

Synthesis and Characterization of Di-Polyester Diamides

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ABSTRACT: A series of di-polyester diamides was synthesized via a nucleophilic ring opening polymerization process. FTIR investigations revealed the spectral characteristics evidencing the newly formed chemical bonds as well as the changes in the relative intensity of the characteristic peaks, due to the increasing side-block lengths of the different members of the series. $^1\text{H-NMR}$ analysis of the described materials confirmed the chemical structures seen by FTIR analysis. The side segment length of the different di-polyester diamides was calculated from the integration ratios in the NMR spectra. The molecular weight results exhibited relatively small deviations from the stoichiometrically calculated values. All the members of the triblock series, with side blocks of up to 120 lactoyl units, were essentially amorphous and glassy at room tempera-

ture. The presence of two separate glass transitions indicated a segmented and microphase separated morphology. It was deduced that the amorphous nature of the relatively long poly(lactic acid) side blocks occurs due to the dominance of the hydrogen-bonded central segment. Synthesis of a di-polyester diamide containing a reduced number of hydrogen-bond-forming groups in the central segment yielded a partial side-block crystallization. The di-polyester diamide with 120 lactoyl unit-long side blocks was eventually able to crystallize in solid state, following thermal treatment during thermal analysis. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: ring opening polymerization; di-polyester-diamide; thermal properties; FTIR; NMR

INTRODUCTION

Degradable di- and triblocks are widely known in various biomedical applications, mainly as implantable materials¹ and drug release devices.² The distinct advantage of using degradable microphase-separated block copolymers as opposed to regular copolymers in biomedical applications is the enhanced ability to accurately tailor both the mechanical properties and the degradation kinetics of the final device. This is mainly achieved by controlling the chemical structure and the size of each of the polymer segments and their ratio.

Among the most extensively studied degradable triblocks for biomedical applications, are those consisting of a central poly(ethylene glycol) (PEG) block and a poly(lactic acid) (PLA) block on each side of the central PEG block.^{1,3,4} In an earlier study,⁵ the synthesis and properties of a series of biomedical degradable poly(ester-ether-urethane)s, based on chain extended poly(caprolactone) (PCL)-PEG-(PCL) triblocks, was presented.

Poly(ester amide) copolymers with alternating amide and ester groups are commonly synthesized via copolycondensation of hydroxy acids and amino

acids or by ring opening of amide esters.⁶ Poly(ester amide) block copolymers were obtained by ring opening polymerization of lactams, as for example caprolactam.⁷

The present article presents a family of di-polyester diamides, synthesized via the nucleophilic ring opening polymerization of lactide, with diamines, exhibiting unique physical properties.

The main purpose in the synthesis of this new molecular family was to obtain materials of prominent rigidity, but with low molecular weights and thus with potentially short degradation periods, as new implantable materials and drug-delivery matrices for biomedical applications.

EXPERIMENTAL

Materials

The following materials were used in this study: diethylenetriamine (DETA) 99% (Sigma-Aldrich); hexamethylenediamine (HMDA) 98% (Aldrich); L-lactide 99.5% (Purac—Purasorb); Tin(II) 2-ethylhexanoate 95% (Sigma); acetone 99.5% (Frutarom), and dimethylsulfoxide (DMSO) d_6 (Aldrich).

Synthesis of di-polyester diamides

The syntheses were performed in a sealed 100-mL glass reactor, with magnetic stirring. The appropriate

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TABLE I
Molar Ratios in the Di-Polyester Diamides

Type of di-polyester diamide	No. of lactoyl units per side segment	Total no. of lactoyl units per molecule	DETA or HMDA/lactide molar ratio
LA ₄ -DETA-LA ₄	4	8	1 : 4
LA ₆₀ -DETA-LA ₆₀	60	120	1 : 60
LA ₆₀ -HMDA-LA ₆₀	60	120	1 : 60
LA ₁₂₀ -DETA-LA ₁₂₀	120	240	1 : 120

reagents were weighed into the reactor, according to the required stoichiometry (Table I) and 0.5 g of catalyst (ethyl-tin-hexanoate) was added. The quantitative calculations were such, as to obtain a final amount of 50 g of polymer in each of the syntheses. The reactor was purged with dry nitrogen gas in order to minimize oxidation during reaction and sealed. The reaction was carried out at 150°C, using oil bath heating. The reactions were carried out for 90 min, after which the contents of the reactor were quickly poured into glass storage vessels and sealed before solidification (vitrification) of the polymers occurred during the cooling process.

Instrumentation

FTIR measurements were carried out on a Perkin Elmer—Spectrum BX FTIR spectrometer. Samples were prepared by dissolving a small amount of the tested material in 2 mL of acetone, and a fraction of the resulting solution was dripped on a NaCl crystal disc and evaporated at room temperature.

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed in parallel, on a simultaneous thermal analysis instrument—STA Scinco S-1500. Samples weighing between 8 and 12 mg were weighed on the instru-

ment scale, in a clean platinum crucible, with an identical empty crucible as reference. The measurements were performed at a heating rate of 10°C/min under nitrogen atmosphere.

Proton nuclear magnetic resonance (¹H-NMR) spectra were recorded at ambient temperature, on a Varian—300 MHz spectrometer. Chemical shifts were referred to tetramethylsilane as internal standard. DMSO *d*₆ was used as solvent for all tested samples.

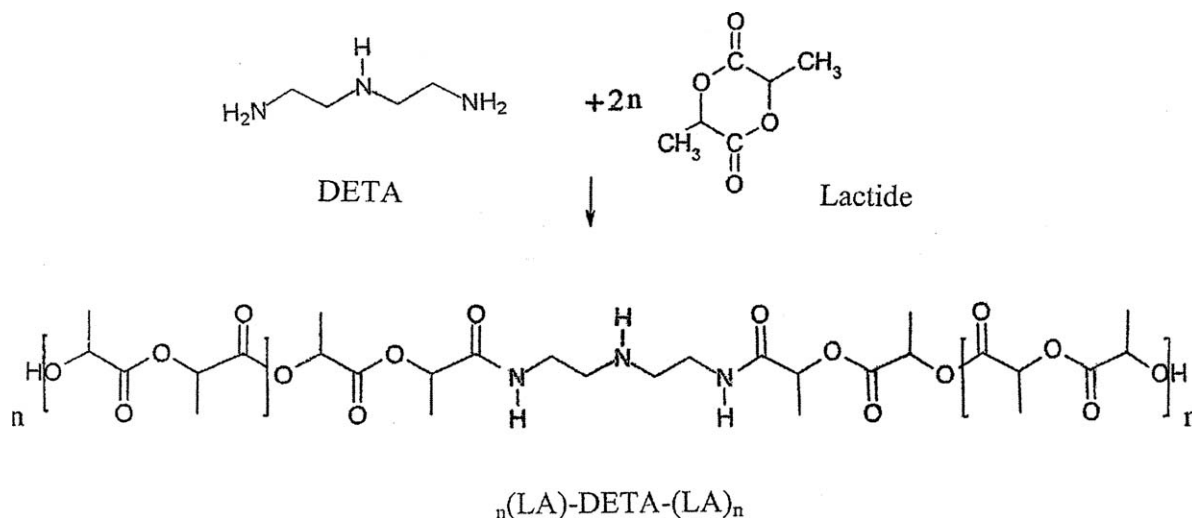
RESULTS AND DISCUSSION

The polymerization process of the di-polyester diamide series described in this article proceeds via a nucleophilic ring-opening reaction, as schematically represented in Scheme 1.

The first and shortest di-polyester diamide of this series (synthesized by reacting DETA with L-lactide at a molar ratio of 1 : 4) consists of the central DETA and four lactic acid (LA) units linked on both sides.

Figure 1(a,b) presents the FTIR analysis spectra of the two reactants, DETA and L-lactide, respectively.

DETA has two primary amines and a central secondary amine, interconnected with two ethylene groups. The spectrum of DETA in Figure 1(a) exhibits the very characteristic absorbances of the primary amine groups: the NH stretching at around 3335 cm⁻¹, which appears as a split peak characteristic for primary amines, is clearly seen in the spectrum (for secondary amines this peak is not split). The sharp absorbance at 1600 cm⁻¹ is due to the NH₂ deformation vibrations of the primary amine group. The broad absorbance in the range of 770–910 cm⁻¹ is due to the NH₂ wagging vibration of the primary amine groups. The ethylene groups of the molecule are represented in the spectrum by the absorbances of the CH stretching vibrations at 2846 and 2929 cm⁻¹ and also



Scheme 1 Schematic representation of the reaction pathway in the polyester diamide triblock synthesis.

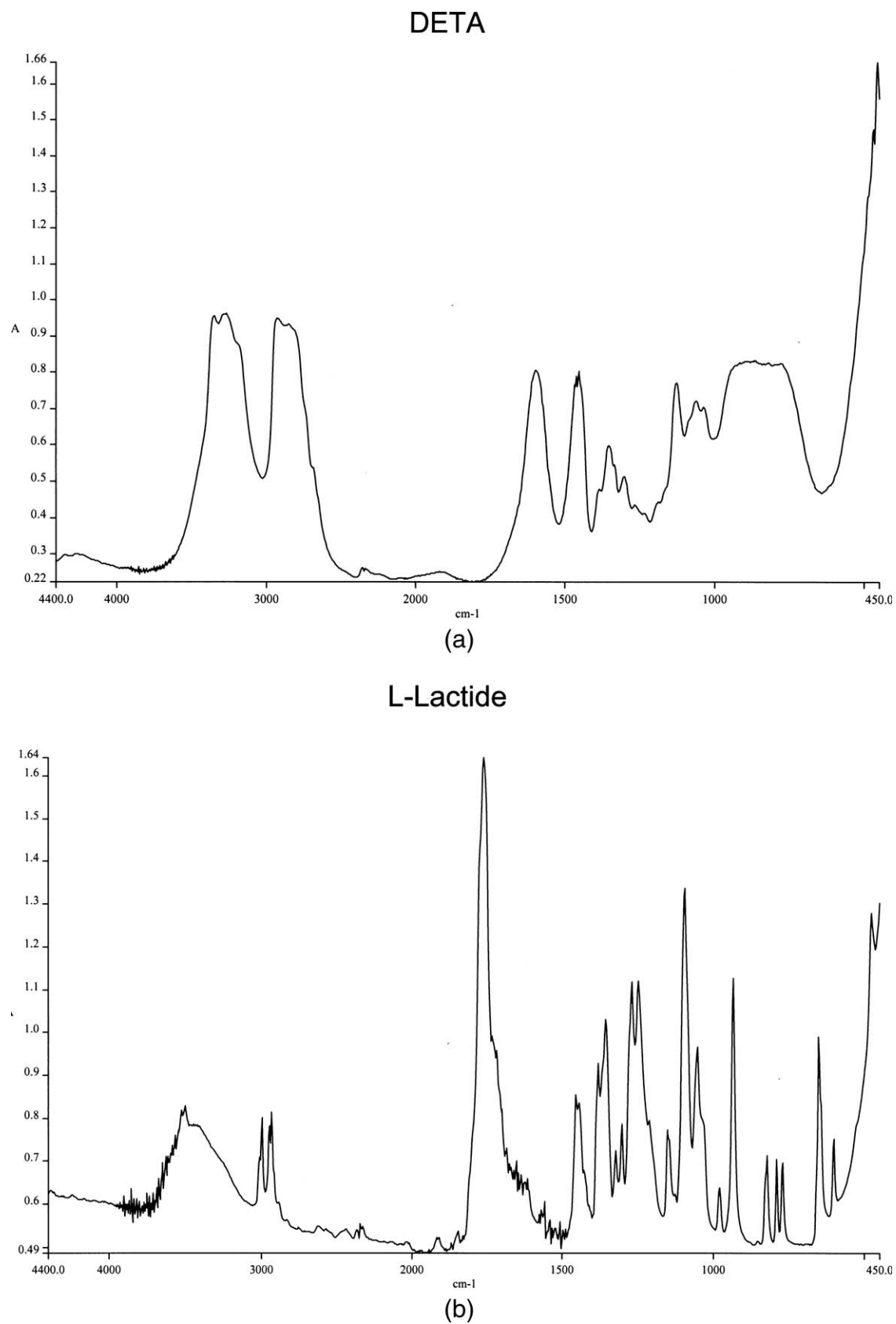


Figure 1 FTIR spectrum of DETA (a) and of L-lactide (b).

DETA-LA4

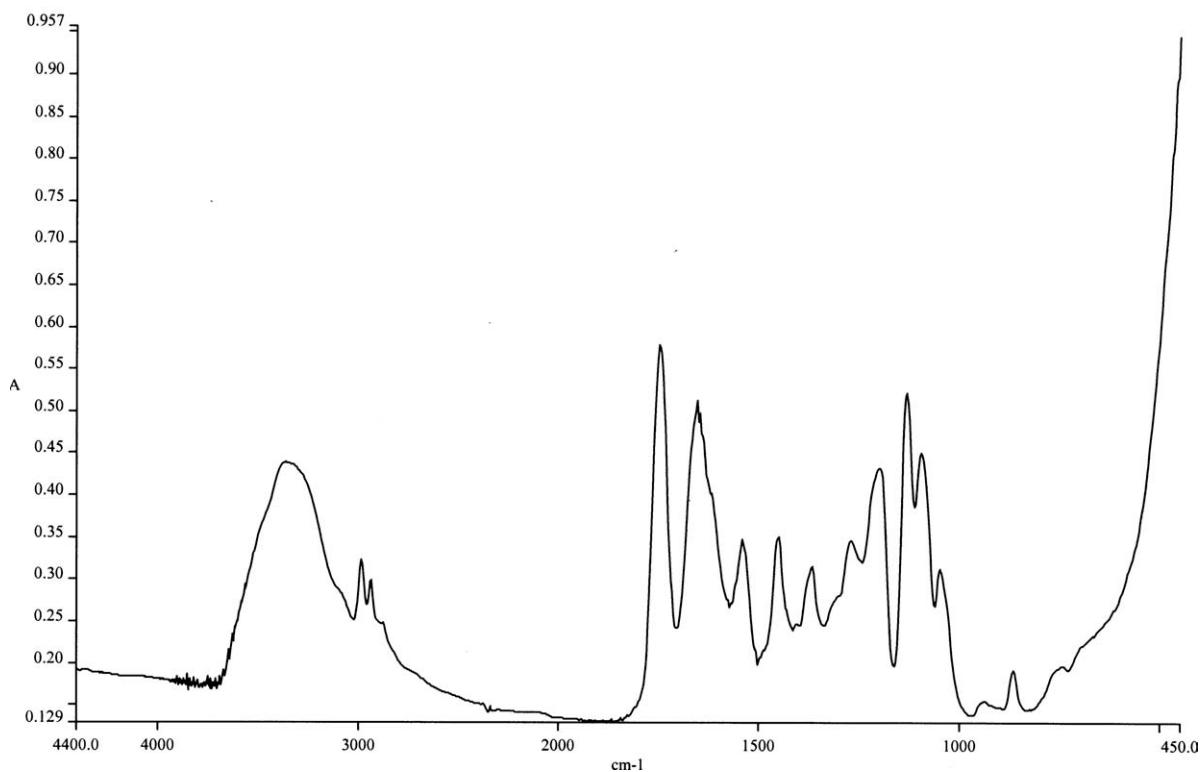


Figure 2 FTIR spectrum of LA₄-DETA-LA₄.

the sharp absorbance of the CH bending vibrations at around 1450 cm^{-1} .

L-Lactide, as schematically represented in the equations mentioned earlier, is a cyclic dimer of two lactic acids and has two ester groups and two pendant methyl groups. The spectrum of L-lactide, in Figure 1 (b), exhibits the very strong and sharp absorbance peak due to the C=O stretching vibrations of the ester group at 1761 cm^{-1} . Also, the sharp peaks in the $1000\text{--}1300\text{ cm}^{-1}$ region represent the C—O—C stretching vibrations of the ester group. C—H stretching vibration absorbances appear at around 2940 and 2997 cm^{-1} , the C—H bending absorbance appears at 1450 cm^{-1} , and the split peak at $1383\text{--}1365\text{ cm}^{-1}$ is due to the C—H bending vibration of the L-lactide CH₃ groups. The wide peak at around 3500 cm^{-1} is most probably due to the presence of adsorbed atmospheric water molecules during FTIR sample preparation.

The FTIR spectrum of the reaction product, LA₄-DETA-LA₄, is illustrated in Figure 2. The strongest, most prominent peak in this spectrum, is the C=O stretching vibration of the ester groups at 1751 cm^{-1} and represents the ester groups formed between the lactoyl repeating units in the short side-blocks (see Scheme 1). Adjacent are two relatively sharp absorbances at 1654 and at 1542 cm^{-1} , which stem from the amide (I) C=O stretching vibrations and amide

(II) C—N—H deformation vibrations, respectively. These characteristic peaks of the amide group indicate the formation of the amide linkages following the first ring opening reaction via the nucleophilic ring opening reaction between the primary amines of DETA and L-lactide. Also, the N—H stretching absorbance at around 3335 cm^{-1} , which was split in the spectrum of DETA (characteristic of primary amines), is not split in the spectrum of LA₄-DETA-LA₄, which is characteristic of the primary amines formed following the reaction (see Scheme 1).

In addition, the presence of the N—H stretching absorbance at around 3335 cm^{-1} , and of the amide (II) C—N—H deformation vibrations in the spectrum of LA₄-DETA-LA₄, is strong proof of the fact that the central secondary amine of DETA did not react. Also, it proves that the newly formed secondary amines (of the new amide groups) also do not react further in the lactide ring opening reactions, because these two absorbances do not appear at all in tertiary amines, where the N—H link does not exist (secondary amines are known to react in epoxy ring opening reactions). On the other hand, the broad absorbance in the range of $770\text{--}910\text{ cm}^{-1}$, which is observed in the spectrum of DETA [in Fig. 1(a)] due to the NH₂ wagging vibration of the primary amine groups, completely disappears in the spectrum of LA₄-DETA-LA₄ (Fig. 2). This also proves the

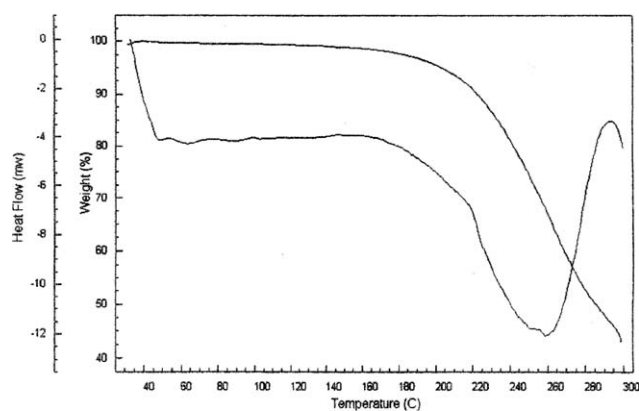


Figure 3 Simultaneous thermal analysis, exhibiting DSC curve (lower) and TGA curve (upper), of LA₄-DETA-LA₄.

conversion of the primary amines to secondary amines, following the first ring opening reactions.

Following the removal of the completed reaction product (in hot liquid form) from the reactor and the cool-down process to room temperature, this very short di-polyester diamide turned into a very hard and glassy material. Pieces broken from it with a hammer led to conchoidal fractures, which further indicated the glassy state of the material.

Simultaneous thermal analysis (combined DSC and TGA) of shattered pieces of the triblock (Fig. 3) revealed that indeed the material is amorphous. A glass transition (T_g) is observed at close to 58°C. This is, by all means, a relatively high T_g , considering the very low molecular weight of this product. A very large thermal decomposition endotherm starts at around 160°C. The TGA curve above the DSC thermogram (Fig. 3) clearly shows the start of weight loss in the sample at approximately the same temperature at which the endotherm starts, sustaining the assumption that the endotherm is due to the thermal decomposition of the material.

It is postulated here that the observed physical properties of this material most probably stem from the hydrogen bonds that can be formed by the three N—H groups in the central segment, with the C=O groups of adjacent molecules, in combination with the relative rigidity and planar structure of the amide groups and to some extent, also of the ester groups of these molecules.

Further, di-polyester diamides consisting of increasingly longer polyester side blocks were synthesized and studied.

A representative di-polyester diamide of this series is described here, LA₆₀-DETA-LA₆₀, having 60 lactoyl units on each side of the central DETA segment. Figure 4 exhibits the FTIR spectrum of the LA₆₀-DETA-LA₆₀ triblock. The most conspicuous change in the spectrum when compared with the former short di-polyester diamide is the very high

and sharp C=O stretching absorbance at 1757 cm⁻¹ of the ester groups in the PLA side blocks. This peak is very much higher in the LA₆₀-DETA-LA₆₀ than in the LA₄-DETA-LA₄, due to the much increased number of ester groups present. Also, the amide (I) C=O stretching vibrations and amide (II) C—N—H deformation vibrations, at 1650 and 1540 cm⁻¹, respectively, are present and clearly seen, but now appear as only small shoulders of the very high ester peak (expectedly indicating that the two amide bonds created in the first two ring opening steps, constitute a much smaller percentage of the much larger PLA side blocks). The broad absorbance at 3420–3500 cm⁻¹ is most probably due to the hydroxyl end groups of the molecule, combined with adsorbed atmospheric water molecules during FTIR sample preparation.

This product (LA₆₀-DETA-LA₆₀), with the same central diamide segment as the first one, but with much longer PLA side blocks, was also almost completely amorphous, transparent, very hard, and glassy. The DSC thermogram in Figure 5 clearly shows the almost completely amorphous nature of this material. Only a very small split endotherm of 1.94 J/g is present at 146°C, with a small shoulder at 141°C. Two very prominent glass transitions are observed in the thermogram. The first T_g , at close to 59°C, and the second, at 88°C, which can be attributed to the PLA segments and the harder, hydrogen-bonded central segment, respectively. The TGA curve in Figure 5 indicates the start of thermal decomposition above 160°C. Another aspect that may be concluded from these results is the occurrence of a relatively efficient microphase separation, between the central diamide segment and side blocks, as reflected in the fact that the material exhibits two separate glass transitions.

It was demonstrated,^{5,8} that in triblocks, the two block types interfere with each others crystallization process. But, even with this interference, it was shown by thermal analysis⁸ that in PLA-PEO-PLA triblocks obtained from a PEO with a molecular weight of 3200, with side blocks consisting of only 18 lactoyl units on each side, the PLA side blocks were able to crystallize. When a central PEO block having a molecular weight of 6000 was used, PLA side blocks of 36 lactoyl units crystallized. Even with a relatively large PEO central block with a molecular weight of 10,000, PLA with 50 lactoyl units on each side were able to crystallize.

In the present study, albeit the central segment of the di-polyester diamides is extremely short, much longer PLA side segments were not able to crystallize, as seen in LA₆₀-DETA-LA₆₀. The possible reason for this phenomenon may most probably be due to the formation of the hydrogen bonds in the central DETA segment regions, which restrict the conformational degrees of freedom of the two connected PLA

DETA-LA60

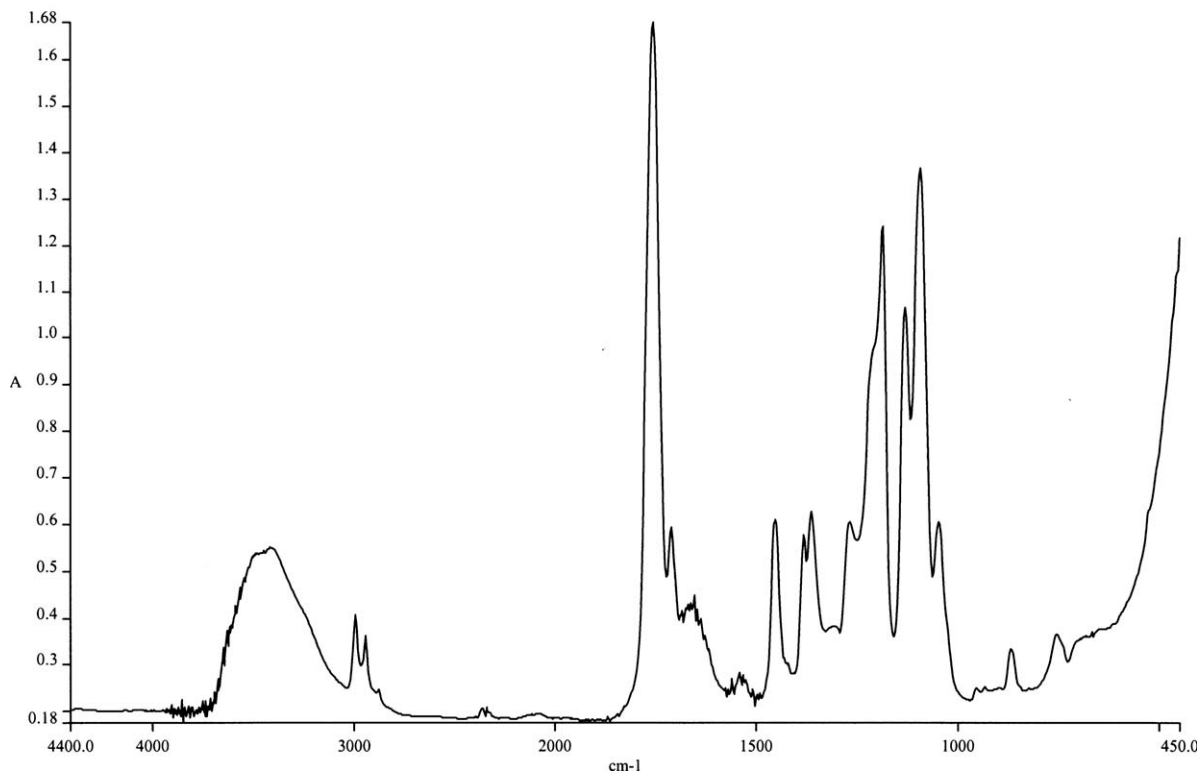


Figure 4 FTIR spectrum of LA₆₀-DETA-LA₆₀.

side blocks, thus restricting their crystallization process. On the other hand, the presence of these hydrogen bonds, in combination with the relative rigidity and planar structure of the amide groups and to some extent, also of the ester groups in the side blocks, is most probably the principle reason for the relatively high glass transitions and apparently enhanced hardness of these materials.

To attempt at further verifying this hypothesis, a di-polyester diamide in which the central segment consisted of hexamethylene diamine (HMDA) was synthesized, with PLA side blocks of 60 lactoyl units on each side. HMDA lacks the central secondary amine present in DETA, thus one less hydrogen bond will be formed in the central segment in the HMDA-containing product. The FTIR spectrum of this new triblock is shown in Figure 6. The strong ester C=O stretching vibration at around 1750 cm⁻¹ is clearly seen as well as the C—O—C vibrations between 1000 and 1300 cm⁻¹. Also, the relatively enhanced C—H bending absorbance at 1450 cm⁻¹, due to the additional methylene groups in the central segment. Again, the occurrence of the first two ring opening reactions, via the two primary amines of HMDA, is evidenced here clearly by the two characteristic amide group absorbances, namely the C—N—H amide (II) at 1539 cm⁻¹ (this absorbance is at a similar location as in the previous DETA-con-

taining triblocks, with maybe a slight shift to the right) and the amide (I) C=O stretching absorbance at 1674 cm⁻¹, exhibits a dramatic shift to the left, when compared with the same absorbance peak in the DETA-containing di-polyester diamide spectra (at 1654 cm⁻¹). This very significant shift of 20 cm⁻¹ is toward a higher wavenumber, that is, a lower wavelength, which means that a higher energy level is required in order to achieve the C=O stretching

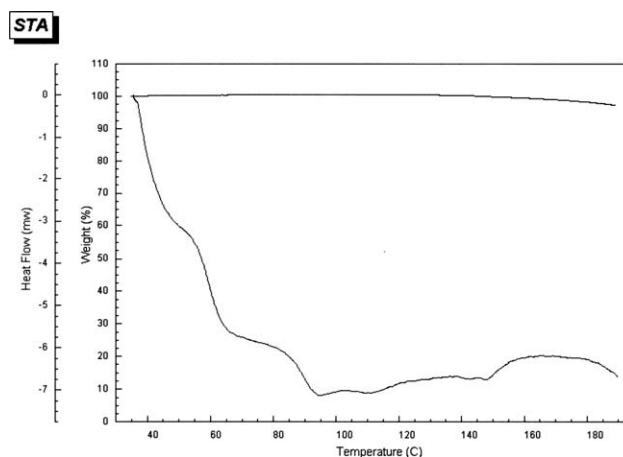


Figure 5 Simultaneous thermal analysis, exhibiting DSC curve (lower) and TGA curve (upper), of LA₆₀-DETA-LA₆₀.

HMDA – LA60

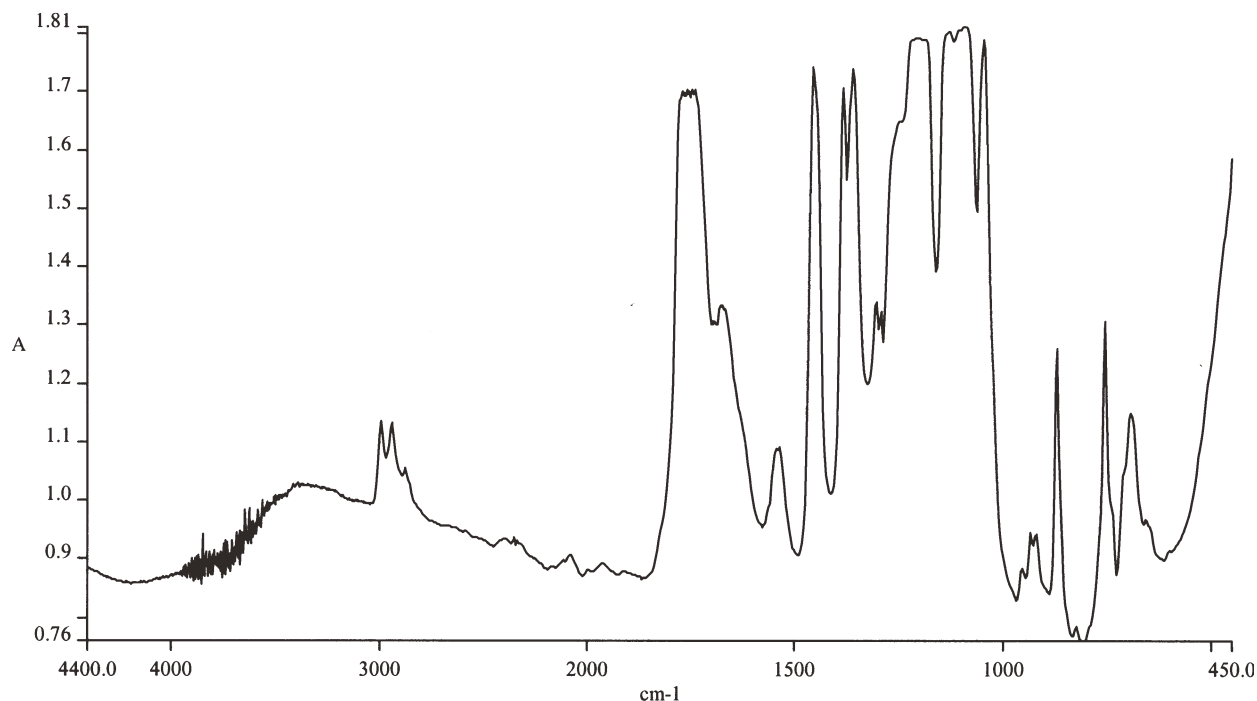


Figure 6 FTIR spectrum of LA₆₀-HMDA-LA₆₀.

vibrations in the HMDA-containing product, in comparison with the DETA-containing product. This shift in the C=O stretching absorbance very likely indicates that the C=O groups in the HMDA-containing product are less hydrogen bonded than in the DETA-containing product. This finding is consistent with the fact that in the HMDA-containing molecules, there are 33% less N–H groups that can form hydrogen bonding with the C=O groups than in the previous DETA-based molecules. The fact that H-bonded C=O groups require a lower energy for the occurrence of stretching vibrations than non-H-bonded C=O groups is widely known.⁹ Another influencing factor, on the extent of H-bonding in the HMDA-containing molecules, is the slightly longer and relatively flexible hexamethylene in the central segment, which may lead to more conformational degrees of freedom, in turn leading to more chain entanglements and consequently less efficient hydrogen bonding.

Thermal analysis of the LA₆₀-HMDA-LA₆₀ (Fig. 7) reveals two prominent glass transitions belonging to the two segment types (at 53 and at 84°C—which are slightly lower T_g temperatures than observed in the DETA-containing di-polyester diamide), but also a relatively significant melting endotherm of 8 J/g at 145°C. This indicates that the decreased amount of hydrogen bonding, as also observed in the FTIR analysis, enabled a partial crystallization of the PLA segments.

These results, as well as the fact that in the case of a central PEO block with no possible H-bonding, much shorter PLA side blocks were able to crystallize,⁸ clearly indicate that the unusually hard, amorphous glassy manifestation of the above described di-polyester diamide series is largely due to the presence of the H-bonding in this molecular family.

In continuation of the LA-DETA-LA series, a di-polyester diamide with 120 lactoyl units on each side of the DETA central block was synthesized, namely LA₁₂₀-DETA-LA₁₂₀. Figure 8 presents the

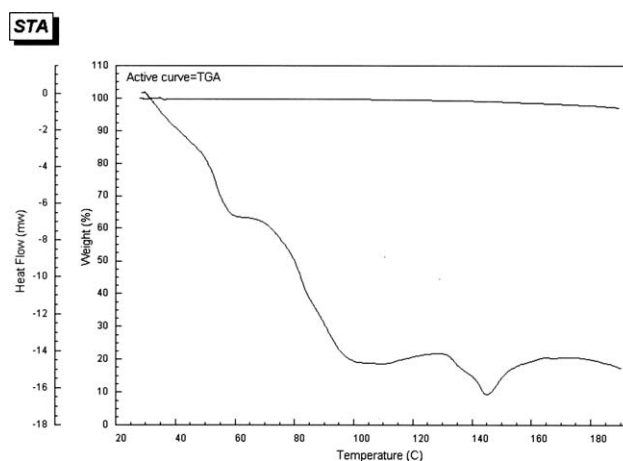


Figure 7 Simultaneous thermal analysis, exhibiting DSC curve (lower) and TGA curve (upper), of LA₆₀-HMDA-LA₆₀.

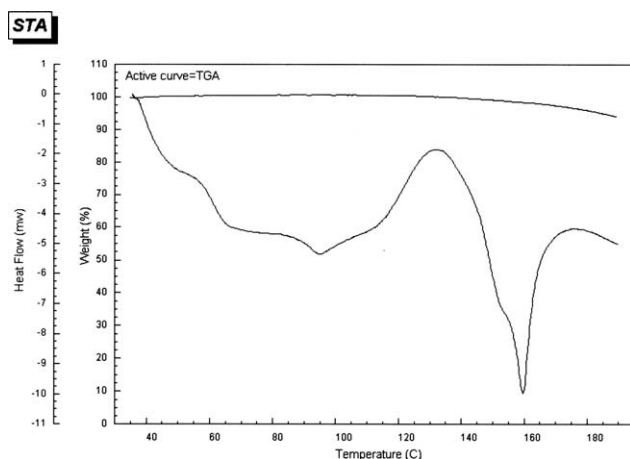


Figure 8 Simultaneous thermal analysis, exhibiting DSC curve (lower) and TGA curve (upper), of LA₁₂₀-HMDA-LA₁₂₀.

thermal analysis of the resulting material. The thermogram exhibits, in addition to the two characteristic glass transitions (at 60 and at 90°C), a relatively large melting endotherm at about 159°C, indicating a massive crystallization of the PLA blocks. Nevertheless, this melting endotherm is preceded by a crystallization exotherm at 131°C, which indicates a solid-phase crystallization process, that is, the rise in temperature of the sample during thermal analysis, results in an increase in the motional degrees of freedom of the segments, which can thus reorganize in a crystalline form. Integration of these peaks showed that the exotherm and endotherm are of similar areas (55 and 59 J/g, respectively); thus, it may be concluded that also this product was essentially amorphous before the heating process during thermal analysis. It may further be concluded here that with long enough PLA side blocks, crystallization eventually occurs.

Observation of the different members of the LA-DETA-LA series, including LA₁₂₀-DETA-LA₁₂₀, by polarized light microscopy with crossed polarizers, revealed an almost complete extinction in all cases, except for very small discrete locations of stress-induced anisotropic areas. This again indicates the essentially amorphous state of these materials.

¹H-NMR studies were performed on all synthesis products described in the present article. Figure 9 presents the NMR spectra of the DETA-containing di-polyester diamides, with side segments consisting of 4, 60, and 120 lactoyl units.

The NMR spectrum of the shortest di-polyester diamide in this series (LA₄-DETA-LA₄) [Fig. 9(a)], reveals a prominent doublet resonance at 1.4 ppm, due to the PLA methyl groups. Adjacent, at 1.2 ppm, a significantly smaller doublet represents the PLA methyl group at the hydroxyl terminus.¹⁰ The quartet at 5.2 ppm represents the resonance of the PLA

methine (CH) groups. The adjacent quartets at 4.94 and 4.8 ppm belong to the methine groups linked to the DETA amides and to the hydroxyl terminuses, respectively. The singlet at 7.79 ppm is due to the resonance of the amide proton (NHCO)¹¹ and indicates the formation of the amide linkages following the first ring opening reaction, which is in agreement with the FTIR analyses described earlier. The triplets at 4.24 ppm and at 3.95 ppm, represent the two types of the DETA methylene (CH₂) groups. The singlet at 4.36 ppm is due to the resonance of the hydroxyl end groups proton. The resonances at 2.52 and at 3.35 ppm belong to the DMSO solvent and water, respectively. The NMR spectrum of the LA₆₀-DETA-LA₆₀ [Fig. 9(b)] reveals a very significant increase of the characteristic PLA resonances described earlier (at 1.4 and 5.2 ppm), in comparison with the characteristic resonances of the DETA central segment (methylene and amide) and of the PLA terminal lactoyl units, reflecting the increased PLA side segments length. In the NMR spectrum of LA₁₂₀-DETA-LA₁₂₀ [Fig. 9(c)], as expected, there is a further significant increase in the PLA methyl and methine resonances.

In LA₄-DETA-LA₄, the integration ratio between the PLA methine resonances and the amide proton resonance integration was 5.5, yielding a total molecular weight of 895 g/mol. The same result was also obtained from the integration ratio of the PLA methine and the 4H DETA methylene resonance at 4.24 ppm. In the higher molecular weight members of the di-polyester diamide family, the concentration of the amide proton was too low in order to perform an accurate enough integration. Nevertheless, integration of the 4H DETA methylene resonance at 4.24 ppm was used, and the ratio with the 5.2 ppm methine resonance was calculated. Accordingly, side segment lengths of 65 lactoyl units were obtained for both LA₆₀-DETA-LA₆₀ and LA₆₀-HMDA-LA₆₀ and 127 lactoyl units for LA₁₂₀-DETA-LA₁₂₀, with total molecular weights of 9462 and 18391 g/mol, respectively. This deviation from the stoichiometrically calculated values is relatively small and does not affect the conclusions described in this work.

CONCLUSION

A series of di-polyester diamides was synthesized, representative members of which were described in this article. FTIR characterization revealed the spectral changes due to the newly formed chemical bonds as well as the transformation of formerly present reactant functional groups. Also, the changes in the relative intensity of the characteristic peaks, due to the increasing side-blocks lengths of the different di-polyester diamides, were clearly seen.

¹H-NMR analysis of the described materials confirmed the chemical structures seen by FTIR

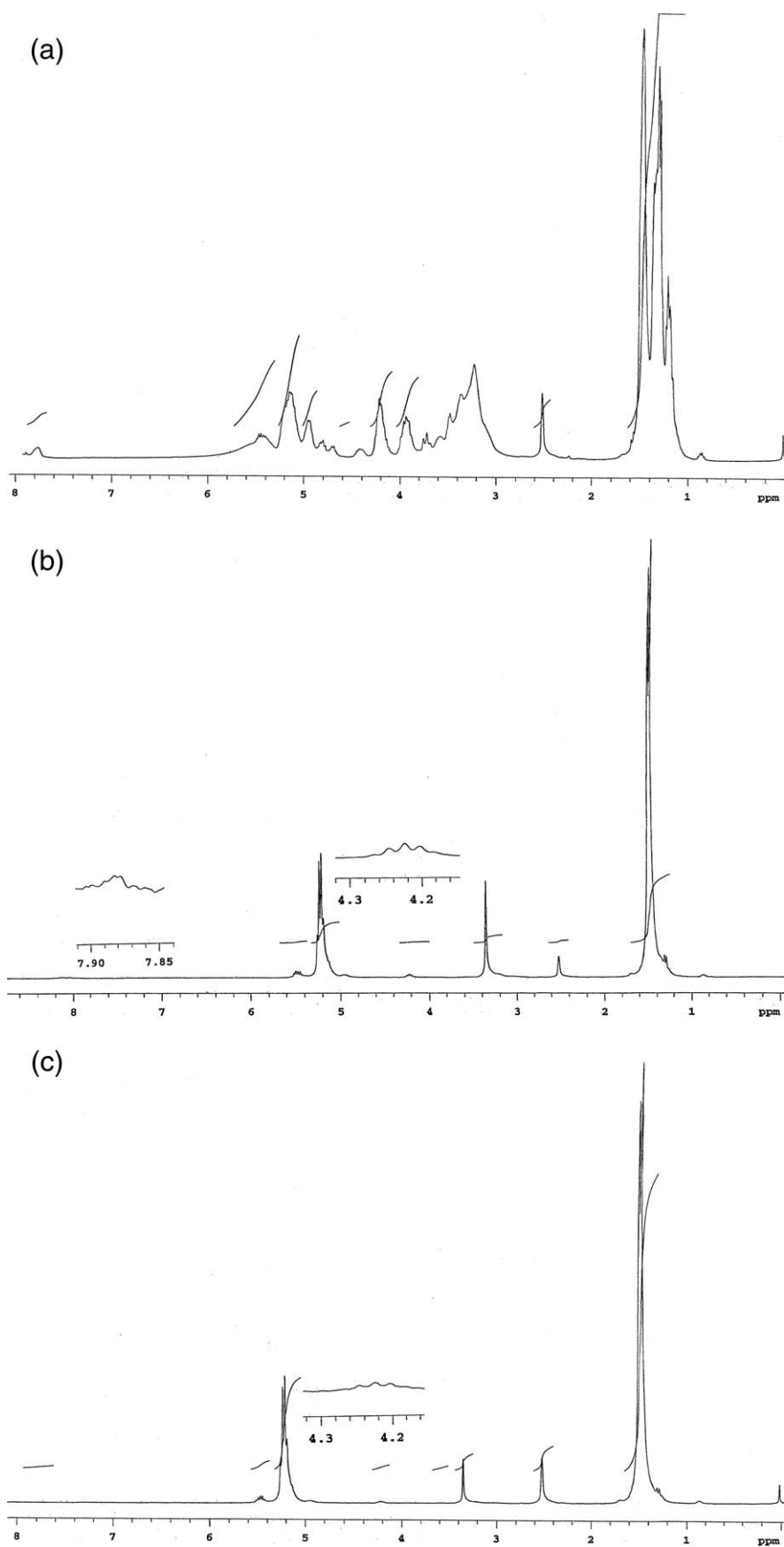


Figure 9 $^1\text{H-NMR}$ spectrum of $\text{LA}_4\text{-DETA-LA}_4$ (a); $\text{LA}_{60}\text{-DETA-LA}_{60}$ (b); $\text{LA}_{120}\text{-DETA-LA}_{120}$ (c).

analysis. Also, the side segment length of the different di-polyester diamides was calculated from the integration ratios in the NMR spectra. The results exhibited only slight deviations from the stoichiometrically calculated values.

The presence of the hydrogen-bonded central segment had a dominant effect on the overall physical properties of the di-polyester diamides, as revealed in the thermal analyses of these materials. Even the shortest member of this family, with side blocks containing only four lactoyl units, was a hard amorphous material with a relatively high glass transition. The amorphous nature of the materials persisted up to 120 lactoyl units and is attributed here to the strong intersegment interference exerted by the dominant H-bonded DETA central segment, thus inhibiting the PLA block crystallization process. The di-polyester diamide containing 120 lactoyl units crystallized in solid state, due to molecular reorganization during thermal analysis. The presence of two separate glass transitions indicated the efficient microphase separation in these materials.

The above-mentioned dominant effect of the H-bonded central segment was further investigated by replacing DETA with HMDA, thus reducing the possible H-bonding in the central segment by a third. Evidence of this decrease in H-bonding was

clearly seen in the FTIR spectrum of the material. Thermal analysis of an HMDA-containing di-polyester diamide with 60 lactoyl units exhibited a relatively significant melting endotherm. These results are consistent with the central segment dominance, hypothesized with respect to the DETA-containing materials.

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