The Action of Chain Extenders in Nylon-6, PET, and Model Compounds

T. LOONTJENS, K. PAUWELS, F. DERKS, M. NEILEN, C. K. SHAM, M. SERNÉ

DSM Research, P.O. Box 18, 6160 MD, The Netherlands

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ABSTRACT: The action of two complementary chain extenders is studied in model systems as well as in poly(ethylene terephthalate) (PET) and nylon–6. Chain extenders are low molecular weight compounds that can be used to increase the molecular weight of polymers in a short time. The reaction must preferably be fast enough to execute this step in an extruder. 1,3-Phenylene bis(2-oxazoline-2) (PBO) and isophthaloyl biscaprolactamate (IBC) are used in this study. Bisoxazolines react quickly with carboxylic acids. With model compounds it is shown that, under processing conditions, high conversions can be reached. However, the conversion is not complete. The high rate and the absence of volatile reactants are the most important characteristics of this reaction. Bislactamates are suitable coupling agents for hydroxy and amino functional polymers. The path of this coupling reaction depends on the type of nucleophile and on the reaction temperature. Under mild conditions the elimination of caprolactam is the main reaction. Under more severe conditions the ring opening mechanism may also be operative. The increase of the viscosity is studied with one as well as with a mixture of the two chain extenders. The effect is larger when both types of chain extenders are used simultaneously. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1813–1819, 1997

Key words: chain extenders; phenylene bisoxazoline; isophthaloyl bislactamate; nylon-6; poly(ethylene terephthalate)

INTRODUCTION

Polyesters and polyamides are commercially produced in melt processes. The attainable molecular weight is limited by the melt viscosity. The average molecular weight of the commercial polymers is in the range of about 20,000. A solid-state polymerization (SSP) can be applied if a higher molecular weight is needed. This SSP process is laborious and costly. An SSP process takes place in about 10–20 h at 200°C. An alternative way to increase the molecular weight of condensation polymers is to treat them with chain extenders.[1–9] Chain extender are low molecular weight chemicals that can increase the molecular weight of polymers in a fast reaction. This process can be performed conveniently in an extruder if the reaction rate is high enough. Because of the small amount of the chain extender needed (about 1%), it is difficult, if not impossible, to investigate the chemistry in detail in polymers. Therefore, we have performed some model reactions that are more appropriate to clarify the chemistry.

To obtain the maximum increase in viscosity it is obviously necessary to utilize both types of endgroups of the polymer. The endgroups in polycondensates are not always equally distributed over the polymer chains. The endgroups (—OH, —NH_2, and —COOH) are in general distributed over the polymer chains in a statistical way. With one type of chain extender only one of the two functional groups can be utilized, and the effect

Correspondence to: T. Loontjens.

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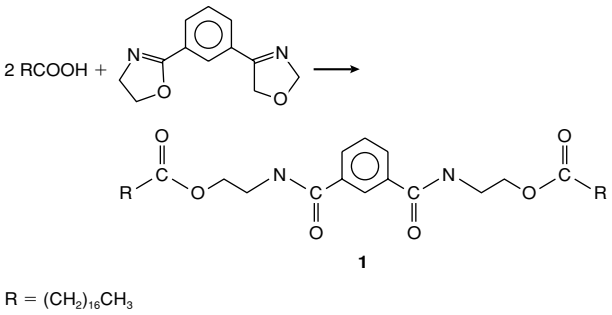
will be limited. Therefore we studied a mixture of two chain extenders. Bisoxazolines are known to react with carboxylic groups and bis-*N*-acyl lactamates with hydroxy or amino groups. Here we report the results with 1,3-phenylene bis(2-oxazoline-2) (PBO) and isophthaloyl biscaprolactamate (IBC) as chain extenders in poly(ethylene terephthalate) (PET), nylon-6, and model compounds.



R = $(CH_2)_{16}CH_3$

Scheme 1

EXPERIMENTAL

Materials

1,3-Phenylene bis(2-oxazoline-2) was obtained from Takeda Chemical Industry, or prepared as described by Witte et al.[10] Isophthaloyl biscaprolactamate was prepared from the acid chloride of isophthalic acid and caprolactam. The acid chloride was obtained from Aldrich, and caprolactam from DSM. Caprolactam (0.20 mol), triethylamine (0.22 mol), and toluene (100 ml) were heated to 95°C. Isophthaloyl chloride (0.1 mol) in 100 ml toluene was added dropwise in 15 min. The temperature was kept at about 100°C for half an hour. Water (50 ml) was added to remove the salt. The organic layer was washed twice with hot water. After cooling, IBC precipitated and was filtered and dried. 5-Nitro isophthaloyl bislactamate was prepared by the same method. The synthesis of the acid chloride was performed according to the method described by Jennings et al.[11] The reaction of thionyl chloride with 5-nitro isophthalic acid lasted longer (48 h) than with isophthalic acid (8 h). 5-Nitro isophthalic acid, thionyl chloride, ethyl benzoic acid, and stearic acid were obtained from Aldrich and used as received.

The reaction product of stearic acid and PBO was prepared by heating the mixture in bulk for 3 h at 170°C under nitrogen in a sealed tube. 2-Hydroxyethyl benzoate (HEB) was prepared according to the method used by Heim et al.[12]

The thermal treatment reactions with the model compounds were performed in a sand bath. The temperatures and reaction times are given in the Results and Discussion section along with information about when thermal treatments were performed during thermogravimetric analysis (TGA).

The PET and nylon-6 were obtained from DSM. The relative viscosity η_{rel} of nylon-6 was measured in formic acid and that of PET in *m*-cresol.

Apparatus

The kneading experiments were done in a Brabender Plasti-corder PLE 651. The ^{1}H NMR spectra were recorded with a Bruker ACF-200 MHz or a Varian Unity 300 MHz spectrometer. The TGA apparatus was a Perkin–Elmer TGA 7.

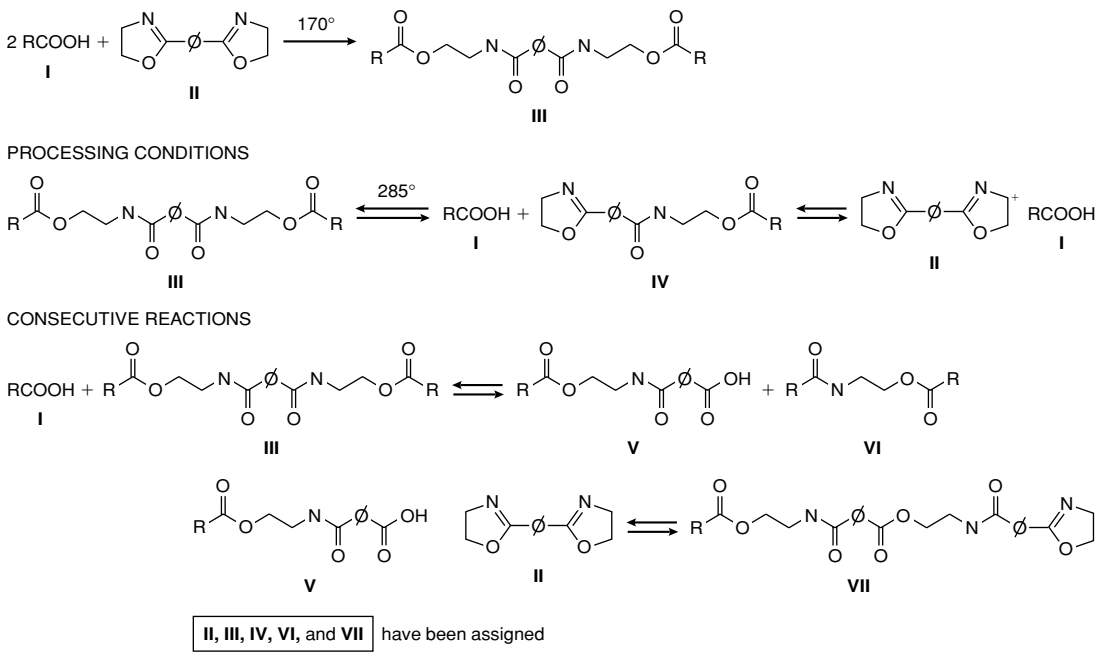
RESULTS AND DISCUSSION

1,3-Phenylene bis(2-oxazoline-2) (PBO)

Several authors have shown[1–9,13,14] that the reaction of bisoxazolines with carboxylic acids is very fast under processing conditions. The reaction goes to high conversions within a few minutes without emitting any volatiles. The reaction between an oxazoline and a carboxylic acid is in principle reversible.[15] To establish whether this reversibility plays a role in the coupling of polymers, we prepared some model components and studied them under processing conditions. Stearic acid (Scheme 1) and ethyl benzoic acid were selected as model acids because of their low volatility. The addition reaction of 2 moles of stearic acid to 1 mole of PBO was performed at 170°C for 3 h to be sure that the equilibrium state had been reached. According to the ^{1}H NMR spectrum of the mixture, the reaction went to completion at that temperature. Vainio et al. found for aliphatic oxazolines that the equilibrium conversion with carboxylic acids, at similar temperatures, is only about 40%.[16]

The processing temperature of polymers is in general between 250 and 300°C. To mimic these conditions, compound 1 was heated in a nitrogen atmosphere at 200, 250, and 285°C.

The ester–amide formed in the reaction between an oxazoline and a carboxylic group is quite stable. When the product is kept at 200°C for 1 h,



Scheme 2

hardly any change in the NMR spectrum can be seen. After heating compound 1 for 1 h at 250°C, some reactions took place. The product mixture comprised one main component, product compound 1, and at least four other products in much smaller quantities.

We separated this mixture by thick layer chromatography and characterized the products by ^{1}H NMR. To explain the analytical data, a reaction mechanism (Scheme 2) is proposed that accounts quite well for the assigned compounds. In the scheme the identified products are indicated. Only the acids in Scheme 2 are not identified. They are probably masked by the other compounds.

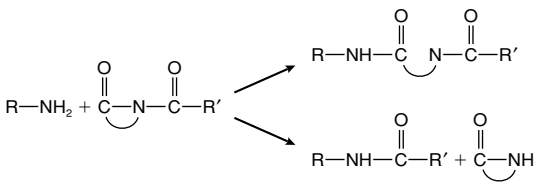
In these experiments we did not quantify the concentration of the products. In order to get information on the extent of the reverse reaction we analyzed the mixture as obtained after heating. The heating was done at 285°C in a closed TGA cup. Because the NMR data of the individual products were known now, it was possible to assign some of the peaks in the mixture. In Table I the molar ratios of the starting compound 1 and the reformed oxazoline is given.

Table I Molar Ratios (Arbitrary Units) of the Products Formed During Heating Compound 1 at 285°C

Heating Time (min)	Cooling Rate (°C/min)	Compound 1	Oxazoline Ring
3	600	86	7
10	13	78	7
10	600	81	9

The other compounds are not mentioned because ^{1}H NMR peaks are not resolved enough to make reliable calculations. Note that the extent of the reverse reaction depends on the reaction time. It can be estimated that about 10–20% of compound 1 is dissociated in 3–10 min under those conditions. About half of the reaction results in the starting materials [an oxazoline and (probably) an acid]. The cooling rate was varied to verify whether the reverse reaction would take place during cooling. The cooling rate seems not to be important.

The reaction was performed in a closed differential scanning calorimetry cup. We tried to avoid the withdrawal some reactants from the equilibrium by keeping the gas phase as small as possible. It is clear that under the applied conditions the bond is not completely stable. The reverse reaction takes place to some extent. However, assuming that the mechanism of Scheme 2 is viable, it can seen that not all of the reactions necessarily



Scheme 3

lead to chain scissions. If the consecutive steps are transesterifications and transamidations, they will not lead to scission.

The acid in PET is terephthalic acid, an aromatic acid. Mülhaupt et al. have shown[14] that the reaction of oxazolines with aromatic acids is faster (at 220°C) than with aliphatic acids. Thus the reverse reaction may differ too. To establish the difference between an aromatic and an aliphatic acid we performed similar experiments with ethylbenzoic acid instead of stearic acid. However the NMR results are much more difficult to interpret. The interchange reactions, as shown in Scheme 2, are in this case less clear because both acids are aromatic. However, some peaks in the NMR spectrum show broadening when the coupled product is heated for 1 h at 250°C. Although it was not possible to give a clear assignment, it was apparent that some (interchange) reactions had taken place. Thus, the reaction of an oxazoline and a carboxylic acid does not go to completion at $T > 250$°C. However, the reaction proceeds nearly to completion, and the side reactions often give coupled products too. Thus, this reaction is certainly good enough to be useful in practice for chain coupling reactions. This will be shown with PET and nylon-6 later in this section.

1,3-Isophthaloyl Biscaprolactamate (IBC)

The use of bislactamtes as chain extenders is known and has been discussed by Akkapeddi et al.[13] IBC can react either by splitting off caprolactam or by a ring opening reaction (Scheme 3). When aromatic amines are used as nucleophiles, it has been shown that the reaction path depends on the size of the lactam ring as well as on the temperature.[17,18] At low temperature the lactam ring is eliminated, whereas at higher temperatures (>200°C) both reactions occur. Nylon-6 contains aliphatic amine endgroups, which might react differently. In this case we measured the increase of the concentration of caprolactam in nylon-6 during the chain extension reaction under extrusion conditions. The polymer was extracted after the reaction, and the composition of the extract was measured by high-pressure liquid chromatography (Table II). Assuming that all the IBC was converted, these results suggest that about the half of the caprolactam is split off. The conclusion is tentative, since the conversion of IBC was not measured. However, in the extract, no IBC was found. Thus, at least half of the IBC reacts by eliminating caprolactam (and probably much more than the half). No model work has been done to investigate the elimination of caprolactam with amines in detail. The emission of caprolactam in nylon-6 is hardly any problem because nylon-6 always contains some caprolactam. Caprolactam, however, is a strange component in polyesters. For some applications in this field, it might be a problem. Therefore, we studied the emission of caprolactam in hydroxy functional polymers in more detail with model compounds. 2-Hydroxyethylbenzoate (HEB) was used to mimic PET. HEB and IBC were heated for 30 min at 120, 130, and 150°C. In Figure 1 the ^{1}H NMR spectrum of the last reaction mixture is given.

It can be seen in Figure 1 that only one type of ester is formed, and this is the product in which caprolactam is eliminated. The free lactam can also be seen clearly (3.20 ppm). There is no evidence for any ring opening reaction of caprolactam. Although the temperature is much lower than the processing conditions, it can be expected also under those conditions that caprolactam will be eliminated to a considerable extent.

We were interested in increasing the reaction rate of hydroxy functional polymers with IBC. It was supposed that electron-withdrawing substitutions in the isophthalic acid would increase the rate. Therefore, we studied the chain extension reaction of hydroxy functional compounds with the lactamate of 5-nitro-isophthalic acid (5-nitro-IBC).

The rate constant, the activation energy, and the collision factor A of the reaction between HEB and IBC or 5-nitro-IBC at 120, 130, and 150°C are given in Table III. The reaction rate of HEB with 5-nitro-IBC at 120°C is about the same as with IBC. However, at higher temperature 5-nitro-IBC appears to be much more reactive. The activation energy (E_a) of 5-nitro-IBC is much higher, but the collision factor is much higher too. Thus, under processing conditions the rate of the chain extension reaction with 5-nitro-IBC is expected to be

Table II Concentration of Caprolactam in Nylon-6 After a Chain Extension Reaction with IBC in Extruder

IBC with Respect to Nylon-6 (%)	Caprolactam Present in IBC (%)	Caprolactam in Extract (%)	% Elimination of Caprolactam (%)[a]
Blank	—	0.19	—
0.5	0.32	0.37	50
1.0	0.64	0.56	58
1.5	0.96	0.68	51

[a] Calculation: [(extract − extract blank)/maximum from IBC] × 100%.

higher (see the subsections below). One can speculate on the mechanism. The mechanism is probably a nucleophilic addition-elimination reaction. One would expect that an electron-withdrawing substituent (nitro group) would decrease E_a. However, it can be seen that E_a is much higher. Probably, the elimination of the negatively charged lactamate is hampered by the more positive charge of the carbonyl group. This suggests the attack of the nucleophile is stimulated (higher A factor) by the attractive force between the nucleophile and the higher positively charged carbonyl group. Also in this case, with 5-nitro IBC, only elimination of caprolactam took place. No ring opening was observed here. It is important to note that the caprolactam, which is formed during the chain extension, can be removed easily in a vented extruder.

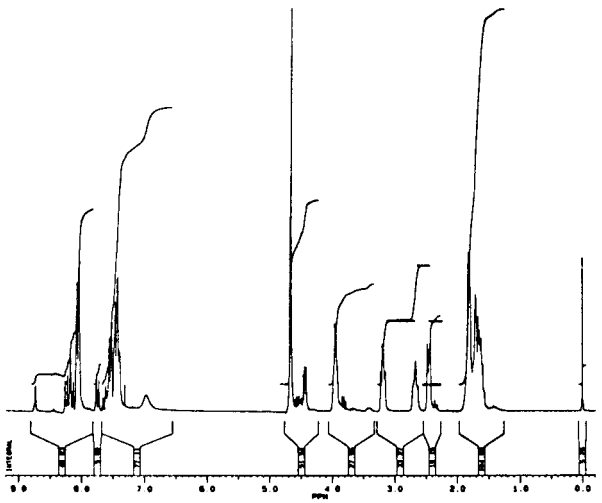


Figure 1 ^{1}H NMR of the reaction mixture of HEB and IBC after heating the mixture for 30 minutes at 150°C.

Chain Extension of Nylon-6

To study the chain extension in polymers we performed some experiments in a Brabender apparatus as well as in an extruder. Because the results are quite similar, we only report the Brabender experiments here. PBO and IBC are used as chain extenders. The chain extender(s) can be added before or after melting the polymer. Both methods give the same results. In Figure 2 the polymer was not melted yet at time = 0. Therefore, in some experiments a decrease in the torque can first be seen followed by an increase. The results are modest if one adds only one chain extender. This was expected and can be calculated too. Only one endgroup of the polymer chain is ultilized now. When both chain extenders are used, the effect on the torque is quite big. If the concentration of the chain extender is matched with the concentration of the endgroups, the rise of the viscosity will be maximized. The η_{rel} increases from 2.50 (blank) to 3.70 in a few minutes.

The crystallization behavior and the mechanical properties (modulus, tensile strength, elongation at break, and mold shrinkage) are measured. These properties are all on the same level as the SSP products, with a corresponding viscosity.

Chain Extension of PET

Similar experiments have been done with PET. The same chain extenders were used as with nylon-6. In addition, 5-nitro-IBC was used. The concentration of the hydroxy endgroups was dissimilar to the concentration of the carboxylic acid end-

Table III Kinetic Data of the Reaction Between HEB and IBC or 5-Nitro-IBC in Bulk

Temperature (°C)	5-Nitro-IBC Rate Constant k_{app}[a] ($l \cdot mol^{-1}s^{-1} \times 10^4$)	IBC Rate Constant k_{app}[a] ($l \cdot mol^{-1}s^{-1} \times 10^4$)
120	0.8	0.7
130	2.3	1.1
150	8.2	2.5
E_a (kJ/mol)	104	60
A ($lmol^{-1}s^{-1}$)	$5.4 \cdot 10^9$	$6.3 \cdot 10^3$

[a] k_{app} is the apparent rate constant.

groups. Once again, when one chain extender is used the results are modest. However, if both chain extenders are added in concentrations matching the endgroups, the rise of the torque is strong again. It can be seen (Fig. 3) that the increase of the torque with an equimolar amount of 5-nitro-IBC (and PBO) is somewhat faster than with an equimolar amount of IBC (and PBO). The viscosity of PET increases with both types of isophthaloyl bislactamate to the same level. The crystallization behavior and the mechanical properties are comparable with the SSP products.

CONCLUSIONS

High molecular weight polycondensates can be obtained by applying SSP. However, this is cumbersome, time consuming, and costly. Similar increases of the molecular weight can be obtained in a few minutes when chain extenders are used. Bisoxazolines react very quickly with carboxylic endgroups of polyesters and polyamides under processing conditions. The reaction is to some extent reversible. The equilibrium lies rather far to the right at 285°C but not completely. Bislactamates react quickly with amino groups or hydroxy groups under processing conditions. During processing, elimination and ring-opening reactions of the of caprolactam ring take place. The elimination reaction is favored at low temperature. Polyesters and polyamides have a statistical distribution of functional endgroups over the polymer chains. If only one chain extender is used, the increase of the viscosity appears to be modest. It is important to use two types of chain extenders in concentrations compatible with the endgroups. Only in that case is a strong increase in the molec-

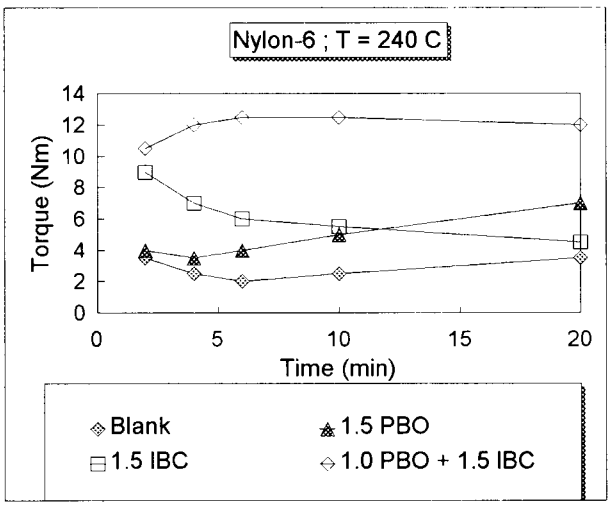


Figure 2 Torque of the Brabender with nylon-6.

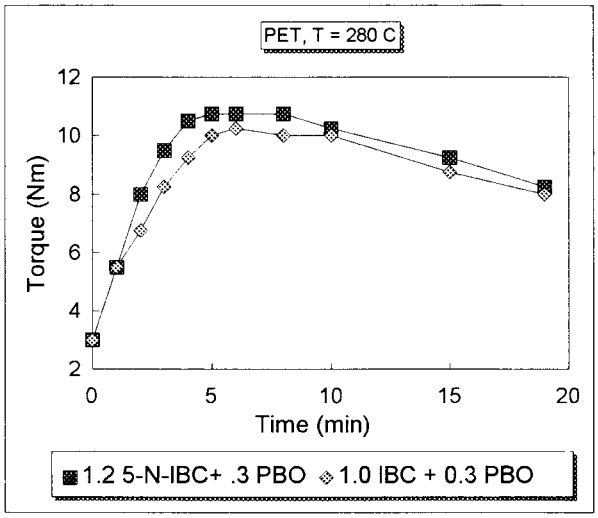


Figure 3 Torque of the Brabender with PET.

ular weight observed within a few minutes in the melt. The properties of the chain-extended polymers are comparable to those obtained in the SSP process.

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