	51200	15000	3.41

<sup>a</sup>[ $\eta$ ] before BOZ treatment.

<sup>b</sup>0.3 mol % pentaerithritol-copolymerized PET.

dices ( $M_w/M_n$ ) for several examples of both the BOZ-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  $M_n$  formed two separate paralleled 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 BOZ-treated PET has the same molecular size distribution, and therefore the same degree of linearity as the ordinary 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:

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

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

## CHEMICAL PROPERTIES

### *Thermal Stability*

To evaluate the thermal stability of the BOZ-treated PET in comparison with the untreated ordinary PET, we carried out two tests (230°C in air and 280°C in nitrogen). In the polymer processing of thermoplastics, the melt stability in an inert atmosphere is important. On the other hand, the thermal stability at the elevated temperatures under  $T_m$  in air is significant to evaluate the practical value of the fabricated thermoplastics. The results from the latter test are summarized in Figure 4. The BOZ-treated PET having a

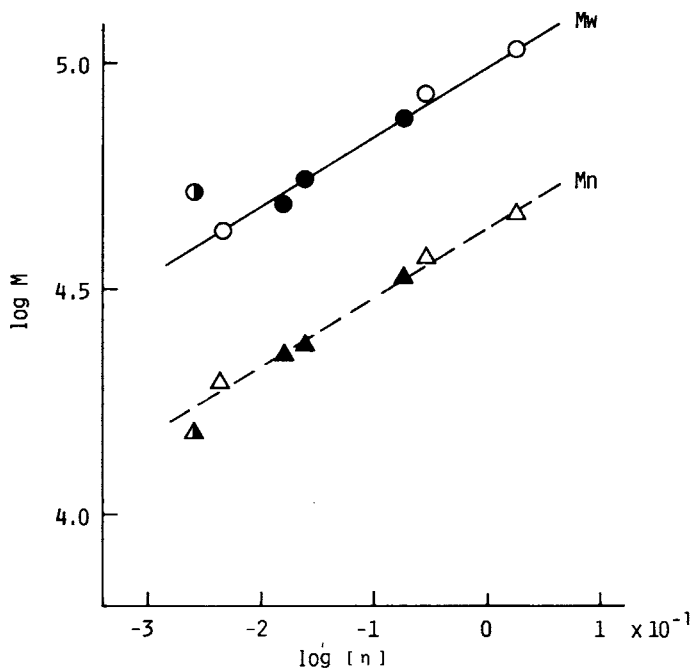


Fig. 3. Relationship between  $M_w$  (—),  $M_n$  (---), and  $[\eta]$  of the BOZ-treated PET (○, △), the ordinary PET (●, ▲), and the branched PET (⊙, ⊔).

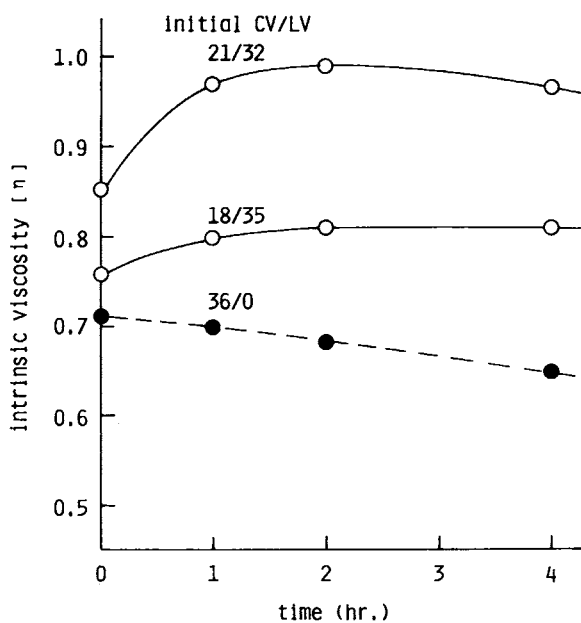


Fig. 4. Thermal stability of the BOZ-treated PET (○) and the ordinary PET (●) at 230°C in air circulation.

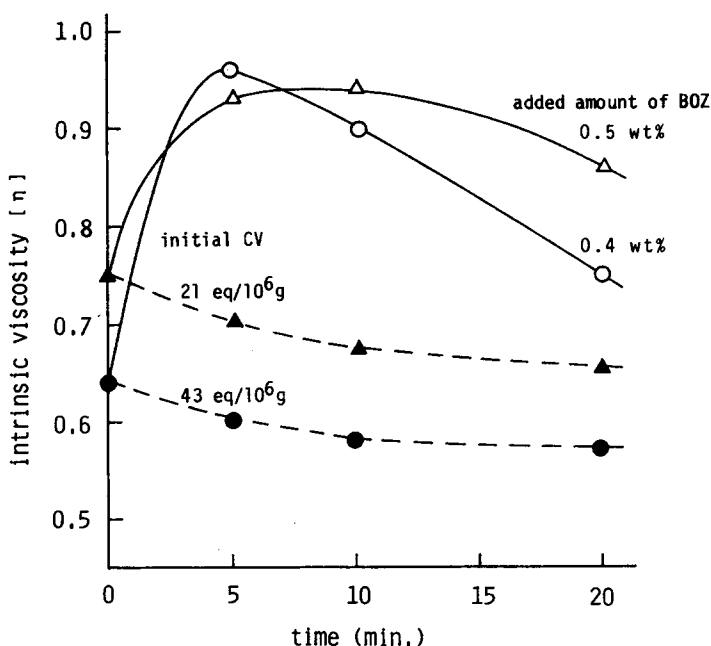


Fig. 5. Melt stability of the BOZ-treated PET (—) and the ordinary (PET) (---) at 280°C under nitrogen flow.

considerable LV showed improved retention of  $[\eta]$ , compared with that of the untreated PET, when heated at 230°C in an air oven. The reason for the improvement is likely to be due to the oxazoline groups remaining unreacted in the treated PET [see eqs. (2) and (3)]. The oxazoline groups can readily react with carboxyl groups generated in the PET by the thermal decomposition (oxidation or hydrolysis) to prevent the decrease in  $[\eta]$ .

In contrast, the BOZ-treated PET showed the inferior melt stability to that of the untreated. Since the predetermined BOZ was added at the start of the test,  $[\eta]$  of the treated polymers abruptly increased once within 10 min by the chain-extending reaction. After that, it fell down more rapidly than that of the untreated (Fig. 5).

It can be demonstrated from the above that the BOZ-treated PET is unstable in the melt, and we have to be careful to select the conditions for melt-processing of the BOZ-treated PET.

The ethylene oxamide unit in the treated PET seems thermally unstable compared with the ethylene terephthalate unit.

#### *Hydrolytic Stabilities*

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>1,2</sup> carboxyl-addition-type chain extenders such as BOZ is very advantageous to produce polyester having a low CV.

In Figure 6 are plotted  $[\eta]$  of various PET chips when they were heated in water at 130°C in a sealed glass tube. The results seems to confirm that the

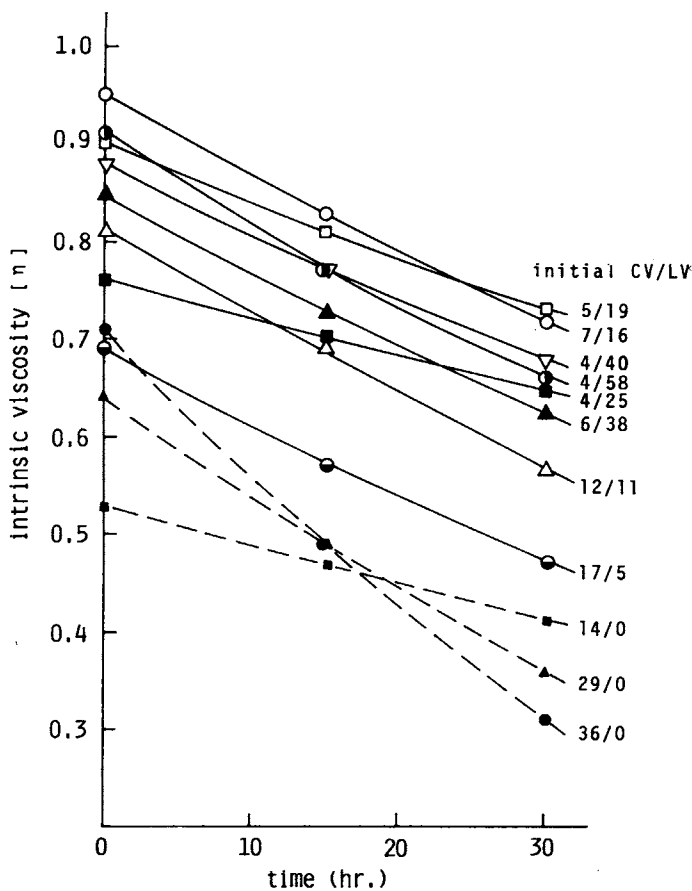


Fig. 6. Hydrolysis of the BOZ-treated PET (—) and the ordinary PET (---).

hydrolytic stability of PET increases with decrease in CV regardless to how CV has been controlled. To understand these results more conveniently, in Figure 7 are plotted the number of scission ( $D$ ) by hydrolysis in 15 h vs. CV of the initial PET.

$D$  was calculated as follows:

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

where  $N_0$  and  $N_d$  mean the numbers of the total terminal groups of the initial polymer and the degraded polymer, respectively. They 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>5</sup> As shown in Figure 7, plots for the chain-extended PET and the ordinary PET fall on the same



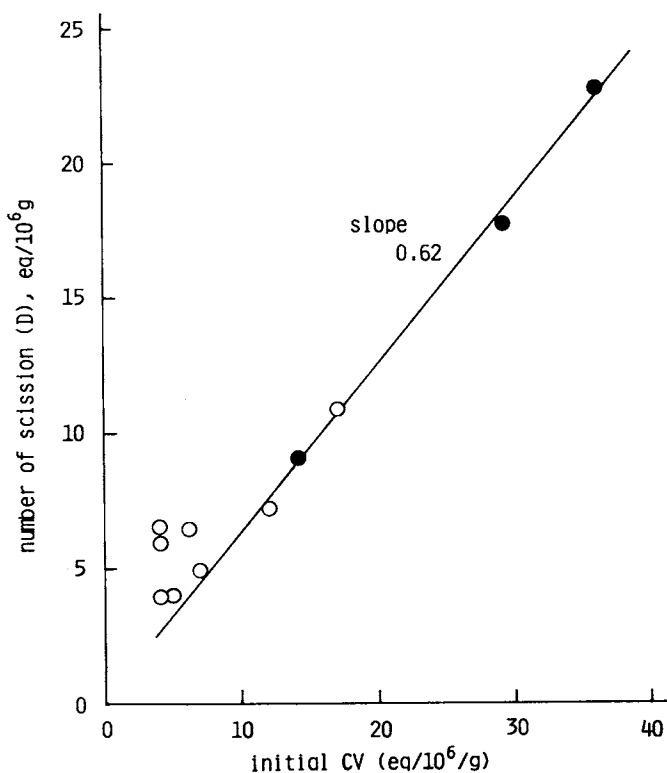


Fig. 7. Relationship between the initial CV and the number of scission ( $D$ ) by hydrolysis at 130°C in water for 15 h: (○) BOZ-treated PET; (●) ordinary PET.

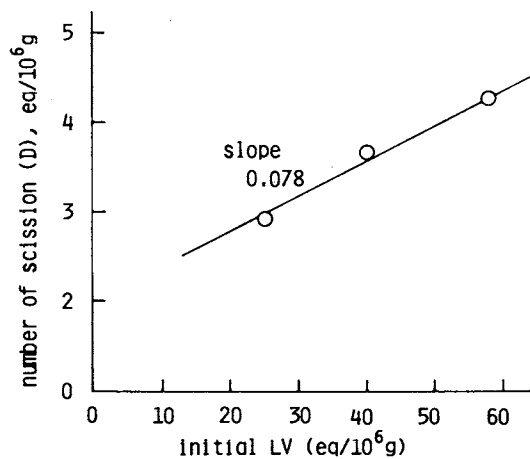


Fig. 8. Relationship between the initial LV and the number of scission ( $D$ ) by hydrolysis at 130°C in water for 15 h using the BOZ-treated PET having CV of 4 eq/10<sup>6</sup> g.

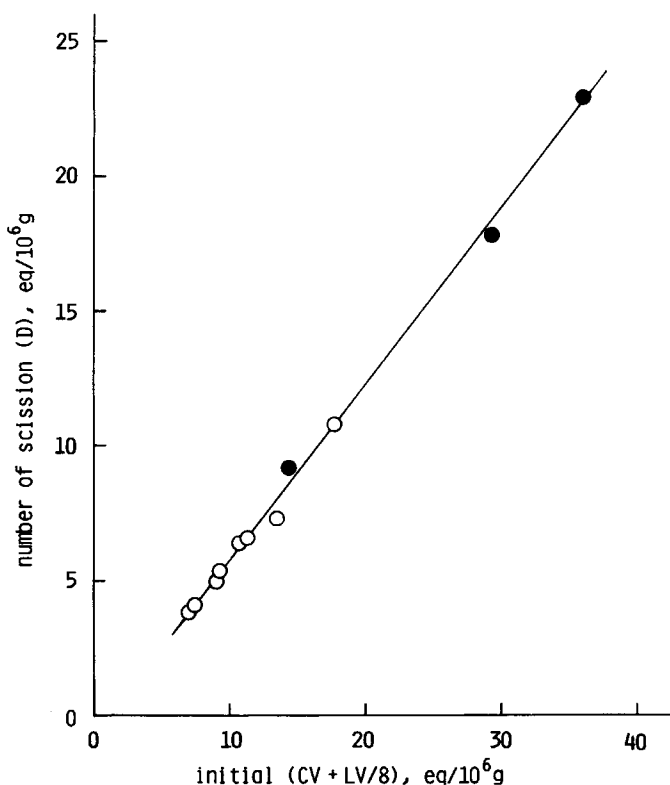


Fig. 9. The number of scission ( $D$ ) by hydrolysis at 130°C in water for 15 h vs.  $(CV + LV/8)$  of the initial polymer: (○) BOZ-treated PET; (●) ordinary PET.

straight line ( $D/CV = 0.62$ ), so far as  $CV$  is above ca. 10 eq/10<sup>6</sup> g. But the  $D$  values for lower  $CV$  appear above the line. This means that the BOZ-treated PET becomes less stable in the region of very low  $CV$ . To pursue the cause of this deviation, we investigated the effect of the remaining oxazoline rings on hydrolysis. In Figure 8 are plotted  $D$  vs.  $LV$  of the various PET having the same  $CV$  (4 eq/10<sup>6</sup> g). Linear relationship has been observed with  $D/LV$  being 0.078. This means that residual oxazoline groups also promote hydrolysis of polyester as well as carboxyl groups, but the effect of the former is about 8 times as small as that of the latter. In Figure 9 are plotted  $D$  vs.  $(CV + LV/8)$  for all cases. Better linear relationship is observable throughout the whole range of  $(CV + LV/8)$ , as is expected.

### CONCLUSION

The PET treated with carboxyl-addition-type chain extender such as BOZ has a similar tendency in its melting point to that of the untreated PET, and almost the same molecular size distribution as compared with the ordinary PET. The BOZ unit incorporated in the polyester chain is relatively thermally unstable compared with the ordinary polyester chain, but oxazoline groups remaining unreacted in polyester can act as a heat stabilizer by further

reacting with carboxyl terminals to prevent decrease in the molecular weight even in the solid state.

The chain-extended PET has a rather low CV and an improved hydrolytic stability. But the presence of unreacted oxazoline groups adversely affects the hydrolytic stability, although the effect was about 8 times as small as that of carboxyl groups.

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