Chain Extenders for Polyester. II. Reactivities of Carboxyl-Addition-Type Chain Extenders; Bis Cyclic-Imino-Ethers

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Synopsis

The reaction behavior of such bis cyclic-imino-ethers as 2, 2'-bis(2-oxazoline), which had been proved in the previous paper to be an effective chain extender to couple carboxyl terminals of linear polyesters through addition reaction, has been studied to evaluate their practical applicability as the chain extenders for poly(ethylene terephthalate) and poly(butylene terephthalate). It has been observed that a wide range of excess use of 2,2'-bis(2-oxazoline) resulted in polyesters of almost similar molecular weight. In addition, when excess amounts of the chain extender were added and the reaction conditions were fixed, the ratio of the coupled carboxyl terminals to the initial carboxyl terminals became constant regardless of the initial molecular weight and carboxyl content (CV). The results indicate that the chain-extended polyesters possess predetermined molecular weight and CV, both of which depend only on the molecular weight and CV of the initial polymers, and not on the amount of the chain extender added.

INTRODUCTION

Poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are well known as commercially important polymeric materials. Many studies have been carried out to improve their performances. Among such studies, a technology to manufacture the polymers of very high molecular weight and low carboxyl content has been regarded as very significant to improve their mechanical and chemical properties such as tenacity and hydrolytic stability. The use of so-called "chain extenders" seems attractive for that purpose. The chain extenders here mean bifunctional compounds which can react with the polymer end groups very readily, when they are added to the polymer melts, resulting in the higher-molecular-weight polymers easily.

For the last several years, we have been making efforts to find more effective chain extenders, especially "addition-type chain extenders," which are reactive with the polymer terminal groups through addition reactions without generating any byproducts.

Our previous paper reported that bis cyclic-imino-ether compounds had been proved to be effective carboxyl-addition type chain extenders.[1] Especially, those having highly electron-withdrawing substituents at the 2-position of the cyclic-imino-ethers, such as 2,2'-bis(2-oxazoline), 2,2'-bis(5,6-dihydro-4H-1,3-oxazine), and N,N'-hexamethylenebis (2-carbamoyl-2-oxazoline) were so highly effective as to result in PET having intrinsic viscosity ([η]) above 1.0 and carboxyl content (CV) below 5 eq/10⁶ g starting from

PET having $[\eta]$ of 0.66 and CV of 46 eq/10^6g within a few minutes at polyester melt temperatures under atmospheric pressure.

In the present paper, we would like to report more detailed evaluation on the reaction behavior of the above bis cyclic-imino-ethers as the chain extenders. As previously reported, the chain extending reaction proceeded so fast that we suspected it might be very difficult to obtain polyesters having predetermined $[\eta]$ and CV with good reproducibility. Therefore, we decided to carry out the present study of evaluating the practical potentiality of the above chain extenders. The results reported here show that the extenders are so far quite promising.

EXPERIMENTAL

Materials

2,2'-Bis(2-oxazoline)[2], 2,2'-bis(5,6-dihydro-4H-1, 3-oxazine),[3] and N,N'-hexamethylenebis (2-carbamoyl-2-oxazoline)[1] were prepared as previously reported.

PET and PBT having various $[\eta]$ and CV were prepared by changing reaction conditions such as temperature, pressure, or time from dimethyl terephthalate and ethylene glycol or 1,4-butanediol by the ordinary polycondensation method, using Sb_2O_3 (0.03 mol %) and $Mn(OCOCH_3)_2 \cdot 4H_2O$ (0.04 mol %) as catalyst and $(CH_3O)_3P{=}O$ (0.05 mol %) as a stabilizer in case of PET, and $Ti(O{-}nC_4H_9)_4$ (0.02 mol %) as catalyst in case of PBT.

CHAIN-EXTENDING REACTIONS

Method A. To a 500-mL three-necked, round-bottom flask, equipped with a mechanical stirrer, a nitrogen inlet, and an 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. All polymer chips were melted in 30 min, and then a prescribed amount of the chain extender was added under stirring. After a predetermined period of the reaction, $[\eta]$ and CV of the resulting polymer were measured.

Method B for PET. A predetermined amount of dry PET chips pulverized to about 10–20 mesh and chain extender were dry-blended well and then melt-extruded by a 30 mmϕ extruder at about 290°C with an average residence time of about 3 min. $[\eta]$ and CV of the extruded polymer were measured.

ANALYTICAL PROCEDURES

$[\eta]$ 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/10^6 g polymer) was measured by the Conix method.[4]

RESULTS AND DISCUSSION

Effect of Added Amount of the Chain Extenders

In chain-extending reactions by bis cyclic-imino-ethers, reaction behavior of carboxyl terminals contained in the initial polymers can be classified into three groups: "blocked (1)," "coupled (2)," and "unreacted (3)," as shown below:
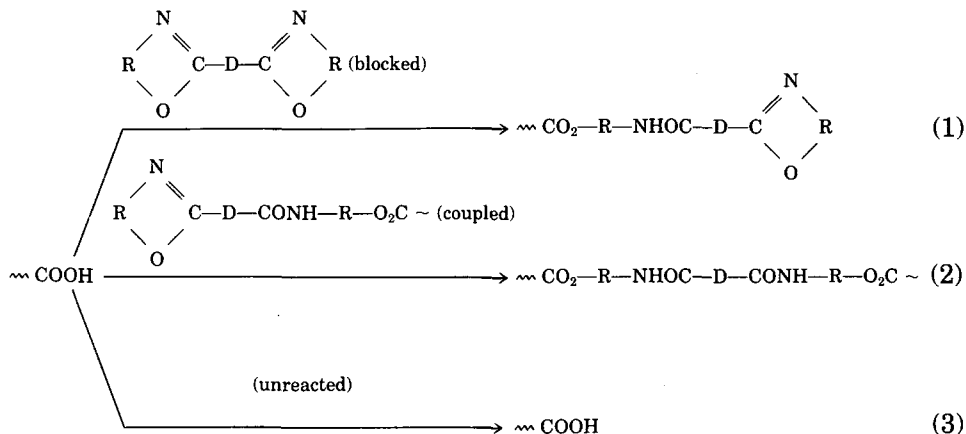
As can be easily understood, theoretically, the chain extender should be added in an equimolar amount to the carboxyl terminals in the initial polymer to result in the highest-molecular-weight polymer after the chain-extending reaction. If an excess amount of the chain extender should be added, the blocking reaction would occur predominantly and the polymer of not-so-much-increased molecular weight but much decreased CV would result. However, if the coupling reaction should proceed much faster than the blocking reaction, the polymer of nearly the highest molecular weight could be obtained even if some excess chain extender is used. From a practical viewpoint, the latter case is much preferred, since the reproducibility of the resulting molecular weight should be much improved even when the CV of the initial polymer is varied, as is often the case in practice. To evaluate such effect, [η] and CV of the resultant polymers for various added amounts of the chain extender "2,2'-bis(2-oxazoline)" have been measured. The results are shown in Figure 1. For better understanding, after a 5-min chain-extending reaction we have calculated the ratios of the "blocked (1)," "coupled (2)," and "unreacted (3)" based on the total carboxyl groups present in the initial polymer. The results are summarized in Figure 2. The parameters used here are calculated as follows.

i. The theoretical amount of the chain extender to be added

$$W = \frac{1}{2}G \cdot CV_0 \times 10^{-4} \quad \text{(wt \% of the initial polymer)} \qquad (4)$$

where G is the molecular weight of the chain extender and CV_0 means CV of the initial polymer.
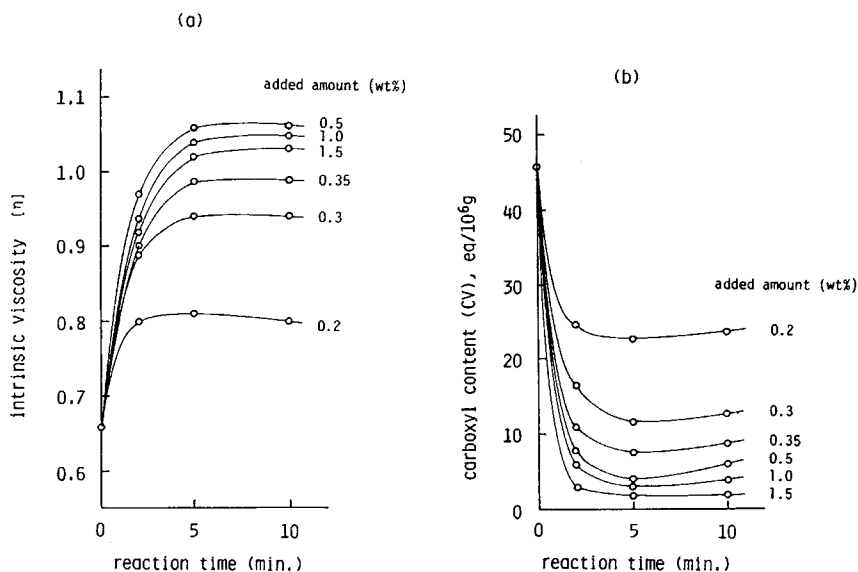
(a)

(b)

Fig. 1.   Effect of the added amount of 2,2'-bis(2-oxazoline) on [η] (a) and CV (b) of the resultant polymer in the chain-extending reactions (method A) of PET (initial [η]/CV of 0.66/46).
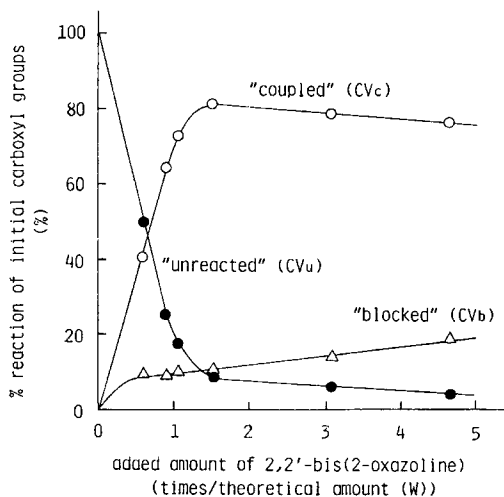

Fig. 2.   Reaction behavior of the carboxyl terminals after 5 min chain-extending reaction (method A) of PET (initial [η]/CV of 0.66/46).

ii. The "coupled" carboxyl groups

$$CV_c = \text{number of the decreased terminal groups} \qquad (5)$$
$$= N_0 - N_r \quad (eq/10^6 \text{ g})$$

where N_0 and N_r mean the numbers of the total terminal groups of the initial polymer and the resulting polymers, respectively. As described in

the previous paper, we have approximated CV_c to the decrease of the total terminal groups, since CV_c cannot be measured directly. N_0 and N_r in eq. (5) can be calculated from $[\eta]$ using the Mark–Houwink equation

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

where M is the number average molecular weight and K and a are such empirical constants as 2.75×10^{-4}, 0.77 for PET[5] and 1.166×10^{-4}, 0.871 for PBT[6], respectively. We defined a percentaged ratio of CV_c to CV_0 as coupling efficiency (CE) in the previous paper.[1]

iii. The "unreacted" carboxyl groups

$$CV_u = CV \text{ of the resulting polymer} \quad (eq/10^6 \text{ g}) \qquad (7)$$

iv. The "blocked" carboxyl groups

$$CV_b = CV_0 - CV_c - CV_u \quad (eq/10^6 \text{ g}) \qquad (8)$$

As can be observed in Figures 1 and 2, CE or CV_c was maximum when 1.5 times as much 2,2'-bis(2-oxazoline) as the theoretical amount (W) was used. This deviation, although not yet confirmed, may be due to the loss of the chain extender during the reaction by sublimation, decomposition, and reaction with newly generated carboxyl terminals. The increase of the carboxyl terminals were observed when the initial polymer was heated in a melt without adding the chain extender as a control in the previous paper.[1]

The more important phenomenon we can see in Figures 1 and 2 is that a wide range of excess use of 2,2'-bis(2-oxazoline) (from 1.5 to 5 times as much as the theoretical amount) resulted in the polymer of rather similar molecular weight or similar CE and CV_c. As discussed before, this is very advantageous from the practical viewpoint.

In addition to 2,2'-bis(2-oxazoline), we have evaluated the effectiveness of 2,2'-bis(5,6-dihydro-4H-1, 3-oxazine) and N,N'-hexamethylenebis (2-carbamoyl-2-oxazoline) similarly. The results are shown in Figure 3, which indicates that the former has similar effect to that of 2,2'-bis(2-oxazoline), but the latter does not show such an advantageous effect.

Both of 2,2'-bis(2-oxazoline) and 2,2'-bis(5,6-dihydro-4H-1,3-oxazine) have structures that two cyclic-imino-ether groups are bonded directly to each other at 2-position, while, in the case of N,N'-hexamethylenebis(2-carbamoyl-2-oxazoline), two rings are located separately by alkylene chains. It is reasonably anticipated that, in the latter case, reactivities of the two oxazoline rings are almost similar even when one of them has reacted with carboxyl groups, and therefore the coupling and blocking reactions proceed in parallel. This can explain the fact that the amount of the added chain extenders has much influence on the $[\eta]$ of the resultant polymer. On the other hand, in the former cases, once one of the two rings has been involved in the blocking reaction, it should affect the reactivity of the other ring. It can be inferred from the above experimental results that the first imino-
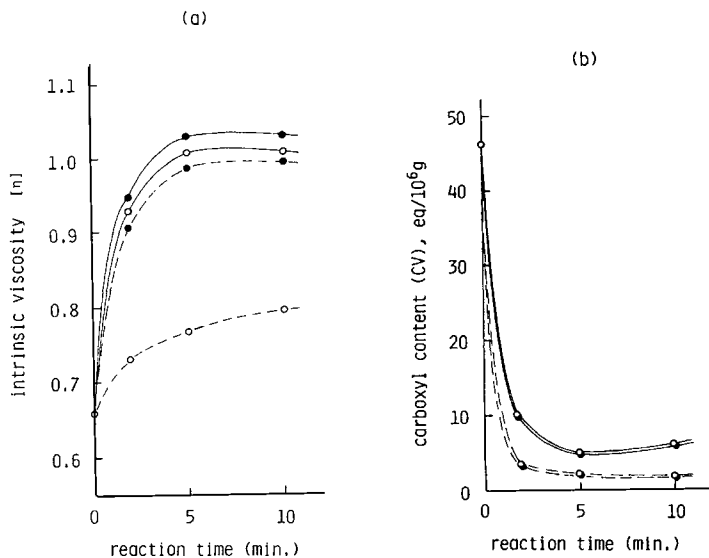
(a)

(b)

Fig. 3.   Effect of the amounts of 2,2'-bis(5,6-dihydro-4H-1,3-oxazine) (●) and *N,N'*-hexa-methylenebis(2-carbamoyl-2-oxazoline) (○) on [η] (a) and CV (b) of the resultant polymer in the chain-extending reactions (method A) of PET (initial [η]/CV of 0.66/46): (——)1.5 times; (---) 4.5 times the theoretical amount.

(a)

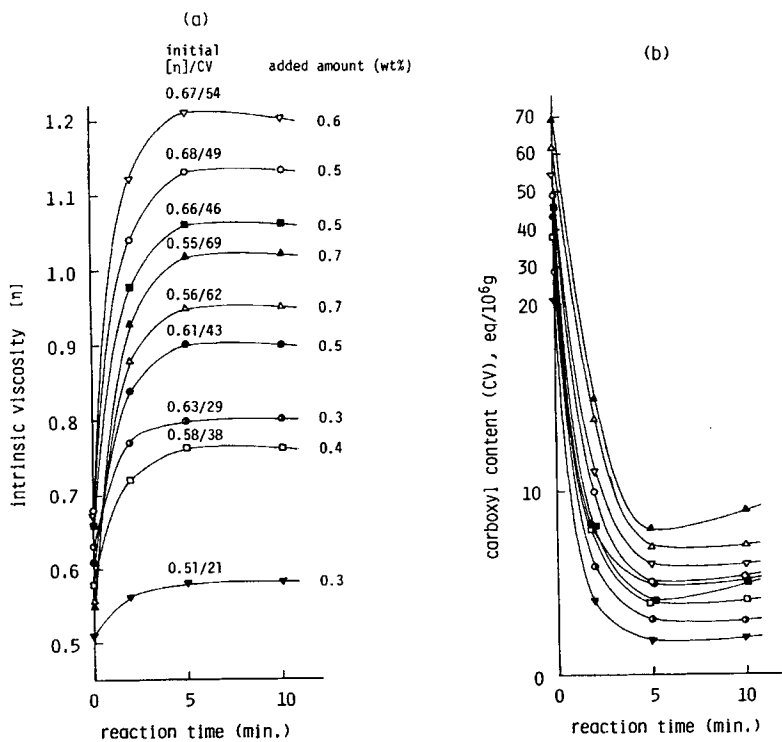initial
[η]/CV   added amount (wt%)

(b)

Fig. 4.   Chain-extension (method A) by 2,2'-bis(2-oxazoline) of PET having various [η] (a) and CV (b).

ether group opened in the blocking reaction accelerates the ring-opening coupling reaction of the other.

We can conclude that bis cyclic-imino-ethers whose two cyclic groups are bonded to each other directly are preferred practically as the chain extender.

Influence of CV and [η] of the Initial Polymers on Those of the Chain-Extended Polymers

Effects of the initial polymers of various [η] and CV on the chain-extending reactions by 2,2'-bis(2-oxazoline) have been investigated. The results are summarized in Figures 4 and 5 (method A) and Table I (method B). In every case 1.5–2 times as much the chain extender as the theoretical amount (W) were added, since it was confirmed to give the maximum CE and [η] to the resultant polymer as can be seen in Figure 2.

We have also calculated CV_c and CV_u in all experiments and plotted them vs. CV_0, as shown in Figure 6. All the dots representing each experiment fell on three straight lines. Each series of the experiments (PET by method A, PBT by method A, and PET by method B) formed each straight line. The slope of the straight lines means CV_c/CV_0 (=CE) and CV_u/CV_0. No matter what [η] and CV of the initial polymers would be, about 81% of initial carboxyl groups are coupled with one another and about 11% remain un-
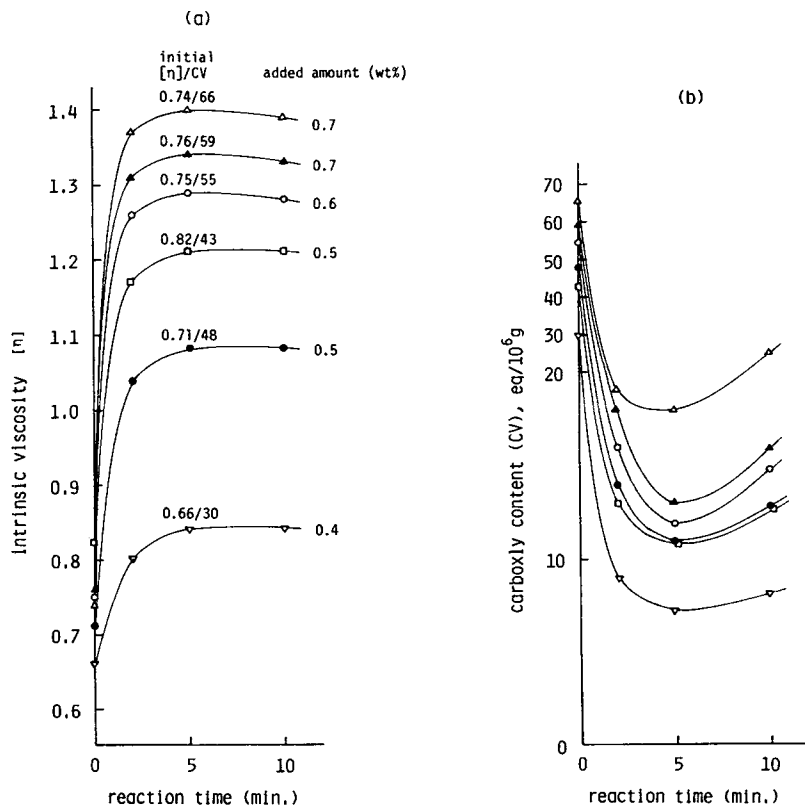

Fig. 5. Chain-extension (method A) by 2,2'-bis(2-oxazoline) of PBT having various [η] (a) and CV (b).

TABLE I
Chain-Extending Reaction (Method B) of PET Having Various $[\eta]$/CV by
2,2'-Bis(2-Oxazoline)

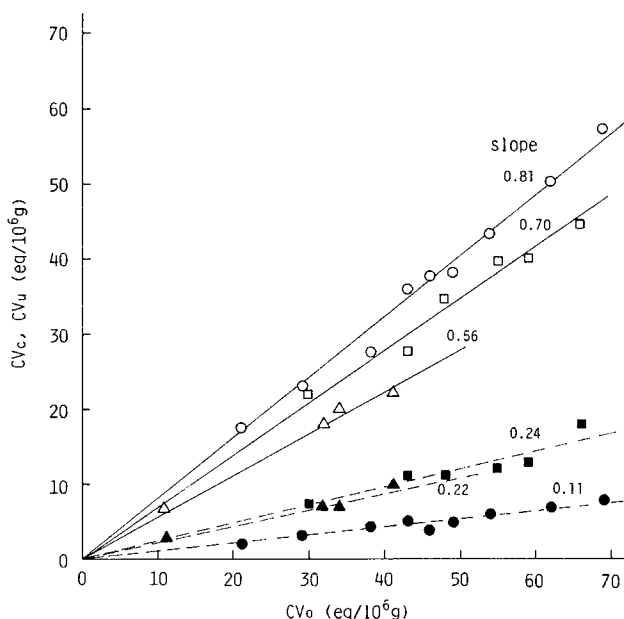| $[\eta]$/CV of initial PET | Added amount of 2,2'-bis(2-oxazoline) | | $[\eta]$/CV of resulting PET | Coupled carboxyl groups $[CV_c]$ (eq/10^6 g) |
	wt %	Times theoretical amount		
0.56/11	0.15	(1.9)	0.59/3	7
0.67/32	0.4	(1.8)	0.81/7	18
0.75/34	0.4	(1.7)	0.97/7	20
0.78/41	0.5	(1.7)	1.07/10	22

Fig. 6. Coupled carboxyls (CV_c) and unreacted carboxyls (CV_u) after chain-extending reaction vs. CV of the initial polymers (CV_0): (○, ●) PET by method A (5 min reaction); (□, ■) PBT by method A (5 min reaction); (△, ▲) PET by method B: (—) CV_c (---) CV_u.

reacted in case of PET by method A. Analogously, CE = 56% and CV_u/CV_0 = 22% in case of PET by method B, and CE = 70% and CV_u/CV_0 = 24% in case of PBT by method A. These results suggest that we can obtain the chain-extended polymers having the predetermined $[\eta]$ and CV by adjusting the $[\eta]$ and the CV of the initial polymers and fixing the reaction conditions, using such chain extenders as 2,2'-bis(2-oxazoline).

EFFECT OF THE USE OF CYCLIC ANHYDRIDES TO INCREASE THE CARBOXYL TERMINALS

According to the above results, the initial polymer having higher CV can result in the polymer of higher molecular weight using 2,2'-bis(2-oxazoline)
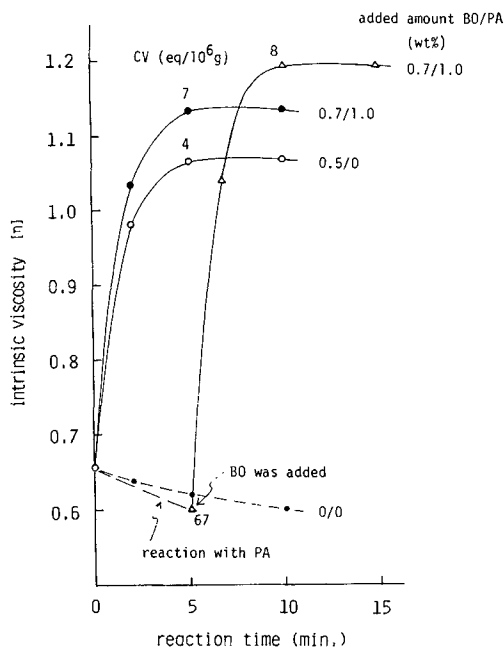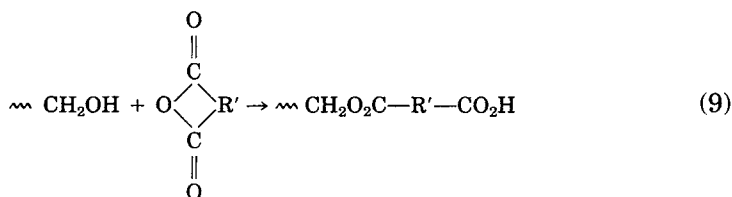
Fig. 7. Effect of phthalic anhydride (PA) used with 2,2'-bis(2-oxazoline) (BO) in chain-extending reaction (method A) of PET on [η] of the resultant polymer: (△) successive addition; (●) simultaneous addition; (○) addition of only BO.

when the initial polymer of similar [η] is used. We can increase the carboxyl terminals by reacting cyclic anhydride with the hydroxyl terminals of starting polymer as shown in the following scheme:

$$
\text{〜 CH}_2\text{OH} + \text{O} \underset{\substack{\text{C} \\ \| \\ \text{O}}}{\overset{\substack{\text{O} \\ \| \\ \text{C}}}{\diagdown}} \text{R}' \rightarrow \text{〜 CH}_2\text{O}_2\text{C—R'—CO}_2\text{H} \tag{9}
$$

Therefore, effects of the combined use of phthalic anhydride and 2,2'-bis(2-oxazoline) have been investigated. Figure 7 shows comparison of the effects of the combined uses (i) by adding them at the same time, and (ii) by successive addition of the anhydride and the chain extender, and (iii) by the single use of the chain extender. The combined uses (i) and (ii) have been proved to result in a polymer of a higher molecular weight than the simple use (iii). The successive addition (ii) was the most effective of the three cases.

CONCLUSION

The above results indicate that such chain extenders as 2,2'-bis(2-oxazoline) can give polyesters having predetermined [η] and CV by selecting the [η] and CV of the initial polymers if the reaction conditions are fixed.

Therefore, these chain extenders have a good practical applicability as the chain extenders for PET and PBT, so far as the reaction behaviors are concerned. The properties of the resulting polyesters will be reported later.

References

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