Chain Extenders for Polyesters. V.
Reactivities of Hydroxyl-Addition-Type
Chain Extender;
2,2′-Bis(4H-3,1-Benzoxazin-4-one)

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Synopsis

In our previous study,[1] 2,2′-bis(4H-3,1-benzoxazin-4-one) (BNZ) was found to be most effective among the tested chain extenders in coupling hydroxyl terminals of linear polyesters through addition reaction. Detailed studies on BNZ chemistry have been made using poly(ethylene terephthalate) and poly(butylene terephthalate) as the polyester. It has been observed that use of BNZ, equivalent amount to the hydroxyl terminals of the initial polymer, resulted in the highest molecular weight. In contrast with the case of 2,2′-bis(2-oxazoline), which was found to be the most effective carboxyl-addition type chain extender and a wide range of its excess use was allowed,[2,3] an excessive use of BNZ resulted in lower molecular weight polymer. Thus, when an equivalent amount of BNZ to the hydroxyl terminals was used, the molecular weight of the resulting polymer could be determined by the carboxyl content of the initial polymer, regardless of its initial molecular weight.

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 (CV) 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 the addition reactions without generating any byproducts.

Our previous papers[1,2] reported that some bis cyclic-imino-ethers and bis cyclic-imino -esters had been proved to be effective as carboxyl-addition type and hydroxyl-addition type chain extenders, respectively. In addition, we have investigated detailed reaction behaviors of 2,2′-bis(2-oxazoline), the most effective carboxyl reactive chain extender among the tested, to confirm it of good practical applicability so far.[3]

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In the present paper, we would like to report the reaction behavior of 2,2′-bis-(4H-3,1-benzoxazin-4-one) (BNZ), which had been proved to be most effective among the tested hydroxyl-reactive chain extenders.

BNZ showed some different reaction behaviours from those of 2,2′-bis(2-oxazoline).

EXPERIMENTAL

Materials

BNZ was prepared as previously reported by the reaction of oxalyl chloride and isatoic anhydride in pyridine[4] followed by recrystallization from nitrobenzene.

N-glycidylphthalimide (NGP) was prepared by the reaction of potassium phthalimide and epichlorohydrin and recrystallized from ethanol, as mentioned in the literature.[5]

Chain-Extending Reactions

The initial PET and PBT polymers having various intrinsic viscosity ($[\eta]$) and CV were prepared by changing reaction conditions such as temperature and pressure under the typical polycondensation method from (i) bis(β-hydroxyethyl terephthalate) using Sb_2O_3 (0.03 mol %) as catalyst (PET-a), (ii) dimethyl terephthalate and ethylene glycol using $Mn(OCOCH_3)_2 \cdot 4H_2O$ (0.04 mol %) and Sb_2O_3 (0.03 mol %) as catalyst and $(CH_3O)_3 P{=}O$ (0.05 mol %) as a stabilizer (PET-b), and (iii) dimethyl terephthalate and 1,4-butanediol using $Ti(O{-}nC_4H_9)_4$ (0.02 mol %) as catalyst (PBT). Then, to the molten polymer under a nitrogen stream and stirring, a prescribed amount of the chain extender was added. The reaction temperature was set at 280°C in case of PET and 240°C in case of PBT. After a predetermined period of the reaction, $[\eta]$ of the resulting polymer was measured.
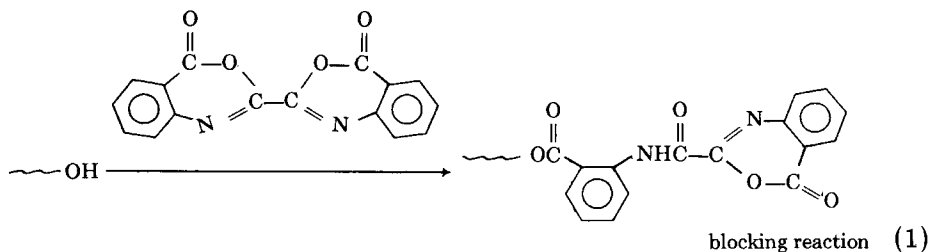
Analytical Procedure

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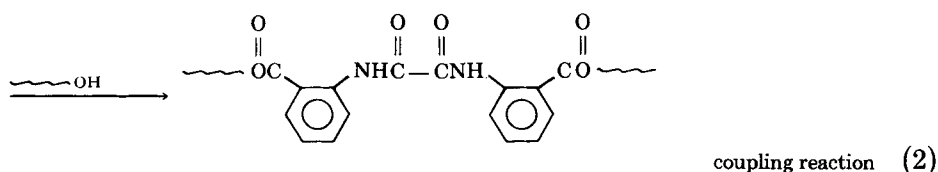
CV (eq/10^6 g polymer) was measured by the Conix method.[6]

RESULTS AND DISCUSSION

Effect of Added Amount of the Chain Extenders

The chain-extending reaction by BNZ proceeds in two steps (blocking and coupling) as shown in the following schemes:

blocking reaction (1)

$$\text{————OH} \longrightarrow \quad \overset{\overset{\displaystyle O}{\overset{\displaystyle \|}{}}}{\text{~~~OC}} \quad \overset{\overset{\displaystyle O \quad O}{\overset{\displaystyle \| \quad \|}{}}}{\text{NHC—CNH}} \quad \overset{\overset{\displaystyle O}{\overset{\displaystyle \|}{}}}{\text{CO ~~~}}$$

<div align="right">coupling reaction   (2)</div>

Theoretically, in addition of the chain extender amounting to the equivalent to the hydroxyl terminals of polyesters will result in the chain-extended polymer of the highest molecular weight.

But, if the coupling reaction (2) would proceed much faster than the blocking reaction (1), the polymer of nearly similar molecular weight to the highest should be obtained even though some excessive amount of the chain extender would be used. As we reported in the previous paper[3] such carboxyl-addition-type chain extenders as 2,2'-bis(2-oxazoline) and 2,2'-bis(5,6-dihydro-4H-1,3-oxazine) in which two cyclic-imino-ether groups are bonded directly to each other at 2-position of the imino-ether ring react in the above fashion.

It is interesting to know how BNZ would behave in the chain-extending reaction since it has an analogous structure, that is, two cyclic-imino-ester groups are connected directly with each other.

To investigate such reaction behaviors of BNZ, various amounts of BNZ were added to the molten polyesters of almost the same $[\eta]$ and CV, and the changes in $[\eta]$ were measured. The results are shown in Figure 1. For better understanding, we plotted the increases of $[\eta]$ ($\Delta[\eta]$) which were calculated by subtracting the initial $[\eta]$ from the maximum $[\eta]$ after 5–10 min reaction vs. the added amount of BNZ as shown in Figure 2. Added amounts of BNZ are shown by the equivalent ratio to the initial hydroxyl terminals (HV_0) calculated as follows:

$$HV_0 \; (\text{eq}/10^6 \text{ g polymer}) = N_0 - CV_0 \tag{3}$$

where N_0 and CV_0 mean the number of the total terminal groups (N) and CV of the initial polymer, respectively. N (eq/10^6 g polymer) can be calculated from $[\eta]$ using the following Mark–Houwink relationship:

$$[\eta] = KM^a = K\left(\frac{2 \times 10^6}{N}\right)^a \tag{4}$$

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[7]) and $a = 0.871$, $K = 1.166 \times 10^{-4}$ for PBT (proposed by Borman[8]).

As can be seen in Figure 2, maximum $\Delta[\eta]$ was obtained when the added amount of BNZ was almost the same equivalent to HV_0. Accordingly, the reaction behavior of BNZ as a chain-extending agent has been proved to be different from that of 2,2'-bis(2-oxazoline).
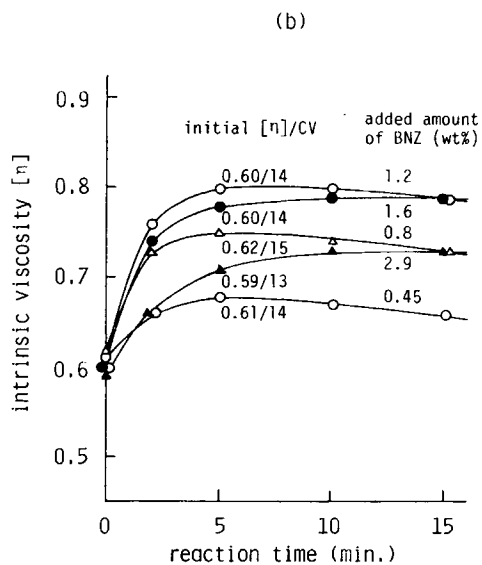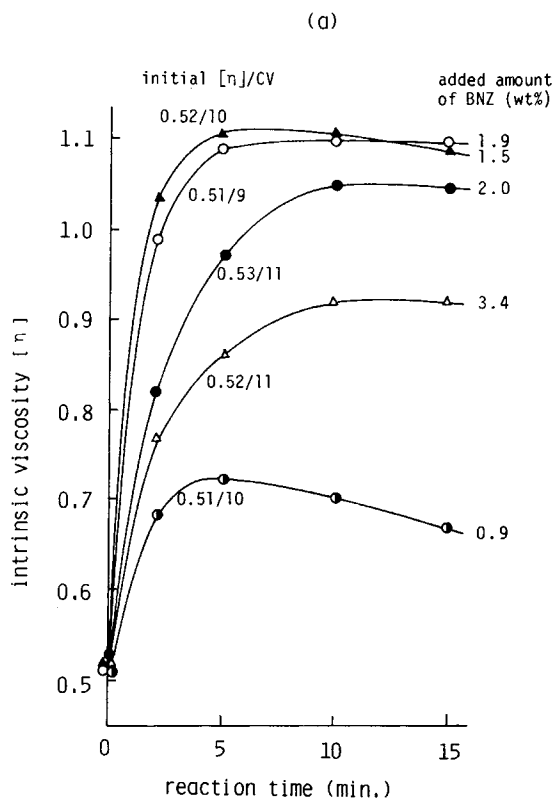
(a)

(b)

Fig. 1. Effect of the added amounts of BNZ on $[\eta]$ in the chain-extending reactions of PET-a (a) and PET-b (b).
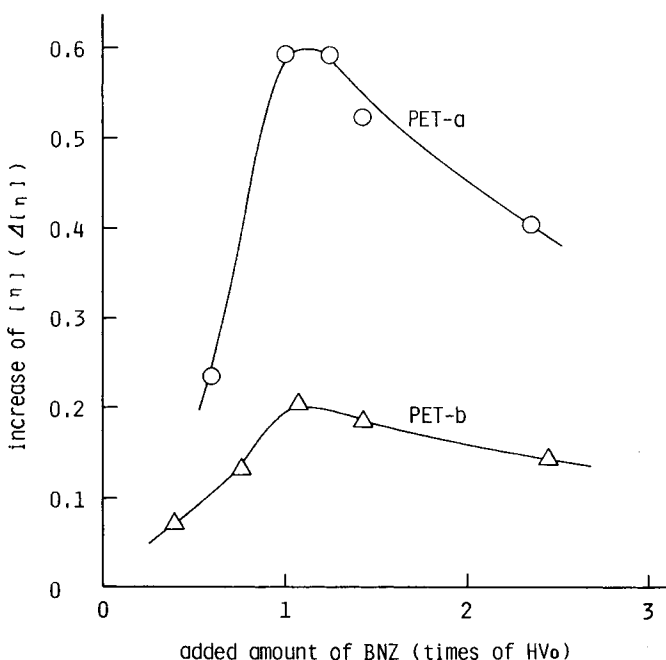
Fig. 2. Effect of the added amounts of BNZ on increase in [η] in the chain-extending reaction. Initial [η]/CV = 0.51–0.53/9–11 (PET-a) and 0.59–0.62/13–15 (PET-b).

Influence of CV and [η] of the Initial Polymers

Effects of CV and [η] of the initial polyesters on the resultant BNZ-treated polymers have been investigated. The results of the experiments are shown in Figures 3–5. In every experiments, BNZ of 1–1.2 times as much as HV_0 was added. We have calculated the number of coupled hydroxyl groups (HV_c) after 5 min reaction, and plotted it vs. HV_0 as shown in Figure 6. We have approximated HV_c to the "decrease of total terminal groups," which can be calculated by measurement of the number-average molecular weight:

$$HV_c = N_0 - N_r \tag{5}$$

where N_r means N of the resulting polymer.

It has been observed in Figure 6 that all dots representing each series of PET-a, PET-b, and PBT fell on a similar straight line and three straight lines thus formed were just parallel to the "ideal line," which means all the initial hydroxyl terminals are used to couple the chain ends.

This leads to the following empirical equation:

$$HV_c = HV_0 - L \tag{6}$$

where L means the deviation from the ideal line and the constant determined by polymer kinds and reaction conditions.
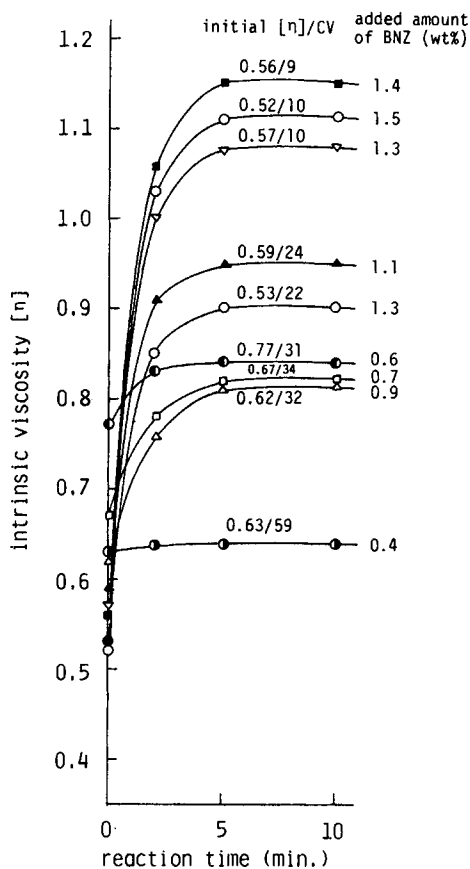
Fig. 3. Chain-extending reactions of PET-a having various [η] and CV by BNZ.
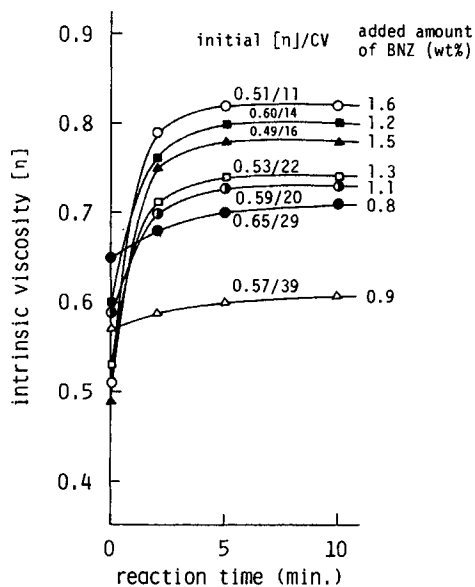
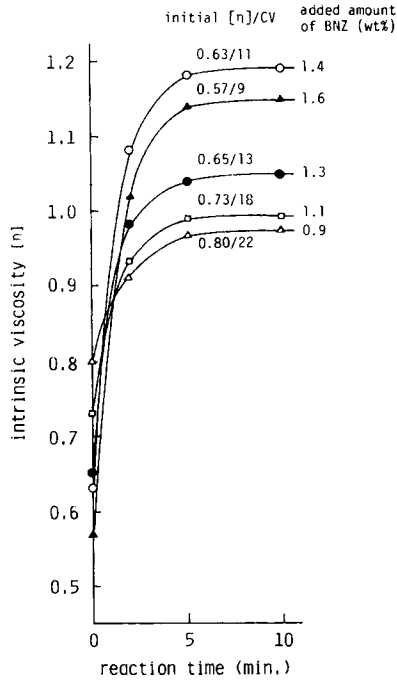Fig. 4. Chain-extending reactions of PET-b having various [η] and CV by BNZ.

Fig. 5. Chain-extending reactions of PBT having various $[\eta]$ and CV by BNZ.
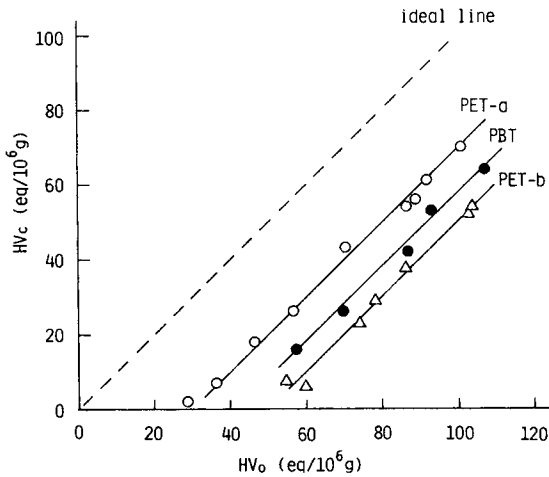

Fig. 6. HVc after 5 min chain-extending reaction vs. HV_0 ($= N_0 - CV_0$).

Combining equations (3), (5), and (6), we can make the following equation:

$$N_r = CV_0 + L \qquad (7)$$

This equation means that the molecular weight (or $[\eta]$) of the resultant polymer is determined only by CV_0 of the initial polymer, regardless of its initial molecular weight. In addition, when HV_0 is below L, the apparent chain-extending reaction does not occur.
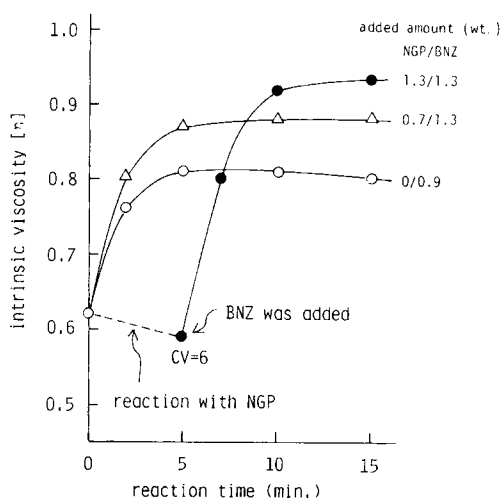
Fig. 7. Effect of combined use of monoepoxy compound (NGP) with BNZ in the chain-extending reaction of PET-a (initial $[\eta]/CV = 0.62/32$): ($\bigcirc$) addition of only BNZ; ($\triangle$) simultaneous addition; ($\bullet$) successive addition.

We can point out many possible reasons for such deviations or threshold values represented by L. If there are chain-terminal groups other than hydroxyl and carboxyl groups such as methyl groups, they should cause at least a part of such a value, since HV_0 was calculated as equal to $(N_0 - CV_0)$. The irreversible decomposition at the chain extended sites might occur simultaneously during the chain-extending reaction. It seems to be unprobable that any single reason can explain the deviation satisfactorily, although we have not yet investigated.

Effect of the Use of Epoxy-Compound To Increase the Hydroxyl Terminals

According to the above results, the initial polymer having lower CV can result in the polymer of higher molecular weight using BNZ as the chain extender. We have tested the effects of monoepoxy compound (NGP), which can be expected to react carboxyl terminals preferentially, resulting in the formation of hydroxyl terminals as shown in the following scheme:

$$\sim\sim CO_2H + CH_2CH-R \rightarrow \sim\sim CO_2CH_2CHOH \overset{R}{\underset{|}{}} \qquad (8)$$
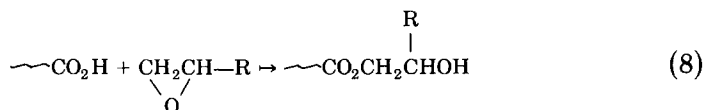
Figure 7 shows comparison of the effects of the combined uses (i) by adding NGP and BNZ at the same time, (ii) by successive addition of NGP and BNZ, and (iii) the single use of BNZ. The combined uses (i) and (ii) have been proved to result in the higher molecular weight polymers. The successive addition (ii) was most effective of the three cases.

CONCLUSION

Such hydroxyl-addition-type chain extenders as 2,2'-bis(4H-3,1-benzoxazin-4-one) can give polyesters having the predetermined $[\eta]$ by selecting CV of the initial polymer if the proper amount of the chain extender is added. Therefore, the compound seems to have a practical applicability, as far as the reaction behaviors are concerned. The properties of the resulting polymers will be reported later.

References

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