Chain Extenders for Polyesters. I. Addition-Type Chain Extenders Reactive with Carboxyl End Groups of Polyesters

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Synopsis

Effective chain extenders for linear polyesters were investigated among some bis-heterocycles, which were capable of coupling carboxyl terminals of the polyesters through addition reaction. Consequently, 2,2'-bis(2-oxazoline), 2,2'-bis(5,6-dihydro-4H-1,3-oxazine) and *N,N'*-hexamethylenebis(carbamoyl-2- oxazoline) were found to be the most effective chain extenders. Starting from a poly(ethylene terephthalate) (PET) having intrinsic viscosity ([η]) of 0.66 and carboxyl content (CV) of 46 eq/10^6 g, one could obtain polyesters with [η] of above 1.0 and CV of below 5 eq/10^6 g in the presence of the chain extenders. Typical reaction condition for the coupling of PET was heating PET under atmospheric nitrogen above its melting temperature with 0.5 mol % of a chain extenders only for several minutes. Bis-2-thiazolines showed no effect under the condition investigated, while in case of bis-2-imidazolines definite degradation was observed. Bis-*N*-acylaziridines and bisiminocarbonates resulted in some gell formation, indicative of side reactions.
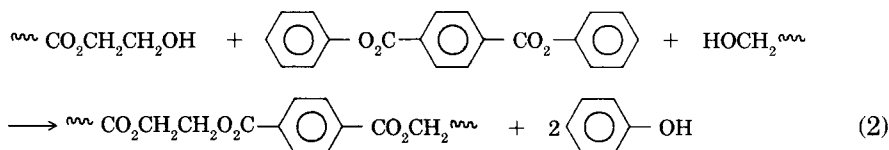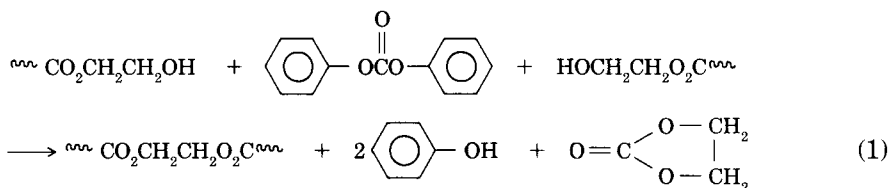
INTRODUCTION

Poly(ethylene terephthalate) (PET) has been one of the most commercially important polymers, which is used as fibers, biaxially-oriented films, blow-molded bottles, and fiber-reinforced plastics. It is well known in practical use of PET that the increase in molecular weight of the polymer and the decrease in the number of the carboxylic end group help to improve significantly the tensile and thermal properties of PET products. Such improvement is desired in most uses of industrial PET yarns.

In a usual melt polycondensation of PET, however, it is very difficult to obtain the polymers having an intrinsic viscosity ([η]) above 0.9 and carboxyl content (CV) below 15 eq/10^6 g. As the polycondensation proceeds, the reaction rate decreases and the degradation of the terminal groups occurs leading to the increase in CV.
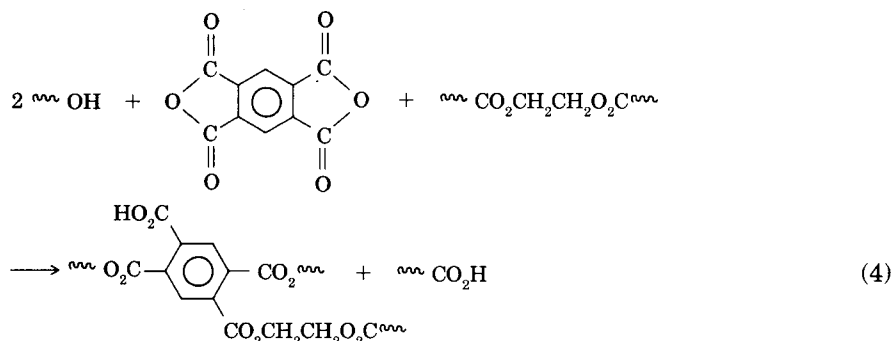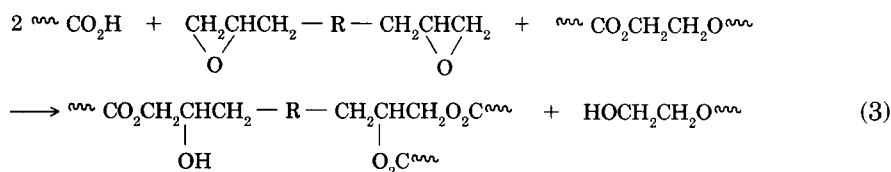
To overcome the above limitations, post-polycondensation in a solid phase has been usually applied. The disadvantages in this case are the very slow reaction rate and the needs for a special equipment for the large scale operation. Another method proposed is to use so-called "chain extender," which can react with the polymer end groups more readily, resulting in the higher-molecular-weight polymers when it is added to the melt polycondensation systems. Such active diesters as diphenyl carbonate, diphenyl terephthalate, diphenyl oxalate, and phenyl orthocarbonate were reported to be effective chain extenders.[1] The following schemes of the chain-ex-

tending reactions show that phenol and ethylene carbonate are the by-products:

$$\sim CO_2CH_2CH_2OH \; + \; \langle\!\bigcirc\!\rangle\!-\!OCO\!-\!\langle\!\bigcirc\!\rangle \; + \; HOCH_2CH_2O_2C\!\sim$$

$$\longrightarrow \sim CO_2CH_2CH_2O_2C\!\sim \; + \; 2\langle\!\bigcirc\!\rangle\!-\!OH \; + \; O\!=\!C\!\underset{O-CH_2}{\overset{O-CH_2}{<}} \qquad (1)$$

$$\sim CO_2CH_2CH_2OH \; + \; \langle\!\bigcirc\!\rangle\!-\!O_2C\!-\!\langle\!\bigcirc\!\rangle\!-\!CO_2\!-\!\langle\!\bigcirc\!\rangle \; + \; HOCH_2\!\sim$$

$$\longrightarrow \sim CO_2CH_2CH_2O_2C\!-\!\langle\!\bigcirc\!\rangle\!-\!CO_2CH_2\!\sim \; + \; 2\langle\!\bigcirc\!\rangle\!-\!OH \qquad (2)$$

Needs for the complete removal of such byproducts having a rather high boiling point from the resultant polymers and contaminations of the re-covered ethylene glycol with them may cause some troubles on applying them to commercial PET productions.

Therefore, "addition-type chain extender" generating no byproduct is much preferred. Uses of bisepoxy compounds, bis(cyclic carboxylic anhy-dride), and diisocyanates as the addition-type chain extenders have been proposed.[2] But, as shown in the followng schemes, the above compounds unavoidably give rise to branching and/or introductions of less thermally stable linkages in the polymer chains.

$$2 \sim CO_2H \; + \; CH_2CHCH_2\!-\!R\!-\!CH_2CHCH_2 \; + \; \sim CO_2CH_2CH_2O\!\sim$$
$$\underset{O}{\diagup\!\!\diagdown} \qquad \underset{O}{\diagup\!\!\diagdown}$$

$$\longrightarrow \sim CO_2CH_2CHCH_2\!-\!R\!-\!CH_2CHCH_2O_2C\!\sim \; + \; HOCH_2CH_2O\!\sim \qquad (3)$$
$$\underset{OH}{|} \qquad\qquad \underset{O_2C\!\sim}{|}$$

$$2 \sim OH \; + \; O\overset{\overset{O}{\parallel}C}{\underset{\underset{O}{\parallel}C}{\diagup}}\!\langle\!\bigcirc\!\rangle\!\overset{\overset{O}{\parallel}C}{\underset{\underset{O}{\parallel}C}{\diagdown}}O \; + \; \sim CO_2CH_2CH_2O_2C\!\sim$$

$$\longrightarrow \sim O_2C\!-\!\underset{CO_2CH_2CH_2O_2C\!\sim}{\overset{HO_2C}{\langle\!\bigcirc\!\rangle}}\!-\!CO_2\!\sim \; + \; \sim CO_2H \qquad (4)$$

In the present paper, we would like to report the results from our attempts to find more effective addition-type chain extenders using such bis-heter-ocyclic compounds as bis-2-oxazolines (I), bis-5,6-dihydro-4H-1,3-oxazines (II), bis-2-thiazolines (III), bis-2-imidazolines (IV), bis-N-acylaziridines (V), and bis-iminocarbonates (VI), which have been known to be reactive with car-

boxyl groups to form addition products. The carboxyl-reacting chain extenders should be more advantageous than the hydroxyl-reacting ones, since the reduction of CV can also be attained simultaneously.

The following are the proposed reaction schemes:

$$\sim CO_2H \;+\; A-D-A \;+\; HO_2C\sim$$
$$\longrightarrow \sim COA^1-D-A^2OC\sim \tag{5}$$
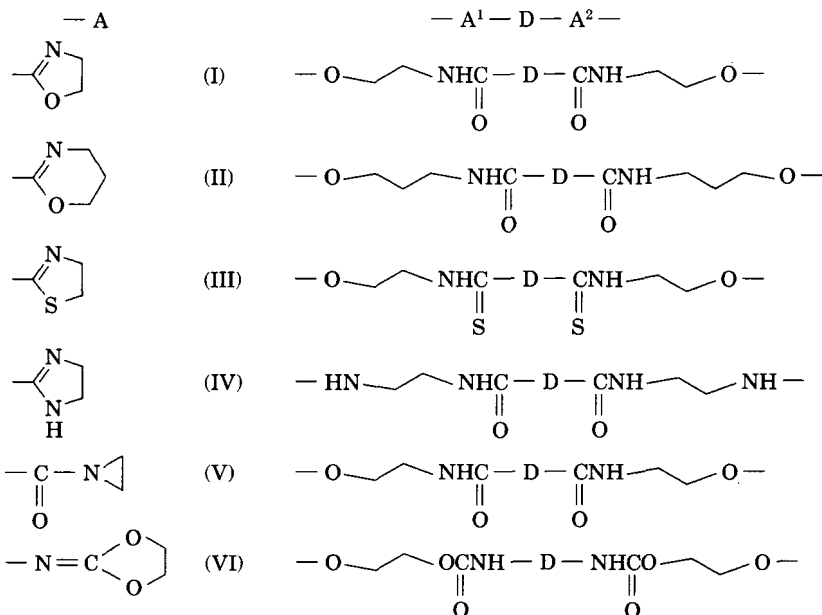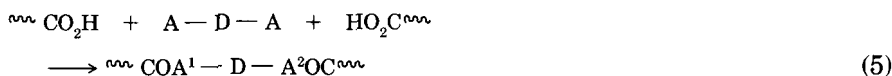
Some of the above compounds have been proved very effective as practical chain extenders.

EXPERIMENTAL

Materials

Bis-2-oxazolines and bis-5,6-dihydro-4H-1,3-oxazines were prepared as previously reported[3] by the cyclizing reaction of the corresponding N,N'-bis-chloroalkylamide under the presence of potassium hydroxide or sodium alcoxide.
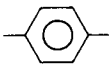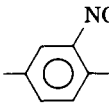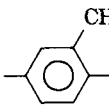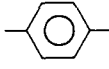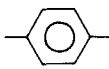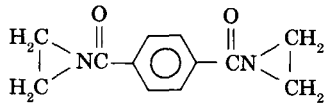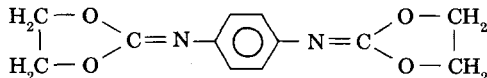
N,N'-hexamethylenebis(2-carbamoyl-2-oxazoline) was obtained according to the following procedure.

A mixture of 18 g of 2-chloroethyl oxamic acid ethyl ester and 5.8 g of hexamethylenediamine was dissolved in 250 mL ethanol, and the solution was refluxed for 30 min. After cooling, to this was added 6.1 g of sodium methoxide, and the reaction was carried out under refluxing of ethanol for 30 min. The reaction product was concentrated by evaporating ethanol, extracted with hot xylene and recrystallized; 9.0 g of N,N'-hexamethylenebis(2-carbamoyl-2-oxazoline) was yielded.

2,2'-p-Phenylenebis(2-thiazoline),[4] 2,2'-bis(2-imidazoline),[5] N,N'-tere-phthaloylbisaziridine,[6] and N,N'-p-phenylenebis(ethylene iminocarbonate)[7] were prepared according to the method described in the literature. Recrystallization solvents and melting points of the compounds prepared here are summerized in Table I.

PET was prepared from dimethyl terephthalate and ethylene glycol by the ordinary melt polycondensation using Sb_2O_3 (0.03 mol %) and $Mn(OAc)_2 \cdot 4H_2O$ (0.04 mol %) as catalysts and $(CH_3O)_3P{=}O$ (0.05 mol %) as a stabilizer. The molten polymer obtained was cooled and pulverized, which had $[\eta]$ of 0.75 and CV of 34 eq/10^6 g.

TABLE I
Synthesis of Bis-Heterocyclic Compounds

Compound			Melting point (°C)	Recrystallization solvent
— R — X —	— D —			
— CH_2CH_2O —	—	(I-a)	213–214	Dioxane
	(phenylene)	(I-b)	> 300	Ethanol
	(phenylene-NO_2)	(I-c)	115–116	Ethanol
	(phenylene-CH_3)	(I-d)	95–96	Ethanol
	— $(CH_2)_4$ —	(I-e)	42–46	Ethanol
	— $CONH(CH_2)_6NHOC$ —	(I-f)	148–151	Xylene
— $CH_2CH(CH_3)O$ —	—	(I-g)	83–85	n–Hexane
	(phenylene)	(I-h)	102–104	Dioxane
— $C(CH_3)_2CH_2O$ —	—	(I-i)	111–114	n-Heptane
— $CH_2CH_2CH_2O$ —	—	(II-a)	192–195	Toluene
	(phenylene)	(II-b)	212–215	Ethanol/NaOH
— CH_2CH_2S —	(phenylene)	(III-a)	168–171	Ethanol
— CH_2CH_2NH —	—	(IV-a)	290–295	Benzonitrile
(V-a structure)		(V-a)	152–154	Acetone
(VI-a structure)		(VI-a)	188–190	Xylene

Poly(butylene terephthalate) (PBT) was prepared from dimethyl tere-phthalate and 1,4-butanediol by ordinary melt polycondensation using Ti(O n-C_4H_9)$_4$ (0.02 mol %) as a catalyst. The resultant PBT had [η] of 0.86 and CV of 39 eq/10^6 g.

Chain-Extending Reaction

To a 500-mL three-necked, round-bottom flask, equipped with a mechanical stirrer, nitrogen inlet, and outlet tube, 100 g of the dry polymer chips 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 in the case of PET and at 250°C in the case of PBT. After 40 min all polymer chips were melted, and a chain extender was added under stirring. The amount of the chain extender added was 0.5 mol % per polymer recurring unit in the case of PET and 0.6 mol % per polymer recurring unit in case of PBT. After a predetermined period of reaction, [η] and CV of the resulting polymer were measured.
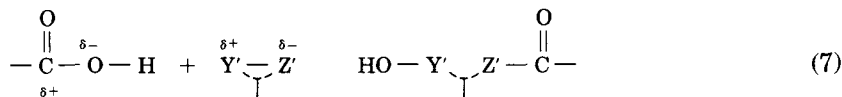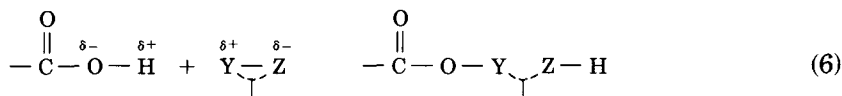
Analytical Procedures

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

CV (eq/10^6 g) was measured by the Conix method.[8]

RESULTS AND DISCUSSION

Selection of Carboxyl-Reactive Chain-Extending Groups

In the addition reactions involving carboxyl groups, the carboxyls can act as either nucleophiles or electrophiles according to reacting groups and reaction conditions, as formularized as follows:

$$-\overset{\overset{\text{O}}{\|}}{\text{C}} - \overset{\delta-}{\text{O}} - \overset{\delta+}{\text{H}} \ + \ \overset{\delta+}{\text{Y}} \cdots \overset{\delta-}{\text{Z}} \qquad -\overset{\overset{\text{O}}{\|}}{\text{C}} - \text{O} - \text{Y} \cdots \text{Z} - \text{H} \tag{6}$$

$$-\overset{\overset{\text{O}}{\|}}{\underset{\delta+}{\text{C}}} - \overset{\delta-}{\text{O}} - \text{H} \ + \ \overset{\delta+}{\text{Y}'} \cdots \overset{\delta-}{\text{Z}'} \qquad \text{HO} - \text{Y}' \cdots \text{Z}' - \overset{\overset{\text{O}}{\|}}{\text{C}} - \tag{7}$$

Here "Y$\cdots$Z" and "Y'$\cdots$Z'" mean multiple bond groups (which may be regarded as two-membered rings) or cyclic groups, and "Y" and "Y'" should have electrophilic or electron-deficient properties while "Z" and "Z'" should be nucleophilic or electron-sufficient atoms. In the polyester chain terminals, hydroxyl groups usually coexist with carboxyl groups. To be the effective carboxyl-reacting chain-extending groups, they have to react with the carboxyl groups more preferentially than hydroxyl groups. In the ester-forming reactions, hydroxyl groups are regarded as stronger nucleophiles than carboxyl groups, since the formers react with the lat-

ters as nucleophiles. From this viewpoint, the chain-extending groups which react as nucleophiles with carboxylic acids seem to be preferable. But it is also well known that there are many exceptional cases, where carboxylic acids react more preferentially than hydroxyl groups with electrophilic groups such as epoxy groups.[2] Accordingly, it may be conclusive that we have to consider both possibilities in selecting the suitable carboxyl-reactive groups.

In case that "Y—Z" and "Y'—Z'" mean multiple bonds they correspond to $>C=C<$, $-C\equiv C-$, $>C=O$, $>C=S$, $>C=N-$, and

$-C\equiv N$. Some ethenyl and ethinyl groups can react with carboxylic acids through addition reactions. But when they are applied in the chain extenders, they are so active as to be subject to polymerization, which leads to crosslinking of the polymers. As is well known, simple carbonyl, thiocarbonyl, imino and cyano groups are not reactive with carboxyl groups in the addition reaction. More reactive allene-type groups such as ketene, thioisocyanate, isocyanate, and carbodiimide groups can easily react with carboxyl groups to form unstable addition products. The ketenes and isocyanates, however, more readily react as electrophiles with hydroxyl groups than carboxyl groups. They may be used as hydroxyl-reactive chain extenders.[2] The use of carbodiimide compounds as a "CV reducer" for PET has already been published.[9] In this case, carbodiimides probably act as dehydrating or condensing agents to form ester linkages and corresponding ureas from hydroxyl and carboxyl terminals. They can be regarded as a variation of the chain extenders, but at least not as addition-type chain extenders. The discussion above may lead to the conclusion that it is very improbable that we can find a new effective carboxyl-reactive addition-type chain extender when "Y—Z" and "Y'—Z'" mean

multiple bonds.

In case that "Y—Z" and "Y'—Z'" mean cyclic groups we can select: (i) carbon atom for "Y" or "Y'" and a naturally electron negative atom such as oxygen, nitrogen or sulfur for "Z" or "Z'", and (ii) carbons for both atoms, either of which is electron negative or positive due to attached groups. In the case of addition reactions of carboxyl groups to cyclic groups, it is very rare that carbon—carbon scission in the cyclic groups occurs, differently from the case of the addition to the multiple bonds mentioned before. We have decided to pursue only the former combinations (i). In this case, "−Z−H" in the resultant linkage corresponds to $-OH$, $-SH$, and $-NH$. But the resultant linkage $-\overset{O}{\overset{\|}{C}}OC\diagdown Z-H$

and $HO-C\diagup Z'C-$ should not contain simple hydroxyl, thiol, and amino groups, which are reactive with esters or carboxyls. To meet the above requirement, the $-OH$, $-SH$, and $-NH$ have to be attached to a carbon atom having a double bond. This means that "$-Z-H$" can be

shown as $(-N=C-OH \rightarrow -NHC=O)$, $(-C=C-OH \rightarrow \,>CH-C=O)$,

$(O=C-NH)$, $(-N=C-NH)$, and $(-N=C-SH \rightarrow -NH-C=S)$ and that

$HOY'-$ can be shown as $(HO-C=N- \rightarrow O=C-NH-)$ and $(HO-$

$C=C< \rightarrow O=C-CH<)$. Accordingly, "Y$\rightleftharpoons$Z" and "Y'$\rightleftharpoons$Z'" can contain

the following linkages; $-C-O-C=N-$, $-C-O-C=C<$, $-C-N-$

$C=O$, $-C-N-C=N-$, $-C-S-C=N-$, $-C-S-C=C,<$ and $-C-$

$N-C=C<$.

Thus we have tried the selection of the functional groups for the carboxyl-reactive addition-type chain extenders using the following requisites:

(i) having a from three- to six-membered ring;

(ii) containing such linkage as $-C-O-C=N-$, $-C-O-C=C<$,

$-C-N-C=O$, $-C-N-C=N-$, $-C-S-C=N-$, $-C-S-C=$
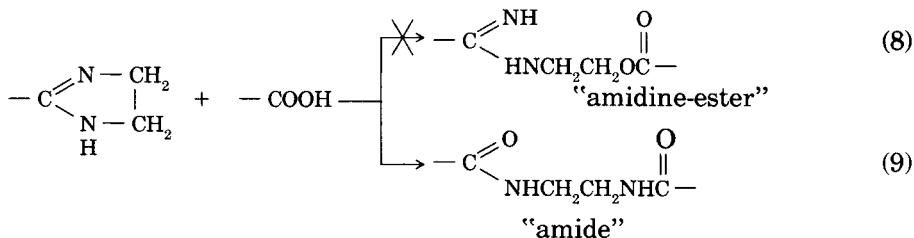
$C<$, and $-C-N-C=C<$,

(iii) being preparable with not too much difficulty, and stable enough to be applied in the polyester melts;

(iv) being known to be reactive with carboxyl groups to form stable addition products.

The resultant candidates are those heterocyclic groups (I)–(VI) mentioned in the Introduction. Most of the above heterocyclic groups have already been applied to the formation of linear or crosslinked polymers using the reaction with carboxyl groups.[6,7,10,11]

There arises a question which reaction scheme of (6) and (7) these heterocycles will take in the addition reactions with carboxyl groups. In the case of (I), (II), and (VI), we cannot judge which is which from the resultant products since the products are the same no matter which scheme the reaction follows. It was reported that 2-oxazolines (I) react with carboxylic acid through the ring opening between the 1- and 5-positions of (I).[10] This means that the above reaction follows eq. (6). It is very likely that 4H-1,3-oxazines (II) and thiazolines (III) react similary to (I), considering the analogous structure of these heterocycles. In case of iminocarbonates (VI) the literature[7] suggests eq. (6). Judging from the reaction product, N-acylaziridines (V) should react with carboxyl groups through eq. (6). In the case of imidazoline (IV), if carboxyl groups react as nucleophiles [eq. (6)], the products should be "amidine–ester" as shown in eq. (8), and if they react as electrophiles [eq. (7)], "diamide" in eq. (9) should result. According to the

literature,[11] the resultant product has been proved to be the latter as shown below.

$$\underset{\text{H}}{-}\overset{\text{N---CH}_2}{\underset{\text{N---CH}_2}{C}} \; + \; -\text{COOH} \longrightarrow \left[\begin{array}{l} \overset{\overset{\displaystyle\times}{}}{-}\overset{\text{NH}}{\underset{\text{HNCH}_2\text{CH}_2\text{OC}\,-}{C}} \qquad \overset{\text{O}}{\underset{}{\|}} \\[2em] \longrightarrow -\overset{\text{O}}{\underset{\text{NHCH}_2\text{CH}_2\text{NHC}\,-}{C}} \qquad \overset{\text{O}}{\underset{}{\|}} \end{array} \right. \qquad (8)$$

"amidine-ester"

"amide"   (9)

Therefore, it can be conclusive that (IV) reacts with carboxyl groups through eq. (7).

Bis Cyclic-Imino Compounds (I)–(IV)

Usually, the remelt of polyester chips is accompanied by the decrease in $[\eta]$ and increase in CV, even when the chips are well dried. Therefore, we confirmed that the value of $[\eta]/\text{CV}$ was changed from 0.75/34 to 0.66/46 in case of PET, and from 0.86/39 to 0.75/55 in case of PBT, immediately after remelting.

The bis cyclic-imino compounds shown in Table I have been evaluated as the chain extenders according to the procedures described in Experimental. The results are shown in Figures 1 and 2.

The data indicated that all the bis cyclic–imino–ether compounds tested here (I-a–i, II-a, b) were effective chain extenders although the effects were
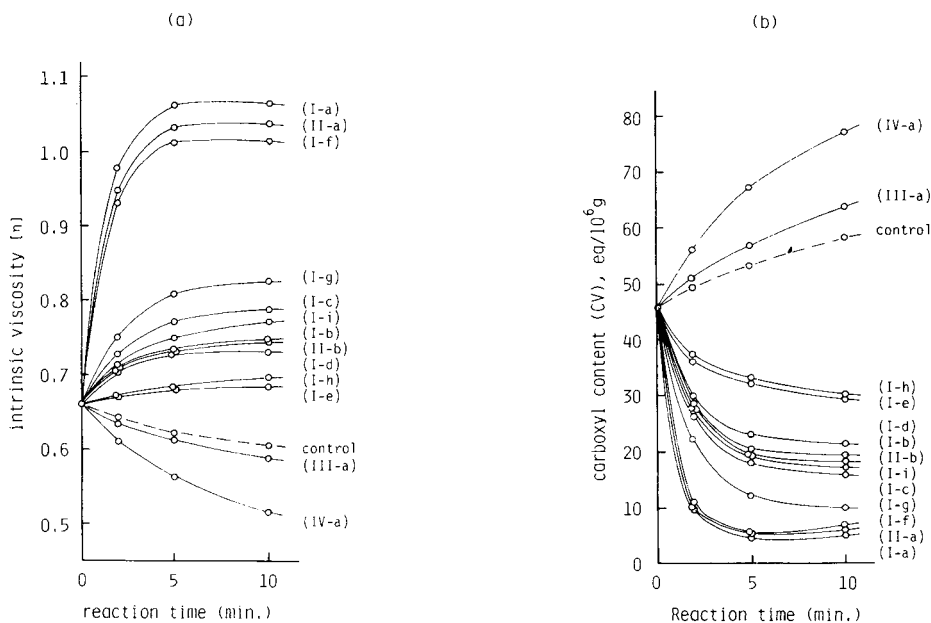

Fig. 1.   Chain-extending reaction of PET with bis cyclic—imino compounds. Variation of $[\eta]$ (a) and CV (b) with reaction time.
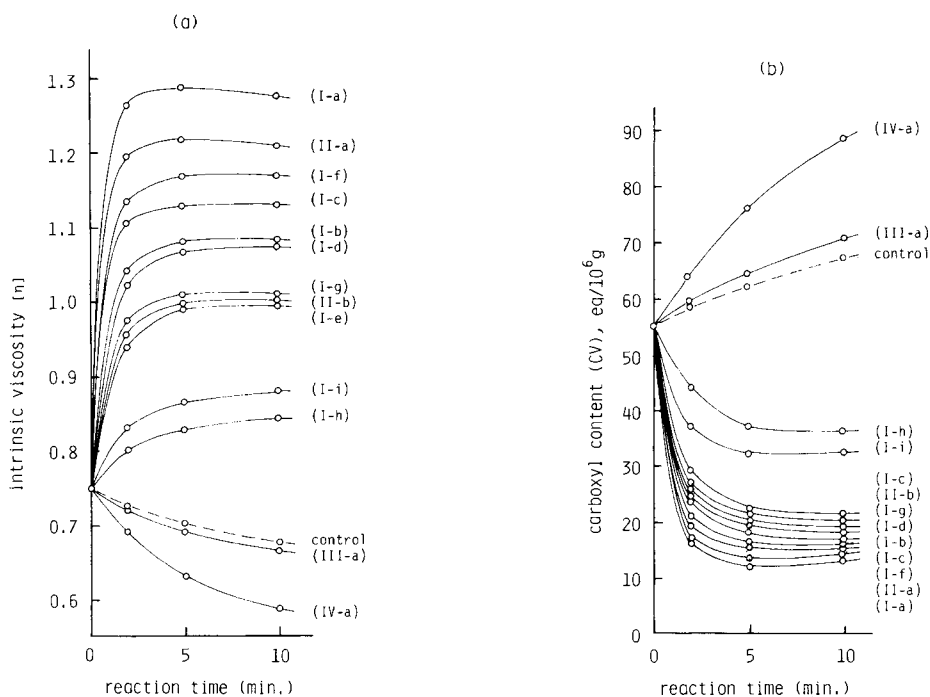
Fig. 2. Chain-extending reaction of PBT with bis cyclic—imino compounds. Variation of [η] (a) and CV (b) with reaction time.

rather varied, whereas bis-2-thiazoline (III-a) showed no effect and bis-2-imidazoline (IV-a) showed a reverse effect.

No effectiveness of bis-2-thiazoline can be attributed to the very low electron-withdrawing property of sulfur atom.

In case of N-unsubstituted imidazolines, they can be regarded to have a secondaly amine, which is reactive with esters and carboxylic acid to form N-acylimidazolines. It is probable that such reaction between bis-2-imidazoline and esters to result in the polyester-chain scission occurs preferentially or at least competitively with the chain-extending reaction. This may be the reason why the bis-2- imidazoline (IV-a) showed a reverse effect in spite of their known high reactivities with carboxylic acids.[11]

To compare the effectiveness (or reactivities) of the chain extenders quantitatively, the parameter we call "coupling efficiency" (CE) has been defined as follows:

$$CE(\%) = \frac{\text{number of terminal carboxyl groups coupled with one another by the chain extenders } [CV_c] \text{ (eq}/10^6 \text{ g)}}{\text{initial CV of the polymer } [CV_0]} \times 100$$

$$= \frac{\text{number of decreased terminal groups } [\Delta N] \text{ (eq}/10^6 g)}{CV_0} \times 100$$

$$= \frac{N_0 - N_r}{CV_0} \times 100 \tag{10}$$

where N_0 and N_r mean the numbers of the total terminal groups of the initial polymer and the resulting polymer, respectively. Simple decrease of the terminal carboxyl groups can be easily calculated by CV measurement, but ΔCCV as defined above cannot be measured by the analogous means. We have approximated it to ΔN, which can be calculated by measurement of the number-average molecular weights. Namely, N_0 and N_r in eq. (10) has been calculated from $[\eta]$ using the Mark–Houwink equation shown below:

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

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 Ward[12]), and $a = 0.871$, $K = 1.166 \times 10^{-4}$ for PBT (proposed by Bormann[13]).

In Table II, the CE values of each bis cyclic–imino compounds in 5-min reaction period are summarized.

Among these bis cyclic–imino–ether compounds, 2,2'-bis(2-oxazoline) (I-a), 2,2'-bis(5,6-dihydro-4H-1,3-oxazine) (II-a), and N,N'-hexamethylenebis(2-carbamoyl-2-oxazoline) (I-f), which have a strong electron withdrawing group at 2-position, have been proved very reactive and gave polyesters having higher $[\eta]$ and lower CV than those of the initial polymer chips before remelting. The CE values for these compounds fell in the range of 80% in the case of PET. This means that about 80% of carboxyl groups in the initial polymer were bonded to each other through bis cyclic–imino–ether moiety, resulting in an increase in $[\eta]$.
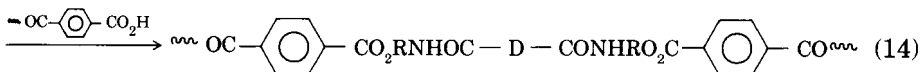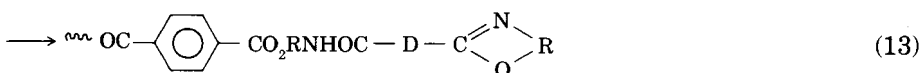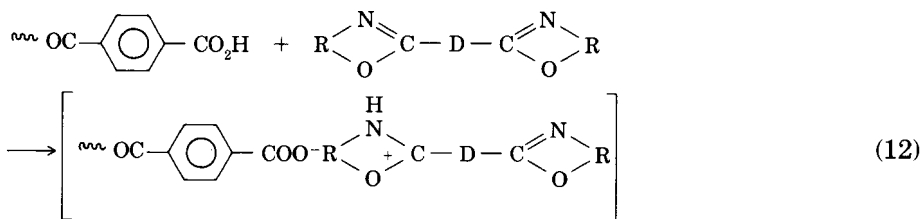
TABLE II
Results of Chain-Extending Reaction of Bis-Heterocyclic Compounds with Polyesters

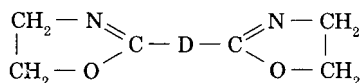| Compound | PET[a] | | PBT[b] | |
	[η]/CV of the resulting polymer after 5 min reaction	CE (%)	[η]/CV of the resulting polymer after 5 min reaction	CE (%)
(I-a)	1.06/4	81	1.29/12	71
(I-b)	0.72/20	22	1.08/18	53
(I-c)	0.77/18	32	1.13/16	58
(I-d)	0.72/23	19	1.07/19	52
(I-e)	0.68/32	7	0.99/15	43
(I-f)	1.01/5	75	1.17/15	62
(I-g)	0.81/12	41	1.01/20	45
(I-h)	0.68/33	7	0.83/37	17
(I-i)	0.75/19	27	0.87/32	24
(II-a)	1.03/5	78	1.22/13	66
(II-b)	0.73/19	22	1.00/21	43
(III-a)	0.61/57	−19	0.69/64	−15
(IV-a)	0.56/67	−42	0.63/75	−34
Not added (control)	0.62/53	−15	0.70/62	−13

[a] [η]/CV of initial polymer is 0.66/46.
[b] [η]/CV of initial polymer is 0.75/55.

The reaction scheme of bis cyclic–imino–ether compounds with polyesters can be shown as follows:

$$\text{OC}-\langle\bigcirc\rangle-CO_2H \ + \ R-\underset{O}{\overset{N}{\diagdown}}C-D-C\overset{N}{\underset{O}{\diagup}}R$$

$$\longrightarrow \left[\text{OC}-\langle\bigcirc\rangle-COO^-R\underset{O}{\overset{H\\N}{\diagdown}}\overset{+}{C}-D-C\overset{N}{\underset{O}{\diagup}}R \right] \tag{12}$$

$$\longrightarrow \text{OC}-\langle\bigcirc\rangle-CO_2RNHOC-D-C\overset{N}{\underset{O}{\diagup}}R \tag{13}$$

$$\xrightarrow{\text{OC}-\langle\bigcirc\rangle-CO_2H} \text{OC}-\langle\bigcirc\rangle-CO_2RNHOC-D-CONHRO_2C-\langle\bigcirc\rangle-CO \tag{14}$$

In Figure 3 are plotted the CE of bis-2-oxazolines

$$\begin{array}{ccc}CH_2-N & & N-CH_2 \\ | & \diagup C-D-C\diagdown & | \\ CH_2-O & & O-CH_2\end{array}$$

in both PET and PBT vs. pKa_1 value of the corresponding dicarboxylic acids ($HO_2C-D-CO_2H$). A linear relationship has been observed.

It is well known that the acidity of a carboxylic acid is dominated by the electron density of the carbon atom to which the carboxyl group is attached, that is, the stronger the electron-withdrawing property of the residual group
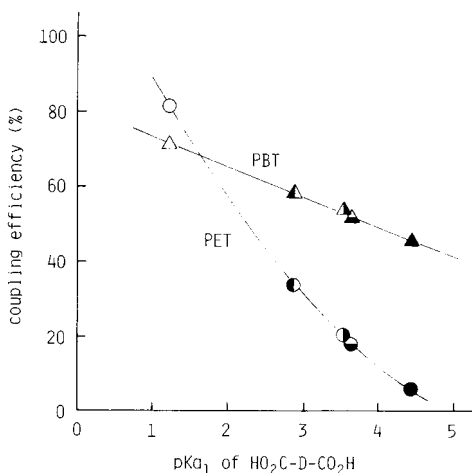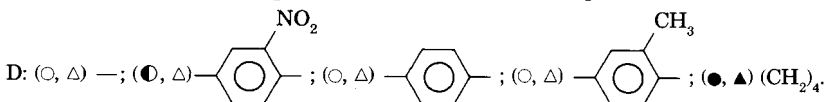

Fig. 3. Polt of CE of $\begin{array}{ccc}CH_2-N & & N-CH_2 \\ | & \diagup C-D-C\diagdown & | \\ CH_2-O & & O-CH_2\end{array}$ vs. pKa_1 of $HO_2C-D-CO_2H$.

D: (○, △) —; (◐, △)—$\langle\bigcirc\rangle$(NO$_2$) ; (○, △) —$\langle\bigcirc\rangle$— ; (○, △) —$\langle\bigcirc\rangle$(CH$_3$)— ; (●, ▲) (CH$_2$)$_4$.

of the carboxylic acid becomes, the more acidic (lower pKa) the carboxylic acid becomes, ruled by the Hammett equation.[14]

Therefore, the relationship observed above means that the reactivity of bis-2-oxazolines as the chain extender is dependent upon the electron-withdrawing property of the substituent at 2-position of the oxazoline ring, and can be predicted by using the Hammett equation.

Figure 3 also shows that the reactivity dependence in the case of PBT is smaller than that in the case of PET. This means that the Hammett's reaction constant (ρ value) for the chain-extending reaction using bis-2-oxazolines is different between PET and PBT. Although we can point out some factors which may cause the difference, such as the polymerization catalyst, the melting behavior, and the reaction temperature, the details have not yet been investigated.

Bis-N-Acylaziridines (V) and Bis-Iminocarbonates (VI)

The evaluation results on (V-a) and (VI-a) as the chain extender in terms of changes in [η] and CV are shown in Figure 4. These data suggest both compounds can act as effective chain extenders. The problem we have found, however, is that some gels are formed during the chain-extending reaction. Both aziridine and iminocarbonate are known to subject to ring-opening polymerization.[15] The gellation here may be caused by such self-polymerization. In conclusion, both bis-N-acylaziridines and bisiminocarbonates are not effective chain extenders for linear polyesters.

CONCLUSION

Among the bis-heterocyclic compounds tested here, bis-2-oxazolines and bis-5,6-dihydro-4H-1,3-oxazines have been proved to be the effective chain extenders for linear polyesters. Especially those having highly electron-withdrawing substituents at 2-position of the cyclic–imino–ethers, such as 2,2'-bis(2-oxazoline) (I-a), 2,2'-bis(5,6-dihydro-4H-1,3-oxazine) (II-a), and N,N'-hexamethylenebis(2-carbamoyl-2-oxazoline) (I-f) were so highly effective as to result in PET and PBT of high [η] (above 1.0) and low CV (below 5 eq/
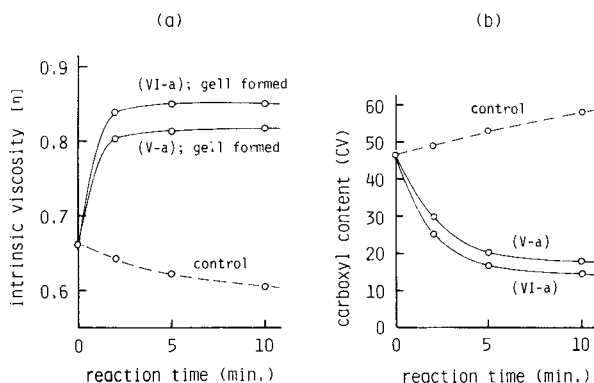

Fig. 4. Chain-extending reaction of PET with bis-N-acylaziridine and bisiminocarbonate. Variation of [η] (a) and CV (b) with reaction time.

10^6 g) within a few minutes of heating under atmospheric nitrogen from usual PET and PBT.

On the other hand, bis-2-thiazolines (III) showed no effect and bis-2-imidazolines (IV) assisted definite degradation of the polyesters.

Bis-*N*-acylaziridines (V) and bisiminocarbonates (VI) were found to form some gells during the chain-extending reaction probably due to their self-polymerization.

Consequently, bis-2-oxazolines and bis-5,6-dihydro-4H-1,3-oxazines are expected to be the most promising classes of compounds for practical chain extenders. More detailed investigation on these compounds, including their reaction behaviors and the properties of the chain-extended polyesters will be reported later.

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