

Chain Extenders for Polyesters. III. Addition-Type Nitrogen-Containing Chain Extenders Reactive with Hydroxyl End Groups of Polyesters

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Synopsis

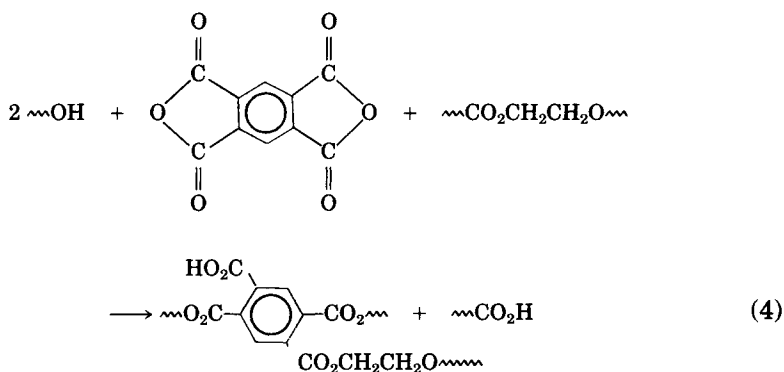
Effective chain extenders for linear polyesters such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) were sought among some nitrogen-containing bis-heterocycles, which were reactive with hydroxyl terminals of the polyesters to form addition linkages. Tested were such bis cyclic-imino-esters as bis[5(4H)-oxazolone]s (OXZ) and bis(4H-3,1-benzoxazin-4-one)s (BNZ), among which BNZ, especially 2,2'-bis(4H-3,1-benzoxazin-4-one) (BNZ-A-1) has been proved to be a very effective chain extender for both PET and PBT. Starting from PET having intrinsic viscosity ($[\eta]$) of 0.52 and carboxyl content (CV) of 10 eq/10⁶ g, addition of 1 mol % BNZ-A-1 resulted in PET having $[\eta]$ of 1.11 and CV of 13 eq/10⁶ g at a polyester melt temperature under atmospheric nitrogen within a few minutes. On the other hand, OXZ which were less thermally stable than BNZ could not act as good chain extenders for PET at a PET melt temperature. But they were effective in the case of PBT, which melted at a lower temperature than PET.

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 some of the applications, where high tenacity or toughness of the fabricated product is very important, PET of a high molecular weight, for instance, that having intrinsic viscosity ($[\eta]$) of above 1.0, is desired. In a conventional melt polycondensation, however, it has been proved difficult to obtain the PET having $[\eta]$ of above 0.9.

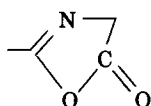
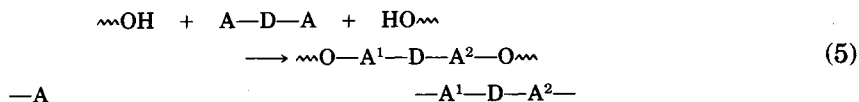
To overcome the difficulty, the use of so-called "chain extender" has been proposed as an attractive method from a practical view point.^{1,2} The chain extenders can be defined as bifunctional compounds which react with the polymer end groups readily to couple the polymer chains with each other, when they are added to the polymer melts, resulting in the higher-molecular-weight polymers.

The chain terminals of the linear polyesters mainly consist of alcoholic hydroxyl groups derived from glycol, and carboxyl groups from dicarboxylic acid moiety. Therefore, the chain extenders for polyesters should be either hydroxyl-reactive or carboxyl-reactive. It is well known that the carboxyl contents (CV) in the polyesters have influence over their hydrolytic stabilities, and the smaller CV leads to the better hydrolytic stability. Accordingly, the carboxyl-reactive chain extenders seem more advantageous than

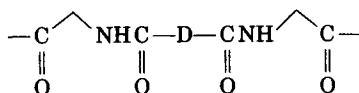


In order to find the improved hydroxyl-reactive chain extenders without such problems mentioned above, we have investigated some nitrogen-containing bis-heterocycles which are reactive with hydroxyl groups to form stable addition linkages. Selected for test were such bis cyclic-imino-esters as bis[5(4H)-oxazolones] (OXZ) and bis(4H-3,1-benzoxazin-4-ones) (BNZ).

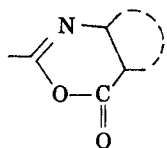
The following are the proposed reaction schemes:



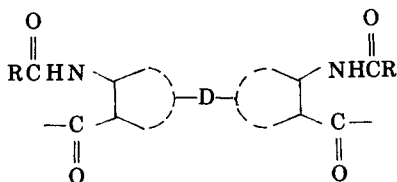
(OXZ)



(BNZ-A)



(BNZ-B)

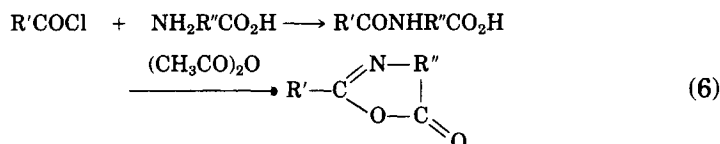


Some of the above compounds have been proved to be very effective chain extenders.

EXPERIMENTAL

Materials

Bis cyclic-imino-esters used here were prepared according to the procedures reported already in the literature.⁵⁻⁸ The general ring-formation schemes can be described as follows. The corresponding bis(acylamino acids) obtained from acyl chlorides and amino acids were cyclized to OXZ or BNZ using acetic anhydride as a dehydrating agent:



2,2'-Bis(4H-3,1-benzoxazin-4-one) (BNZ-A-1) was prepared by the reaction of oxalyl chloride and isatoic anhydride in pyridine.⁹

2,2'-*p*-Tolylenebis(4H-3,1-benzoxazin-4-one) (BNZ-A-3) was prepared as follows. Methylterephthaloyl chloride (21.7 g) in 200 mL dioxane was added to a solution of 27.4 g of anthranilic acid in 100 mL pyridine. The mixture was stirred for 1 h at room temperature. The reaction mixture was poured into cold water under stirring, followed by acidification with hydrochloric acid. The precipitate was filtered and dried. The resulting *N,N'*-*p*-tolylenebis (anthranilic acid) was heated in 300 mL of acetic anhydride under reflux for 2 h. After cooling the reaction mixture, the resulting precipitate was filtered and recrystallized from pseudocumene.

ANAL. Calcd for $\text{C}_{23}\text{H}_{14}\text{N}_2\text{O}_4$: C, 72.25%; H, 3.69%; N, 7.33%. Found: C, 72.42%; H, 3.57%; N, 7.35%.

2,2'-(Nitro-*p*-phenylene)-bis(4H-3,1-benzoxazin-4-one) (BNZ-A-4) was prepared from 24.8 g of nitroterephthaloyl chloride and 27.4 g of anthranilic acid similarly to the above. Nitrobenzene was used as recrystallization solvent.

ANAL. Calcd for $\text{C}_{22}\text{H}_{11}\text{N}_3\text{O}_6$: C, 63.93%; H, 2.68%; N, 10.17%. Found: C, 63.77%; H, 2.72%; N, 10.36%.

6,6'-Methylenebis[2-(4-nitrophenyl)-4H-3,1-benzoxazin-4-one] (BNZ-B-5) was prepared from 37.1 g of *p*-nitrobenzoyl chloride and 28.6 g of bis(4-aminophenyl)methane-3,3'-dicarboxylic acid using similar procedure to the above and recrystallized from nitrobenzene.

ANAL. Calcd for $\text{C}_{29}\text{H}_{16}\text{N}_4\text{O}_8$: C, 63.51%; H, 2.94%; N, 10.22%. Found: C, 63.70%; H, 2.88%; N, 10.14%.

The compounds prepared here are summarized in Table I with their melting points and recrystallization solvents.

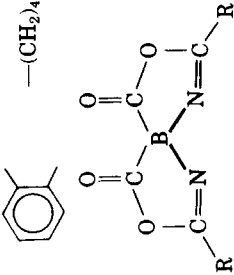

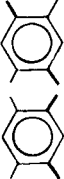
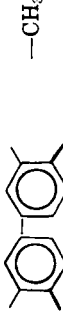

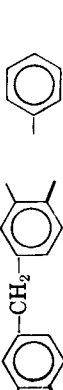
CHAIN-EXTENDING REACTION

In the Case of PET. To a 500-mL three-necked round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and an outlet tube, 127 g of

TABLE I
Synthesis of Bis Cyclic-Imino-Esters

Compound	Melting point (°C)	Recrystallization solvent
	264–267	Xylene
	252–255	Dioxane
	>300	Nitrobenzene
	>300	<i>o</i> -Dichlorobenzene
	277–279	Pseudocumene
	>300	Nitrobenzene

TABLE I (continued)
Synthesis of Bis Cyclic-Imino-Esters

Compound	Melting point (°C)	Recrystallization solvent
	212-218	Dioxane
(BNZ-A-5) ⁶		
		
mixture	261-264	<i>o</i> -Dichlorobenzene
(BNZ-B-1) ⁷		
	>300	<i>N,N'</i> -dimethyl acetamide and acetic anhydride
(BNZ-B-1) ⁸		
	266-269	Acetic anhydride
(BNZ-B-3) ⁶		
	290-294	Xylene
(BNZ-B-4) ⁶		
	>300	Nitrobenzene
(BNZ-B-5)		

bis(β -hydroxyethyl terephthalate) and 0.044 g of Sb_2O_3 were added, and the polycondensation was carried out at 280°C by the ordinary procedure until $[\eta]$ of the molten polymer reached within the range of 0.5–0.6. Then, under a nitrogen stream and stirring, 0.005 mol (1.0 mol % based on the polymer recurring unit) of the chain extender was added. After a predetermined reaction period, $[\eta]$ and CV of the resulting polymer were measured.

In the Case of Poly(butylene Terephthalate) (PBT). PBT was prepared from 97 g of dimethyl terephthalate and 67.5 g of 1,4-butanediol by the ordinary melt polycondensation using 0.034 g of $\text{Ti}(\text{O}-n\text{C}_4\text{H}_9)_4$ as catalyst at 240°C in a flask similar to that used above, until $[\eta]$ of the polymer reached between 0.6 and 0.7. Then, 0.005 mol (1.0 mol % per the polymer recurring unit) of a chain extender was added, and the chain-extending reaction was carried out similarly to the above.

ANALYTICAL PROCEDURE

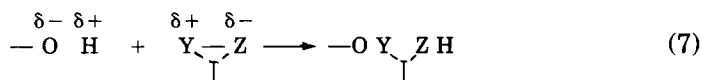
$[\eta]$ of PET was measured in *o*-chlorophenol at 35°C and $[\eta]$ of PBT was measured in 60/40 (w/w) phenol–tetrachloroethane at 30°C .

CV (eq/10⁶ g) was measured as follows. The finely-ground polymer (0.1 g) was dissolved in 10 mL 60/40 (w/w) phenol–tetrachloroethane at 140°C . After cooling, the solution was titrated with 0.1*N* sodium hydroxide in benzyl alcohol using tetrabromophenolphthalein blue as an indicator.

RESULTS AND DISCUSSION

Selection of Hydroxyl-Reactive Chain-Extending Groups

In the addition reactions involving alcoholic hydroxyl groups, they act as nucleophiles. Such reactions can be formulated as follows:



wherein $\text{Y}-\text{Z}$ can mean either a cyclic group or a multiple bond group (which may be regarded as a two-membered ring), and Y means an electrophilic or electron-deficient atom while Z should have a nucleophilic or electron-sufficient property. In this report we would like to describe only the cases that $\text{Y}-\text{Z}$ means a cyclic group.

As for Y and Z in the cyclic group $\text{Y}-\text{Z}$, there can be the following two combinations: (i) a carbon atom for Y, and an electron-negative atom such as oxygen and nitrogen for Z, and (ii) carbons for both Y and Z, either of which is electron negative or positive due to the attached group on it.

In the ring-scission reactions of cyclic groups by the addition of alcoholic groups, it is very rare that carbon—carbon single-bond scissions in the cyclic groups occur. Accordingly, we have decided to pursue the possibilities of

only the combination (i). In this case, $-ZH$ in the resultant linkage corresponds to $-OH$ and $>NH$. But the linkage $-OY$ $\begin{array}{c} | \\ -ZH \end{array}$ should not contain

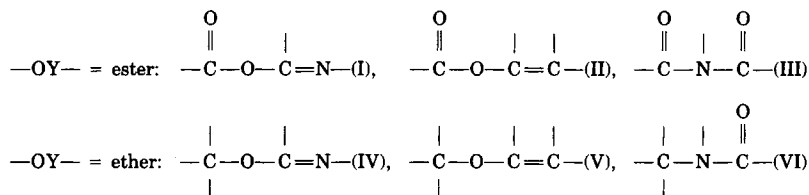
simple hydroxyl, amino (imino), or carboxyl groups, because they are reactive with polyesters and cause branching and crosslinking. To meet the above requirement, in the case that $-ZH = -OH$, the $-OH$ must mean

the hydroxyl of enol form such as amide ($-N=C(OH) \rightarrow -NHC(=O)$) or ketone ($>C=C(OH) \rightarrow >CH-C(=O)$), and in the case that $-ZH = >NH$,

HN must be a part of amide linkage ($\begin{array}{c} | \\ -C-NH \\ || \\ O \end{array}$).

On the other hand, $-OY-$ should be a stable linkage comparable to ester linkages. This leads to the selection of ethers and esters for $-OY-$.

The following linkages as Y $\begin{array}{c} | \\ -Z \end{array}$ can be picked out by combining both of the above requirements:



As reported in the preceding paper,³ linkages (IV), (V), and (VI) had been selected as suitable linkages for carboxyl-reactive chain-extending groups, and most of them had been proved to be effective as carboxyl-reactive chain-extending groups even in the presence of a large amount of alcoholic hydroxyl terminals. This means that such linkages (IV), (V), and (VI), as would be expected to form the ethers by the addition reaction with hydroxyl groups, actually react with carboxyl groups more readily to result in ester linkages. Similarly the simplest case, epoxy groups are known to react more readily with carboxyl groups resulting in the ester linkages than with alcoholic hydroxyl groups to form the ether linkages.¹⁰

Therefore, linkages (IV)–(VI) cannot be regarded as hydroxyl-reactive chain-extending groups and only the linkages (I), (II), and (III) are to be investigated.

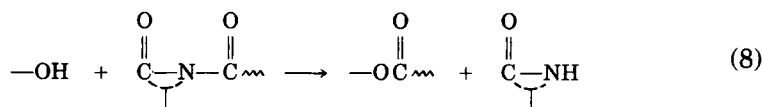
As for cyclic groups containing linkage (III), two types can be picked out.

The one is a cyclic imide shown as $\begin{array}{c} O \quad O \\ || \quad || \\ C-N-C \\ | \end{array}$ and the other is a *N*-acyl lactam

described as $\begin{array}{c} O \quad O \\ || \quad || \\ C-N-C- \\ | \end{array}$. The former is well known to be very stable even

at a high temperature, so it is unsuitable for a chain-extending group. In the latter case, if the lactam is of the 5–7-membered, the lactam ring itself

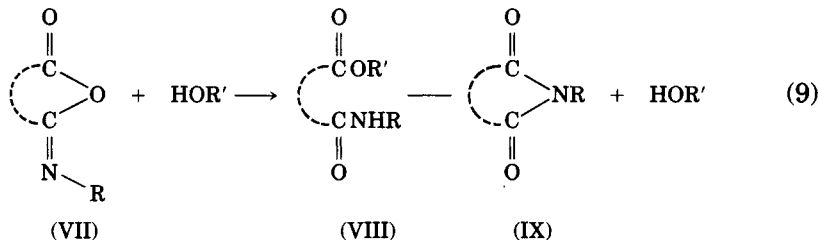
usually would not act as a hydroxyl-reactive group but as a leaving group shown in the following scheme:



Highly-strained lactams, such as the 4-membered β -lactams, may be subject to ring opening preferentially in the reaction with hydroxyl groups. But use of such lactams would not be of practical value since their preparations are difficult.

As for comparison of linkages (I) and (II), (I) can be predicted to be more reactive than (II) due to electron-negativity of the nitrogen atom contained in (I).

Thus, we conclude that bis-heterocyclic compounds containing linkage (I) are potentially promising candidates for hydroxyl-reactive addition-type chain extenders. There are two types of cyclic groups having linkage (I) according to the position of the nitrogen, namely, the position within the ring (cyclic-imino-esters) and the exposition (imino-lactones). Imino-lactones (VII) are known to react with alcoholic hydroxyl groups readily, but the resultant ester-amides (VIII) are easily cyclized again on heating to form stable cyclic imides (IX) as shown in the following scheme (9).¹¹ So this type of cyclic compound cannot act as an effective chain extender.



In conclusion, we have selected bis(five- or six-membered cyclic imino-esters) as the most promising candidates for hydroxyl-reactive addition-type chain extenders.

CHAIN-EXTENDING REACTIONS

The bis cyclic-imino-esters shown in Table I have been evaluated as chain extenders according to the procedure described in Experimental. The results are shown in Figures 1–3, which indicate that all of the bis(4H-3,1-benzoxazin-4-ones) (BNZ-A-1 to 5, B-1 to 5) tested here were effective chain extenders, although the effects were rather varied. Bis[5(4H)-oxazolones] (OXZ-1, 2) have been proved to be very effective in case of PBT, but rapid decrease in $[\eta]$ after a slight increase has been observed in the case of PET. This is probably due to the thermal degradation of the compounds.

To compare the effectiveness of the hydroxyl-reactive chain extenders quantitatively, the parameter we call "coupling efficiency (CE)" has been

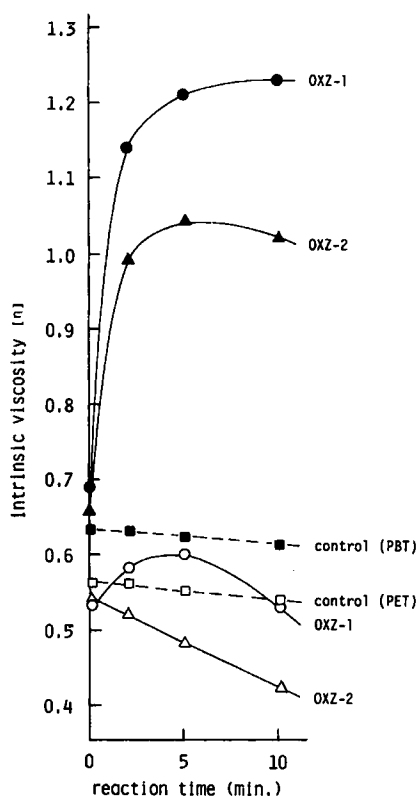


Fig. 1. Chain-extending reaction of PET (○, △) and PBT (●, ▲) with OXZ.

defined as follows, similarly to the case of the carboxyl-reactive chain extenders^{3,4}:

$$\begin{aligned}
 \text{CE}(\%) &= \frac{\text{number of terminal hydroxyl groups} \\ &\quad \text{coupled with one another by the chain} \\ &\quad \text{extender (HV}_c\text{) (eq/10}^6\text{ g)}}{\text{number of the terminal hydroxyl} \\ &\quad \text{groups of the initial polymer} \\ &\quad \text{(HV}_0\text{) (eq/10}^6\text{ g)}} \times 100 \\
 &= \frac{\text{number of decreased terminal} \\ &\quad \text{groups (eq/10}^6\text{ g)}}{\text{HV}_0} \times 100 \quad (10) \\
 &= \frac{N_0 - N_r}{N_0 - CV_0} \times 100
 \end{aligned}$$

where N_0 and N_r mean the numbers of total terminal groups of the initial polymer and the resulting polymer, respectively, and CV_0 means the CV of the initial polymer. We have approximated HV_c to $(N_0 - N_r)$ since only hydroxyl terminals are supposed to be involved in the hydroxyl-reactive

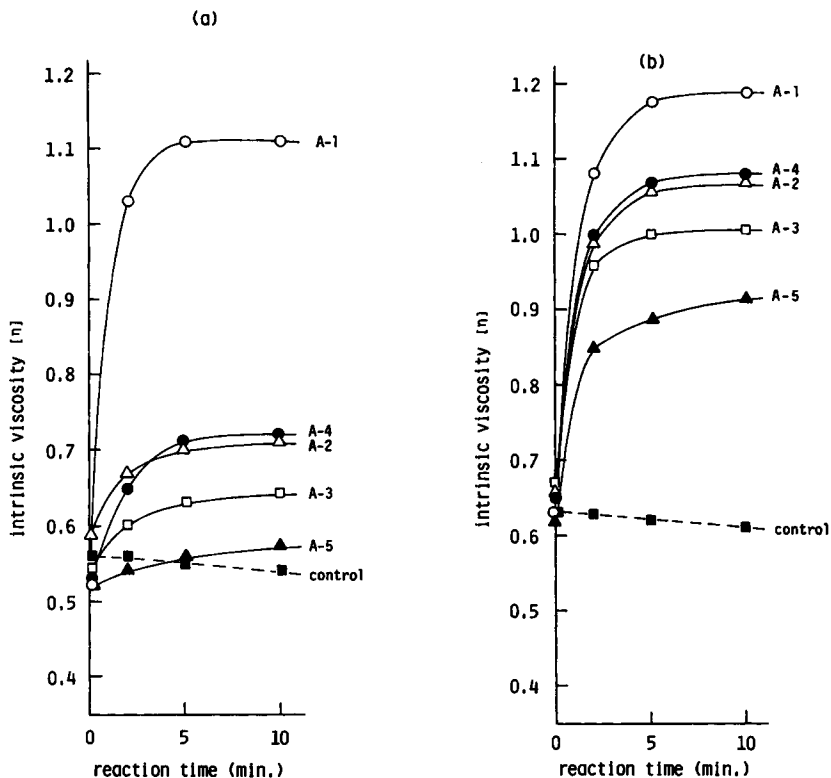


Fig. 2. Chain-extending reaction of PET (a) and PBT (b) with BNZ-A.

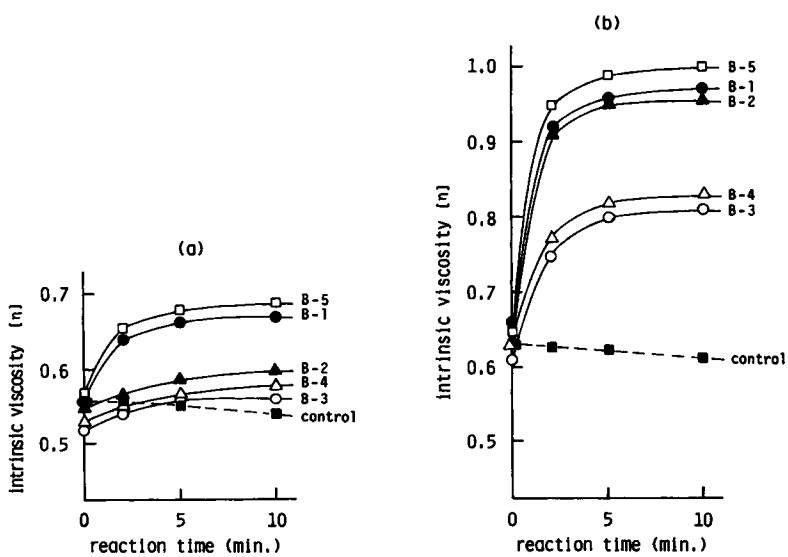


Fig. 3. Chain-extending reaction of PET (a) and PBT (b) with BNZ-B.

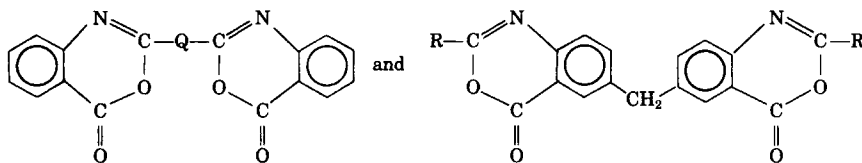
chain-extending reactions. N in eq. (10) can be calculated from $[\eta]$ using the following Mark-Houwink relationship:

$$[\eta] = KM^a = K \left(\frac{2 \times 10^6}{N} \right)^a \quad (11)$$

where M is the number-average molecular weight, and K and a are such empirical constants as $a = 0.77$, $K = 2.75 \times 10^{-4}$ for PET (proposed by Ward¹²) and $a = 0.871$, $K = 1.166 \times 10^{-4}$ for PBT (proposed by Bormann¹³).

In Table II, the CE values of each bis cyclic-imino-ester compounds in a 5-min reaction period are summarized. Among these compounds, 2,2'-bis(4H-3,1-benzoxazin-4-one) (BNZ-A-1) has been proved very reactive. The CE value of this compound is 69% in case of PET. This means that 69% of hydroxyl groups in the initial polymer were bonded to one another through bis cyclic-imino-ester moiety to result in the increase in $[\eta]$.

In Figure 4 are plotted the CE values of BNZ



in both PET and PBT vs. pKa values of the corresponding carboxylic acids ($\text{HO}_2\text{C}-\text{Q}-\text{CO}_2\text{H}$ and $\text{R}-\text{CO}_2\text{H}$). A linear relationship has been observed,

TABLE II
Results of Chain-Extending Reactions of
Bis Cyclic-Imino-Esters with Polyesters

Compound	PET,	CE (%)	PBT,	CE (%)
	change of $[\eta]$ /CV by 5 min chain-extending reaction		change of $[\eta]$ /CV by 5 min chain-extending reaction	
OXZ-1	0.53/10 \rightarrow 0.60/24	16	0.69/13 \rightarrow 1.21/16	55
OXZ-2	0.54/11 \rightarrow 0.48/32	-18	0.66/12 \rightarrow 1.04/15	46
BNZ-A-1	0.52/10 \rightarrow 1.11/13	69	0.63/11 \rightarrow 1.18/14	57
BNZ-A-2	0.59/13 \rightarrow 0.70/15	23	0.66/12 \rightarrow 1.06/15	48
BNZ-A-3	0.54/11 \rightarrow 0.63/13	20	0.67/12 \rightarrow 1.00/16	42
BNZ-A-4	0.52/10 \rightarrow 0.71/12	35	0.64/11 \rightarrow 1.07/14	49
BNZ-A-5	0.52/10 \rightarrow 0.56/13	10	0.62/10 \rightarrow 0.89/13	38
BNZ-B-1	0.56/12 \rightarrow 0.66/14	22	0.66/12 \rightarrow 0.95/15	40
BNZ-B-2	0.55/11 \rightarrow 0.59/14	10	0.64/11 \rightarrow 0.95/14	41
BNZ-B-3	0.52/10 \rightarrow 0.56/13	10	0.61/10 \rightarrow 0.80/14	29
BNZ-B-4	0.53/10 \rightarrow 0.57/13	10	0.63/11 \rightarrow 0.82/14	29
BNZ-B-5	0.57/12 \rightarrow 0.68/14	23	0.56/11 \rightarrow 0.99/14	43
Not added (control)	0.56/12 \rightarrow 0.55/14	—	0.63/11 \rightarrow 0.62/14	—

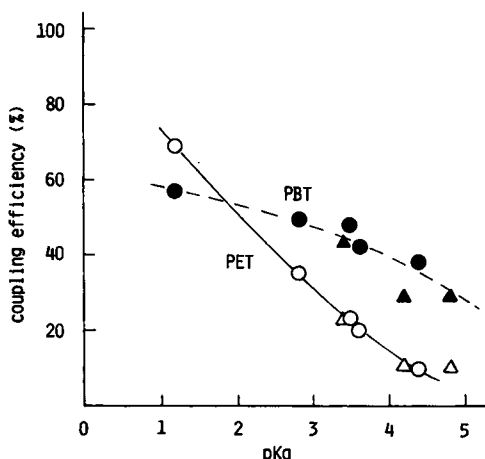


Fig. 4. Plot of CE of BNZ-A $\left(\text{C}_6\text{H}_4 \text{--} \text{N} \text{--} \text{C} \text{--} \text{Q} \text{--} \text{C} \text{--} \text{N} \text{--} \text{C}_6\text{H}_4 \right)$ vs. $\text{pK}a_1$ of $\text{HO}_2\text{C--Q--CO}_2\text{H}$

[PET (○), PBT (●)] and CE of BNZ-B $\left(\text{R--C} \text{--} \text{N} \text{--} \text{C}_6\text{H}_4 \text{--} \text{CH}_2 \text{--} \text{C}_6\text{H}_4 \text{--} \text{N} \text{--} \text{C} \text{--} \text{R} \right)$ vs. $\text{pK}a$ of $\text{R--CO}_2\text{H}$
 [PET (△), PBT (▲)].

and, the more acidic (lower $\text{pK}a$) the carboxylic acid becomes, the higher the CE of the corresponding BNZ becomes.

It is well known that the acidity of a carboxylic acid is determined by the electron density of the carbon atom to which the carboxyl group is attached. Therefore, the reactivity of BNZ as the chain extender depends upon the electron-withdrawing property of the substituent at the 2-position of the 4H-3,1-benzoxazin-4-one-ring, and can be predicted by using Hammett equation.

Figure 4 also show that the reactivity dependence in the case of PBT is smaller than that in the case of PET. Similar behavior was observed in case of carboxyl-reactive addition-type chain extenders.³ Although we can point out some factors which may have caused the difference, such as the polymerization catalyst, the melting behavior, and the reaction temperature, details are yet to be investigated.

CONCLUSION

Bis cyclic-imino-ester compounds tested here have been proved to be effective hydroxyl-reactive addition-type chain extenders for linear polyesters. Especially those having highly electron-withdrawing substituents at the 2-position of the cyclic-imino-esters, such as 2,2'-bis(3,1-benzoxazin-4-one)

(ENZ-A-1) were so highly effective as to give PET and PBT of high $[\eta]$ (above 1.0) within a few minutes of heating under atmospheric nitrogen starting from usual PET and PBT.

More detailed investigation of the reaction behavior of these compounds and the properties of the resulting polymers will be reported later.

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