Synthesis of Bis-*N*-acyllactams Type Chain Extenders for Polyesters and Polyamides

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ABSTRACT: This article shows the synthesis of chain extenders derived from the group of bis-*N*-acyllactams. These chain extenders may not only increase the molecular weight of polyesters or polyamides but also permit a flexible modification at the same time by incorporating an arbitrary functionality in the polymer chains. The chain extenders are synthesized by a two step process starting from terephthaloyl chloride, ε-caprolactam, and the functional moiety R which derives from a diol HO—*R*—OH or diamine H_2N—*R*—NH_2. For five chain extenders varying in the moiety R, the synthesis is explicitly shown and the thermal stability is investigated. It can be shown that the chain extenders are thermal stable up to 260°C at least. The chain extenders may thus be useful to increase the molecular weight and to modify many important thermoplastic polyesters and polyamides during the melt extrusion process. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 425–432, 2007

Key words: chain extenders; coupling reactions; modification; molecular weight increase

INTRODUCTION

High molecular weight polyesters or polyamides are often used for special applications e.g., for the production of technical textiles. Such high molecular weight polymers are usually obtained by a solid state polycondensation (SSP) process which follows after polymer synthesis.[1–3] The SSP, however, is a time and energy consuming process. An alternative to produce high molecular weight polyesters or polyamides is the use of chain extenders which are added to the polymer melt after the polymer synthesis or during the melt extrusion process.[4–7]

Chain extenders are molecules which have the capability to connect two or more polymer molecules with each other by reacting with the polymer endgroups in a fast reaction. In the following, we confine our considerations on chain extenders which have two reactive groups and thus may connect two polymer molecules with each other. The amount of chain extender added to the polymer melt is determined by the number of polymer end groups. From a theoretical point of view[8] the highest increase of the molecular weight is expected if equimolar quantities of chain extenders are added where the molar ratio r of the chain extender groups to the polymer end groups is $r = 1$ (the theory makes the assumption that the coupling reaction is described with only one kinetic constant).

Chain extenders may divided in two groups, namely (a) chain extenders of the condensation and (b) of the addition type. It should be noted, however, that this classification can only be done roughly because the addition type chain extenders may also considerably undergo elimination reactions as discussed later.

In the case (a) the chain extender molecules react with the polymer end groups (e.g., hydroxyl end groups) according to an elimination mechanism where a small molecule is eliminated. Such chain extenders are for example diphenyl carbonate or diphenyl isophthalate eliminating phenol during reaction.[4] The disadvantage of this type of chain extender is that the byproduct (e.g., phenol) remains in the polymer and thus may cause problems in the following processing steps or in the later polymer application.[5] In contrast, chain extenders of the addition type (case (b)) react preferably according to an addition mechanism where no byproduct molecules are eliminated during the coupling step. Important representatives in this group are the bis-*N*-acyllactams reacting with hydroxyl end groups in polyesters or amino end groups in polyamides. As shown elsewhere,[6,7] bis-*N*-acyllactams are effective chain extenders with respect to the increase of the molecular weight. However, as pointed out by Loontjens et al.[6] the path of the coupling reaction (elimination of caprolactam versus ring opening mechanism) depends on the type of the nucleophile and on the reaction temperature. Under mild conditions the

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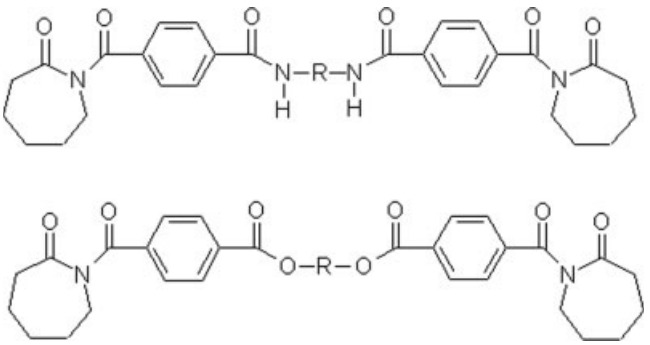

Figure 1 Chain extenders of the bis-*N*-acyllactam type which may incorporate a functionality *R* in the polymer chain during chain extension where *R* denotes an arbitrary organic moiety.

elimination of caprolactam is the main reaction. Under more serve conditions the ring opening mechanism (addition mechanism) may also be operative. Furthermore, as pointed out by Akkapeddi and Gervasi,[7] the use of terephthaloyl biscaprolactam (TBC) was ineffective in chain extending PET whereas the use of terephthaloyl bislaurolactam (TBL) leads to a high molecular weight polyester where in the latter case the authors assumed that a ring opening reaction (addition mechanism) is predominant. In the case of chain extending polyamide 6, however, both compounds TBC, as well as, TBL were effective chain extender resulting in a high molecular weight polyamide.

Our aim was to develop novel chain extenders on the basis of bis-*N*-acyllactams which may not only increase the molecular weight, but also modify the polymer at the same by incorporating covalently an arbitrary functionality *R* in the polymer chain. Since chain extenders will achieve economic acceptance only if they are easy to manufacture, and based on commercially low cost raw materials we therefore developed chain extenders that can be synthesized from terephthaloyl chloride, ε-caprolactam, and the functional moiety *R* which derives from a diol HO—*R*—OH or diamine H_2N—*R*—NH_2. Figure 1 shows the general structure of the chain extenders of the bis-*N*-acyllactam type which may incorporate a functionality *R* in the polymer chain during chain extension.

The aim of this article is to demonstrate a general route to synthesize chain extenders that can be derived from Figure 1. For five different chain extenders, we show explicitly the synthesis where the compounds are characterized by nuclear magnetic resonance spectroscopy (NMR). Furthermore, the thermal stability of these chain extenders is shown since the thermal stability is an important property in view of processing the chain extenders with polyesters or polyamides where melt temperatures are applied exceeding often 260°C.

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich company. The 1,4-dioxane was dried over molecular sieves (effective diameter of 4 Å) and the pyridine was purified by distillation before use.

Chain extender synthesis

a. *Synthesis of terephthaloyl monocaprolactam chloride:* In a 500 mL three-neck flask fitted with a $CaCl_2$ drying tube 15.82 g (0.2 mol) pyridine or 20.24 g (0.2 mol) triethylamine is added to 40.60 g (0.2 mol) terephthaloyl chloride in 220 mL 1,4-dioxane under a nitrogen flow. The reaction mixture is cooled to 15°C and 22.64 g (0.2 mol) ε-caprolactam is added to the solution within 1 h under stirring. The resulting pyridinium chloride is filtered off and the solvent is evaporated. The yield is determined to be 96.2%.
b. *Reaction of terephthaloyl monocaprolactam chloride with 1,3-phenylenediamine to 1,3-phenylenediamine-bis(terephthaloyl-N-caprolactam):* In a 500 mL three-neck flask fitted with a $CaCl_2$ drying tube 5.59 g (0.02 mol) of terephthaloyl monolactam-chloride of synthesis (a) is dissolved in 20 mL 1,4-dioxane under nitrogen. After addition of 1.74 g (0.022 mol) pyridine, 1.08 g (0.01 mol) 1,3-phenylenediamine in 20 mL 1,4-dioxane is added to the solution within 10 min at 20°C. The reaction mixture is stirred for additional 30 min. Subsequently, the mixture is poured into ice water resulting in a white solid which is filtered off and washed with water. After drying the crude product is recrystallized with chlorobenzene resulting in a white product with a melting point of 209°C. The yield is found to be 47.7%. The product is characterized by ^{1}H NMR in $CDCl_3$ (ppm: arom. CH(terephth) = 7.67–7.70 and 7.40–7.43; —NH—Ph—NH— = 8.67; arom. N—Ph—N = 7.28–7.12; N—CH_2(lactam) = 3.95; N—CO—CH_2(lactam) = 2.63; CH_2 (lactam) = 1.82).
c. *Reaction of terephthaloyl monocaprolactam chloride with 1,4-phenylenediamine to 1,4-phenylenediamine-bis(terephthaloyl-N-caprolactam):* The synthesis corresponds to the synthesis (b) in which 1,3-phenylenediamine is replaced by 1,4-phenylenediamine. The dried crude product is recrystallized from N,N-dimethylacetamide (DMA) resulting in a white product with a melting point of 330°C. The yield is determined to be 51.1%. The product is characterized by ^{1}H NMR in d-DMSO (ppm: arom. CH (terephth) = 7.94–7.97 and 7.60–7.64; —NH—Ph—NH— = 10.37; arom. N—Ph—N = 7.76; N-CH_2(lactam) = 3.96;

N—CO—CH_2(lactam) = 2.71; CH_2(lactam) = 1.77).

d. *Reaction of terephthaloyl monocaprolactam chloride with polyethylene glycol 1000 to polyethylene glycol-bis(terephthaloyl-N-caprolactam)*: In a 250 mL three-neck flask fitted with a $CaCl_2$ drying tube 5.59 g (0.02 mol) of terephthaloyl monolactam-chloride of synthesis (a) is dissolved in 40 mL 1,4-dioxane under nitrogen. To the solution 1.74 g (0.022 mol) of pyridine is added. Subsequently, within 20 min a solution of 10 g (0.01 mol) of polyethylene glycol 1000 in 100 mL 1,4-dioxane is added. The reaction mixture is stirred for 2 h at 30°C. After isolating the solid by filtration the solvent of the filtrate is evaporated resulting in a highly viscous liquid. The crude product is solved in a few amount of water and shaken with chloroform in a separatory funnel. The solvent of the chloroform phase is evaporated resulting in a white highly viscous liquid. The product is not further purified and characterized by ^{1}H NMR in $CDCl_3$. (ppm: arom. CH(terephth) = 8.06–8.21 and 7.52–7.62; O—CH_2 = 3.64; N—CH_2(lactam) = 4.01; N—CO—CH_2(lactam) = 2.71; CH_2(lactam) = 1.86).

e. *Reaction of terephthaloyl chloride with caprolactam and ethylenediamine to ethylenediamine-bis(terephthaloyl-N-caprolactam):* In a 250 mL three-neck flask fitted with a $CaCl_2$ drying tube, 4.06 g (0.02 mol) of terephthaloyl chloride is dissolved in 50 mL 1,4-dioxane at 15°C under nitrogen. After addition of 3.48 g (0.044 mol) pyridine 2.26 g (0.02 mol) ε-caprolactam is added within 1 h under stirring. To the reaction mixture 0.60 g (0.01 mol) ethylenediamine in 20 mL 1,4-dioxane are added within 20 min and the mixture is stirred for 1 h in addition. The mixture is poured in ice water resulting firstly in an emulsion transforming afterwards in a solid. The crude product is isolated by filtration and the dried crude product is recrystallized from 1,4-dioxane yielding 16.4% of the purified compound. The recrystallized product has a melting point of 225°C and is characterized by ^{1}H NMR in d-DMSO (ppm: arom. CH(terephth) = 7.83–7.86 and 7.54–7.57; NH = 8.72; N—CH_2 = 3.45; N—CH_2(lactam) = 3.93; N—CO—CH_2(lactam) = 2.67; CH_2(lactam) = 1.75).

f. *Reaction of terephthaloyl chloride with caprolactam and ethylene glycol to ethylene glycol-bis(terephthaloyl-N-caprolactam)*: The synthesis corresponds to synthesis (e) in which ethylenediamine is replaced by 0.62 g (0.01 mol) ethylene glycol. The dried crude product is recrystallized from butyl acetate resulting in a white solid with a melting point of 172°C and a yield of 56.3%. The product is characterized by ^{1}H NMR in $CDCl_3$ (ppm: arom. CH(terephth) = 8.06–8.09 and 7.53–7.56; O—CH_2 = 4.66; N—CH_2(lactam) = 4.00; N—CO—CH_2(lactam) = 2.71; CH_2(lactam) = 1.85).

g. *Synthesis of 3,6-dioxaoctanediyl-biscaprolactam:* 5.0 g (0.028 mol) of 3,6-dioxaoctanedioic acid is refluxed with 50 mL of thionyl chloride for 8 h. The excess of thionyl chloride is evaporated under vacuum. The resulting acid chloride is dissolved in 80 mL of 1,4-dioxane and 4.75 g (0.06 mol) pyridine is added. After addition of 6.34 g (0.056 mol) of ε-caprolactam, the reaction mixture is stirred at room temperature for 1 h. The resulting pyridinium chloride is removed by filtration and the solvent of the filtrate is evaporated leading to a yellow colored oily product transforming in a solid after ~72 h. After recrystallization with cyclohexane a white solid with a melting point of 95–97°C is obtained. The yield is found to be 59.0%. The product is characterized by ^{1}H NMR in $CDCl_3$ (ppm: —O—CH_2—CH_2—O— = 4.66; —O—CH_2—CON— = 3.80; N—CH_2(lactam) = 3.92; N—CO—CH_2(lactam) = 2.71; CH_2(lactam) = 1.72).

Determination of the terephthaloyl monocaprolactam chloride yield by HPLC

The high pressure liquid chromatography (HPLC) analysis is carried out with a Kroma system 2000 of Kontron Instruments using a Spherisorb Si column and a precolumn of Waters. The column has a length of 25 cm and a diameter of 0.4 cm and is filled with 5 μm silica particles. The mobile phase is a mixture of *n*-hexane and 1,4-dioxane (50 : 50 vol %). The flow rate is adjusted to be 1 mL/min where the eluate is detected at 254 nm with a UV detector. The amount of acid halogenides cannot be determined directly by HPLC. Therefore, the acid halogenides are transferred into theirs methyl esters as follows: after finishing the first reaction stage (reaction of equimolar amounts of terephthaloyl chloride with caprolactam in the presence of pyridine or triethylamine) the precipitated salt is filtered off and the solvent of the filtrate is evaporated. In the following step, 0.5 g of the reaction mixture is added to 20 mL of 1,4-dioxane where 0.6 g of triethylamine is added subsequently. After addition of 0.6 g of methanol and a reaction time of 10 min at room temperature, the reaction mixture is filtered with a Teflon filter (0.45 μm) and the filtrate is diluted with 1,4-dioxane in a ratio 1:20. The solution is taken for the HPLC analysis. The retention time of terephthaloyl monocaprolactam monomethylester is 8.13 min, whereas

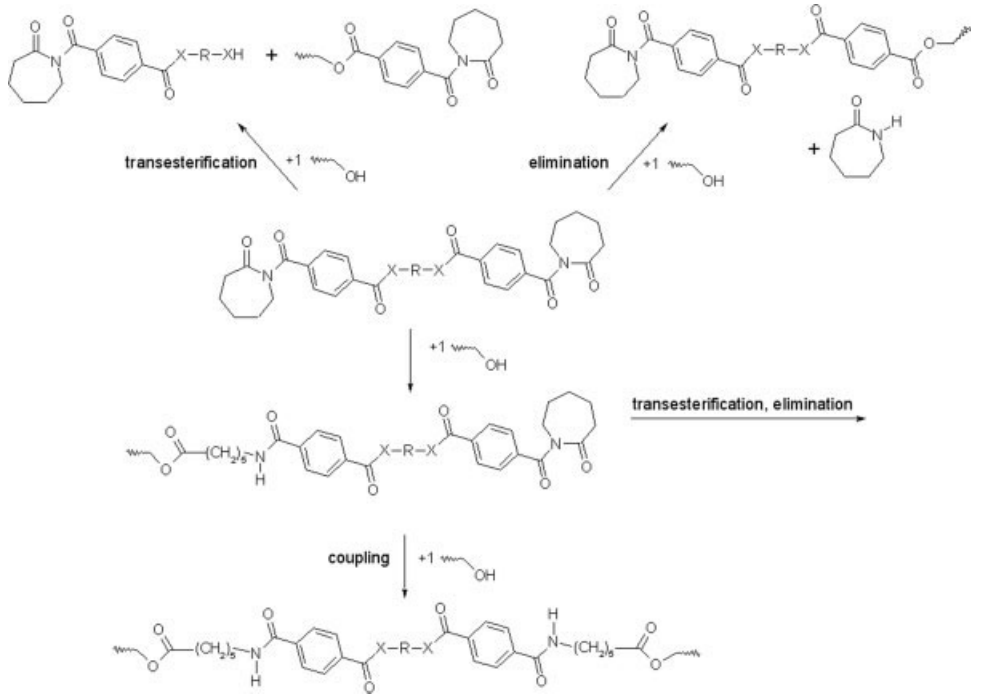

Figure 2 Reaction possibilities of a chain extender molecule derived from Figure 1 with the hydroxyl end groups of a polymer chain where X corresponds either to NH or to O.

the reference compounds dimethyl terephthalate and TBC show a retention time of 6.38 and 12.02 min, respectively. From the area under the signals the yield of terephthaloyl monocaprolactam chloride is calculated.

NMR spectroscopy

The ^{1}H NMR characterization of the different chain extenders is carried out on a Bruker DPX 250 MHz.

Thermogravimetric analysis

The thermogravimetric investigations are carried out with a TGA 7 Thermogravimetric Analyzer of the company Firma Perkin–Elmer where synthetic air is applied and the heating rate is set to be 10 K/min.

RESULTS AND DISCUSSION

The chain extenders given in Figure 1 have two acyllactam moieties able to react with the hydroxyl- or amino-groups of a polymer. In addition, the chain extenders have an aromatic system in their structure that will promote the thermal stability as discussed later. Finally, the main characteristic of the chain extenders in Figure 1 is the functional moiety *R* which may incorporate covalently in a polymer chain during coupling and thus modify or functionalize the polymer during the chain extension process. In comparison to the well known chain extender TBC the chain extenders derived from Figure 1 have additional ester or amid groups in their structure. Therefore, their reaction behavior with respect to the polymer end groups may discussed different as shown in Figure 2 where a chain extender reacts exemplarily with the hydroxyl end groups of a polymer.

The transesterification and the elimination of caprolactam shown in Figure 2 are two undesired reactions where the resulting products may be involved in further reactions with the polymer end groups and may also contribute to an increase of the molecular weight. The main desired reaction is the addition mechanism where the first caprolactam moiety reacts with a polymer end group under ring opening. However, on this stage the formed intermediate may also undergo further undesired transesterification or elimination reactions with other polymer end group as discussed above. The desired chain extension or coupling reaction takes only place if the second caprolactam moiety reacts under an addition mechanism as shown in Figure 2. The resulting product consists of the functionalized moiety *R* that is covalently incorporated between two polymer chains. How the ratio or the magnitude of transesterification, elimination, and coupling reactions are, cannot be estimated or proved at the moment. The above discussion, however, demonstrates that the chain extenders derived from Figure 1 may undergo a multitude of different reactions with the polymer end groups in a polymer melt.

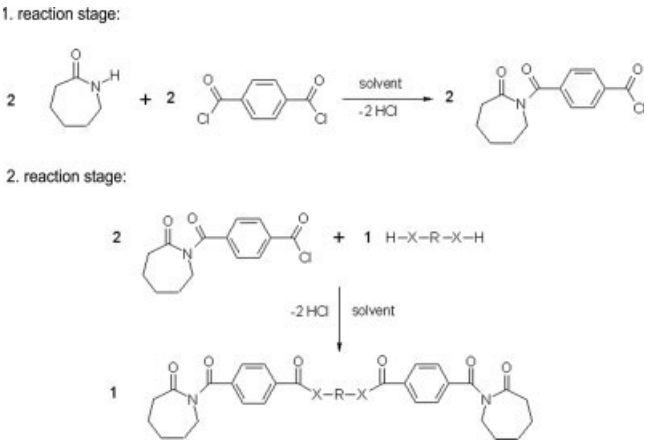

Figure 3 Reaction schema to synthesize chain extenders given in Figure 1 by a two step process where X corresponds either to NH (diamine) or to O (diol).

Synthesis

For the synthesis of the chain extender given in Figure 1, we developed a two step process as shown in Figure 3. In the first stage equimolar amounts of ε-caprolactam and terephthaloyl chloride react in an inert organic solvent under inert anhydrous atmosphere. The reaction is carried out between 15 and 30°C. To accelerate the reaction an organic base is added, capable to link the hydrogen chloride eliminated during the course of the reaction. As base triethylamine or pyridine have turned out to be suitable resulting in a precipitation of triethylammonium chloride or pyridinium chloride during reaction.

Since at the first reaction stage a bifunctional molecule (terephthaloyl chloride) is converted with a monofunctional molecule (ε-caprolactam) one would expect theoretically that a mixture of terephthaloyl chloride, terephthaloyl monocaprolactam chloride, and TBC in a molar ratio of 1 : 1 : 1 will result if both acid chloride groups have the same reactivity. However, we find under the experimental conditions applied that the terephthaloyl monocaprolactam chloride is formed in a high yield as determined by HPLC. To separate and to quantify the reaction mixture formed during the first synthesis stage by HPLC, we transform the acid chloride in its methyl ester since the acid chlorides cannot be analyzed directly by HPLC. Therefore, the HPLC diagram in Figure 4 shows the terephthaloyl monocaprolactam monomethylester in comparison to the both reference compounds dimethyl terephthalate and TBC where also two further byproducts are formed in small quantities that cannot be assigned to a molecular structure. Form Figure 4 we can determine the yield of terephthaloyl monocaprolactam chloride resulting in the first reaction stage to be 72%. According to this high yield, we can conclude that the reactivity of the second acid chloride group in terephthaloyl chloride will decrease after the first acid chloride group has reacted with ϵ-caprolactam. This observation is consistent with the investigations of Entelis et al.[9] in the case of the reaction of terephthaloyl chloride with ethylene glycol in 1,4-dioxane.

During the second reaction stage a diol HO—*R*—OH or a diamine H_2N—*R*—NH_2 is converted with the terephthaloyl monocaprolactam chloride of the first stage in a molar ratio of 1 : 2 to the final chain extender. In accordance with the first stage this reaction is also carried out in an inert solvent in the presence of an organic base where the latter links the hydrogen chloride eliminated during the second reaction stage. After the conversion has finished, the product is separated from the triethylammonium chloride or pyridinium chloride and is subsequently purified (e.g., by recrystallization).

The synthesis strategy discussed and given by Figure 3 is particularly suitable because the terephthaloyl monocaprolactam chloride can be obtained in a high yield after the first reaction stage. It should be noted that the synthesis strategy can be managed without the use of costly protecting group technique making this route attractive in view of economic aspects. However, Figure 3 represents only an idealized synthesis path without any side reactions. As shown by the HPLC diagram in Figure 4 unreacted terephthaloyl chloride is present leading to side products. Under the assumption that the acyllactam groups do not react with HX-*R*-XH molecules under elimination of ε-caprolactam, we would expect mainly two different types of side products A and B as given in Figure 5 where the A-type molecules should only occur in a low concentration. Nevertheless, to avoid possible corrosion of metal generated by the presence of acylchlorides during the extrusion process a purification step of the chain extender

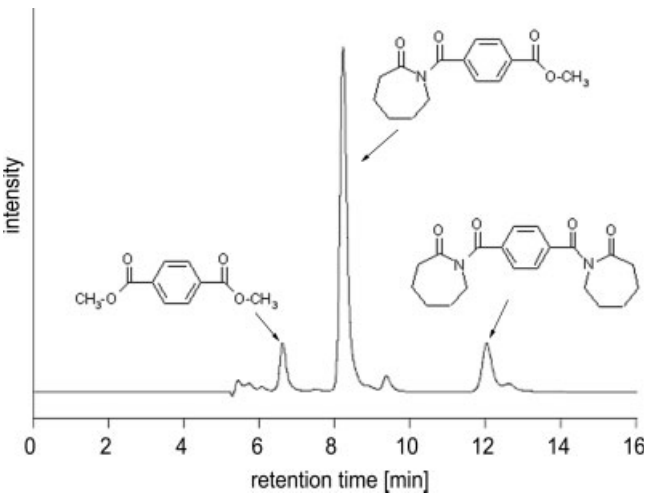

Figure 4 HPLC diagram of terephthaloyl monocaprolactam monomethylester in comparison to the both reference compounds dimethyl terephthalate and TBC.

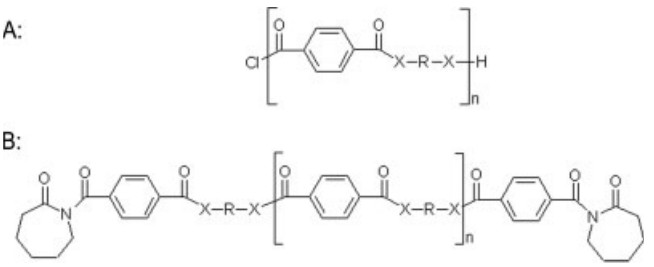

Figure 5 Two different types of side products A and B which can be formed during the second reaction step.

should be carried out before usage at high temperatures.

Figure 6 shows five different chain extenders synthesized according to the route given by Figure 3 where the functionalized moiety R base either on ethylene glycol, or polyethylene glycol, or ethylenediamine, or 1,4-phenylenediamine, or 1,3-phenylenediamine. The chain extenders are purified by recrystallization technique and characterized by ^{1}H NMR. Figure 7 shows exemplarily the ^{1}H NMR spectra of 1,3-phenylenediamine-bis(terephthaloyl-*N*-caprolactam) and the assignment of the protons to the structure. The chemical shift of the protons of the bis (terephthaloyl-*N*-caprolactam) moiety are nearly identical for all chain extenders shown in Figure 6. The spectra mainly differ in the X-*R*-X moiety. In the experimental section the complete assignment of the ^{1}H NMR peaks and the melting point data of the five chain extenders can be found. According to the ^{1}H NMR spectra, the chain extenders have a high purity after recrystallization which can be estimated to be more than 95 mol %. It should be noted that traces of the recrystallization solvent may be incorporated in some of the synthesized chain extenders during the recrystallization process. This will be obvious in the NMR spectra as well as in the TGA curves shown later.

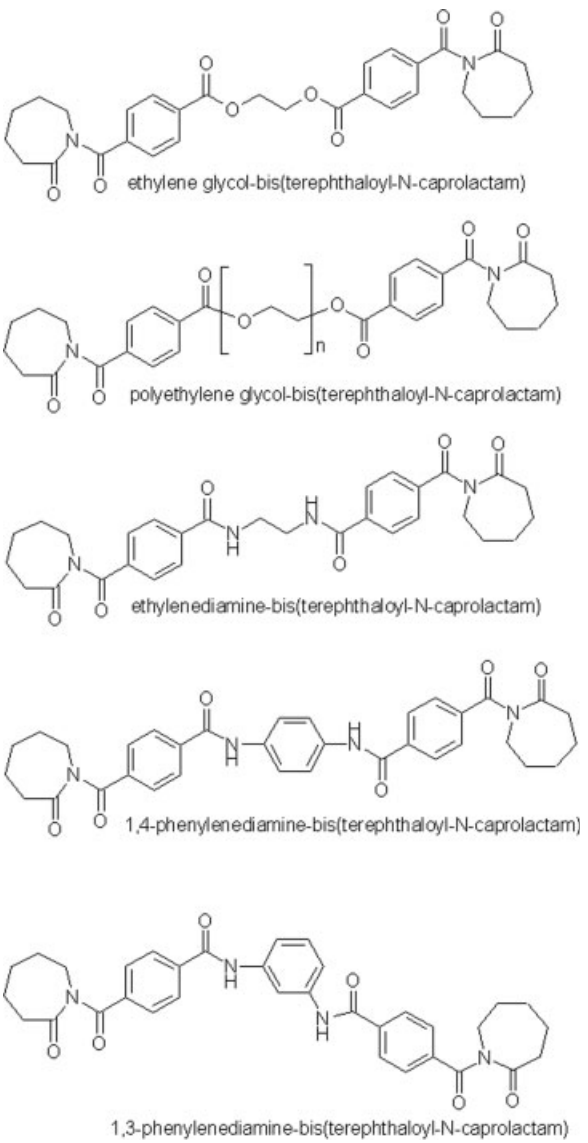

Figure 6 Bis-*N*-acyllactams basing on the general structure of Figure 1 with different functional moieties *R*.

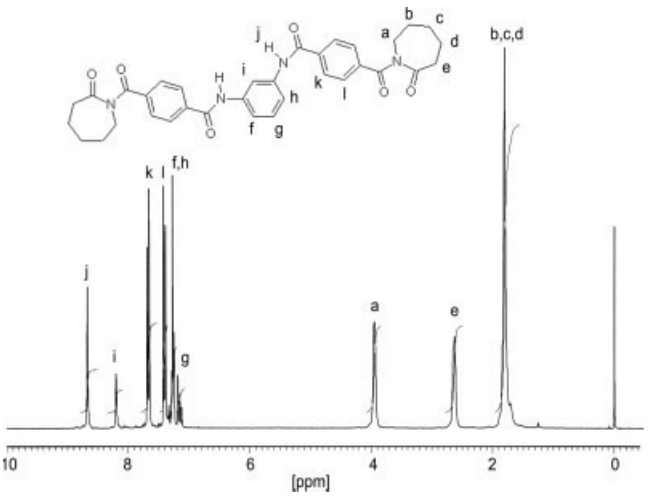

Figure 7 ^{1}H NMR spectra of 1,3-phenylenediamine-bis(terephthaloyl-*N*-caprolactam) and the assignment of the protons to the structure.

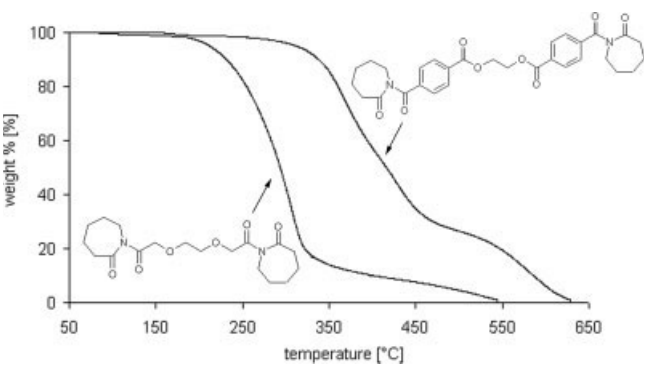

Figure 8 TGA of ethylene glycol-bis(terephthaloyl-*N*-caprolactam) in comparison to 3,6-dioxaoctanediyl-biscaprolactam under synthetic air.

TABLE I
Thermal Stability Characterized by the Onset and Inflection Point Temperature for Different Chain Extenders Determined by Thermogravimetric Analysis

	Onset temperature (°C)	Inflection point temperature (°C)
Ethylene glycol-bis(terephthaloyl-*N*-caprolactam)	334	368
Polyethylene glycol-bis(terephthaloyl-*N*-caprolactam)	287	340
Ethylenediamine-bis(terephthaloyl-*N*-caprolactam)	297	312
1,4-phenylenediamine-bis(terephthaloyl-*N*-caprolactam)	339	351
1,3-phenylenediamine-bis(terephthaloyl-*N*-caprolactam)	310	359

The five chain extenders have different property profiles where for example polyethylene glycol-bis (terephthaloyl-*N*-caprolactam) is a flexible chain extender which may improve the dyeability of polyethylene terephthalate (PET) fibers if the chain extender reacts with the PET chains in the polymer melt. In contrast with 1,4-phenylenediamine-bis(terephthaloyl-*N*-caprolactam) and 1,3-phenylenediamine-bis(terephthaloyl-*N*-caprolactam), we have stiff chain extenders. According to Figure 2 the stiff moieties can be incorporated in polyester or polyamide chains to improve the mechanical properties of the polymer material.

Thermal stability

The thermal stability of chain extenders is a crucial point since processing temperatures of polyesters or polyamides are usually at high temperatures. For example, polyamide 6 is extruded at temperatures of 260°C whereas for PET temperatures of ~ 280°C are applied.

Figure 8 shows the TGA of ethylene glycol-bis(terephthaloyl-*N*-caprolactam) in comparison to 3,6-dioxaoctanediyl-biscaprolactam under synthetic air. As shown in Figure 8, the introduction of an aromatic system in the structure of a chain extender may significantly improve the thermal stability of the chain extender. Therefore, the chain extenders in Figure 1 have two aromatic systems in their structure that should make high processing temperatures possible. Table I shows a comparison of the onset and inflection point temperature obtained from the TGA of the five chain extenders given in Figure 6 where the complete TGA curves of the five chain extenders are shown in Figure 9.

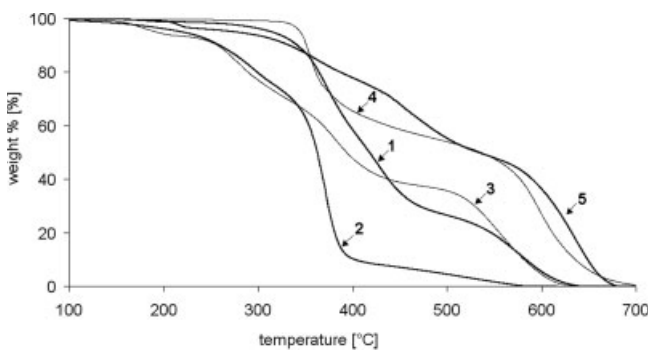

Figure 9 TGA of (1) ethylene glycol-bis(terephthaloyl-*N*-caprolactam); (2) polyethylene glycol-bis(terephthaloyl-*N*-caprolactam); (3) ethylenediaminebis(terephthaloyl-*N*-caprolactam); (4) 1,4-phenylenediamine-bis(terephthaloyl-*N*-caprolactam); (5) 1,3-phenylenediamine-bis(terephthaloyl-*N*-caprolactam) under synthetic air.

According to Table I and Figure 9, the chain extenders can be processed at temperatures up to 260°C at least which will be sufficient for most thermoplastic polyesters or polyamides. With respect to these results we expect for any further chain extenders derived from Figure 1 a corresponding high thermal stability.

CONCLUSIONS

We have shown a general route to synthesize chain extenders of the bis-*N*-acyllactam type by a two step process without applying protecting group techniques. The chain extenders synthesized may react with the hydroxyl- or amino-polymer end groups increasing the molecular weight of the polymer and simultaneously incorporating covalently an arbitrary moiety R in a polymer chain able to modify the polymer properties. The advantage of this kind of chain extenders is that high molecular polymers with functionality can be obtained directly during the melt extrusion process. Therefore, by using the chain extenders given in Figure 1, it would be possible to replace on the one hand the modification or functionalization of the polymer during the polymer synthesis and on the other hand the cost and time consuming SSP process.

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