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Synthesis and characterization of bisester-amide segments of uniform and random length

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Abstract

The synthesis and characterization of bisester-oligoamides segments with varying segment length that can be used in segmented block copolymers were studied. The bisester-oligoamides segments were made form diamines and terephthalate or isophthalate esters. The diamines used were *p*-xylylene diamine, *m*-xylylene diamine and hexamethylene diamine. The esters used are dimethyl terephthalate, diphenyl terephthalate, dimethyl isophthalate and diphenyl isophthalate. Uniform bisester-diamide, bisester-(tetra-amides) and bisester-(hexa-amide) segments were synthesized in steps and characterized by ^{1}H NMR, MALDI-TOF and DSC. The uniformity of these segments was studied by MALDI-TOF.

With the uniform amide segments and polypropylene oxide segments, block copolymers were prepared by high temperature melt polymerization. The amide segment length distribution, which is susceptible to randomization was studied. The analysis of the amide segment distribution after hydrolysis of the ester-linkage groups was by MALDI-TOF. The amide segments were found to have the same narrow distribution as the starting bisester-oligoamide, which strongly supports the fact that randomization of the amide segments during melt polymerization does not take place. The uniformity of the amide segments is, therefore, preserved during high temperature melt polymerization.

Keywords: MALDI-TOF; Block copolymer; Transamidation

1. Introduction

Segmented polyether(ester)s (PEE) synthesized from diesters and telechelic polyethers like Arnitel® and Hytrel® are examples of commercial PEE's. These segmented blockcopolymers belong to the class of so-called thermoplastic elastomers (TPE's) [1]. Normally, commercial TPE's contain rigid crystallisable segments, which have a broad segment length distribution. The majority of these segmented blockcopolymers is synthesized from poly (tetramethylene oxide) (PTMO) or poly(ethylene oxide) (PEO) as the polyether segment and a minor part is made from poly(propylene oxide) (PPO). PPO contains secondary hydroxyl end groups and has, therefore, a lower reactivity in the PEE syntheses as compared to PTMO and PEO. Recently, a PPO end-capped with ethylene oxide (PEO-*b*-PPO-*b*-PEO) has become commercially available which has an enhanced reactivity [2]. However, this PPO still contains a small amount of secondary hydroxyl groups [3], which hinders the formation of high molecular weight PEE block copolymers [4,5]. High molecular weight PPO-based polyether(ester) (PEE) and polyether(ester-amide) (PEEA) segmented block copolymers can be obtained if a terephthalic diester is used that contains phenolic ester end groups, like: diphenyl terephthalate [5].

The properties of segmented polyurethanes, PPE and PEEA segmented block copolymers depend strongly on the structure regularity of the crystallisable segment used. The higher the structure regularity the faster the crystallization and the higher the crystallinity in the resulting block copolymer [1]. The structural regularity of the crystallisable segments is usually higher for those containing *p*-phenylene groups as compared to *m*-phenylene groups. Another kind of structure regularity can be found in the segment length

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distribution of the crystallisable segments. The smaller the segment length distribution, the faster the crystallization and the higher the crystallinity [6–8]. A third parameter of interest is the length of the crystallisable segment used in segmented block copolymers. Block copolymers with tetra-amide segments were found to have enhanced elasticity over block copolymers with di-amide segments [9].

New and interesting types of TPE's are block copolymers, which comprise crystallisable segments with narrow segment length distribution; the so-called uniform segments [9–13]. A major problem of block copolymers with segments of uniform length is the loss of uniformity at high temperatures due to transreactions. These transreactions are fast for segmented polyurethanes, polyureas and polyesters [14]. However, with oligoamide segments melt polymerization and melt processing seems possible without losing the uniform character of these segments [9,11].

Segmented block copolymers with crystallisable amide segments of uniform length can be made by a conventional copolymerization using uniform bisester-amide segments. The synthesis of some biester-diamide and bisester-(tetra-amide) segments have been reported before [15,16]. These bisester-oligoamides segments were synthesized, starting with a diamine and a diester. The reaction of a diamine (X) with a terephthalic diester (T) may proceed by the following reaction scheme [15]:

1. X+2 T→TXT (diamide).
2. 2 X+T→XTX.
3. XTX+2 T→TXTXT (tetra-amide).
4. 2 X+TXT→XTXTX.
5. XTXTX+2 T→TXTXTXT (hexa-amide).

A very large excess of diamine favors oligo-amide sequences having amine end groups and vice versa with a large excess of diester. If bisester-oligoamides of uniform length are required, the longer segments can best be prepared in steps. For instance, the tetra-amide segments ($x=2$) can be synthesized in two steps [16]. First, by reacting an excess diamine with the diester and subsequent purification (2). Secondly, the extended diamine, here XTX, was added to an excess diester (3). Even if a large excess of diamine or diester is used there may still be a distribution of segment length. One hundred percent uniform segments are, therefore, difficult to obtain and purification steps are needed to obtain a high uniformity. The uniformity of the synthesized bisester-oligoamide segments was determined by ^{1}H NMR and MALDI-TOF and is defined as the mol fraction of segments with the desired segment length. In a one-pot synthesis bisester-oligoamide segments with a random segment length distribution can be prepared. The extent of randomization of the amide segments during the polymerization is difficult to determine by ^{1}H NMR as the average length of these segments remains constant.

For the synthesis of segmented block copolymers based on the low reactive poly(propylene oxide) the use of uniform bisester-amide segments with phenolic ester end groups is an advantage [5]. The bisester-oligoamide segments in our studies are segments with varying structural regularity and length (Fig. 1). The structure regularity of bisester-oligoamides was varied by using either isophthalic or terephthalic groups and *p*-xylylene diamine, *m*-xylylene diamine or hexamethylene diamine groups. Also the uniform length bisester-oligoamides is varied ($x=1$, 2 or 3).

In this paper, the preparation of random and uniform biester-oligoamide segments is studied. Also studied is whether the uniformity of the segments is maintained on copolymerization at high temperature with a telechelic hydroxyl functionalized poly(propylene oxide). The uniformity of the segments is studied by ^{1}H NMR and MALDI-TOF. For analysis of the amide segment length distribution in the block copolymers, the polymers were first hydrolyzed before the remaining blocks were analyzed by MALDI-TOF.

2. Experimental

2.1. Materials

Dimethyl terephthalate (DMT), diphenyl isophthalate (DPI), terephthaloyl dichloride, phenol, *p*-xylylene diamine, 1,6-diamino hexane, tetra-isopropyl orthotitanate ($Ti(i\text{-}OC_3H_7)_4$), ethanol, *m*-xylene, toluene, chloroform, *N*-methyl-2-pyrrolidone (NMP) and dimethyl formamide (DMF) were purchased from Aldrich (BIOSOLVE). Irganox 1330 was obtained from CIBA. *m*-Xylylene diamine was a gift from Mitsubishi Gas Chemical Company (Japan). These materials were used as received. Poly (propylene oxide) end capped with 20 wt% ethylene oxide (EO) and a molecular weight of approximately 2300 g/mol (PPO-2300) was a gift from Bayer AG (Acclaim Polyol PPO-2220 N).

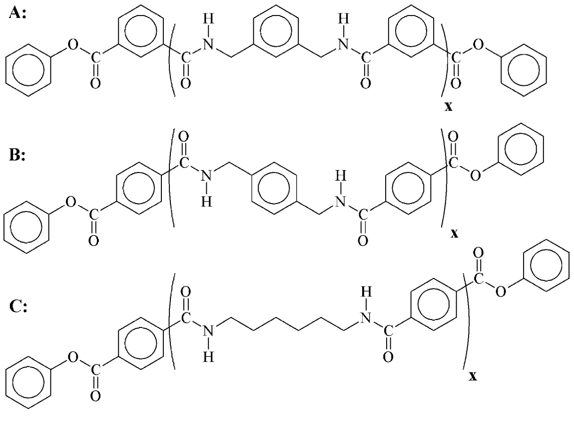


Fig. 1. Structure of the bisester-oligoamide monomers with amide segment length x and phenolic ester end groups. A, isophthalic ($I(X_mI)_x$); B, terephthalic ($T(X_pT)_x$); C, terephthalic/aliphatic ($T(6T)_x$).

2.2. Synthesis of diphenyl terephthalate (DPT)

Terephthaloyl dichloride (540 g, 2.66 mol) was added to a solution of phenol (500 g, 5.32 mol) in toluene (500 ml), which was kept at 80 °C in a round-bottomed flask of 2000 ml equipped with a magnetic stirrer, condenser and nitrogen inlet. The condensation product hydrochloric acid (HCl) was neutralized by leading the gas through a NaOH-solution in water. After all was added, the mixture was heated to 95 °C and maintained for 1 h at this temperature and a suspension was formed. Thereafter, the suspension was cooled, washed with de-ionized water and filtered. The residue, a white product, was washed three times with hot ethanol (80 °C) and subsequently dried overnight in vacuum at 70 °C. The yield was 90% and the purity as determined by ^{1}H NMR and FT-IR was $>98\%$. DSC-experiments also indicate a high purity ($T_m = 200.5$ °C, $\Delta H_m = 158.4$ J/g) [17].

2.3. Synthesis of uniform diamide IX$_m$I-diphenyl ($x=1$)

A mixture of *m*-xylylene diamine (12.9 g, 0.076 mol) and DPI (250 g, 0.79 mol) was heated to 80 °C in a 1000 ml flask charged with 300 ml toluene and equipped with magnetic stirrer, condenser, calcium chloride tube and nitrogen inlet. The reaction mixture was stirred at 80 °C for 24 h under a nitrogen atmosphere and a suspension was formed. The precipitated product was collected on a glass filter (pore size 4) and washed three times with toluene and dried in vacuum at 70 °C overnight. The yield was 72%.

2.4. Synthesis of uniform diamide TX$_p$T-diphenyl ($x=1$)

A mixture of *p*-xylylene diamine (14.7 g, 0.11 mol) and DPT (202 g, 0.64 mol) was heated to 80 °C in a 1000 ml flask filled with 1200 ml toluene and 50 ml DMF equipped with magnetic stirrer, condenser, calcium chloride tube and nitrogen inlet. The reaction mixture was stirred at 80 °C for 24 h under a nitrogen atmosphere and a suspension was formed. The precipitated product was collected on a glass filter (pore size 4) and washed three times with hot *m*-xylene (120 °C) and dried in vacuum at 70 °C overnight. The yield was 75%.

2.5. Synthesis of uniform diamide T6T-diphenyl ($x=1$)

The synthesis was similar to the synthesis of TX$_p$T-diphenyl using 1,6-diamino hexane instead of *p*-xylylene diamine. The yield was 76%.

2.6. Synthesis of uniform tetra-amide IX$_m$IX$_m$I-diphenyl ($x=2$)

At first DPI (28.8 g, 0.090 mol) was added to an excess of *m*-xylylene diamine (220 g, 1.6 mol) at 80 °C under nitrogen flow (no solvent). The reaction mixture was stirred at 80 °C for 24 h under a nitrogen atmosphere. After addition of diethylether a viscous transparent liquid X$_m$IX$_m$-diamine was formed. The toluene–diethylether mixture was decanted and the viscous liquid was washed three times with diethylether (at 30 °C). The yield of X$_m$IX$_m$-diamine was 50%. The purity as determined by ^{1}H NMR was $>98\%$. The X$_m$IX$_m$-diamine (25.9 g, 0.045 mol) was added to a solution of DPI (170 g, 0.53 mol) in 300 ml NMP in a 500 ml flask equipped with magnetic stirrer, condenser, calcium chloride tube and nitrogen inlet. After a short time at 120 °C a homogeneous mixture was formed and stirring was continued at 120 °C for 24 h. The product was precipitated in diethylether and collected on a glass filter (pore size 4). Subsequently the product was washed three times with hot toluene (70 °C). The material was dried in vacuum at 70 °C overnight before use. The yield was 68%.

2.7. Synthesis of uniform tetra-amide TX$_p$TX$_p$T-diphenyl ($x=2$)

At first DMT (41.0 g, 0.21 mol) was added to an excess of *p*-xylylene diamine (173 g, 1.3 mol) at 80 °C under nitrogen flow (no solvent). The reaction mixture was stirred at 120 °C for 24 h under a nitrogen atmosphere. After 2 h reaction *m*-xylene was added. The reaction mixture was introduced into a soxhlet extraction thimble and extracted overnight. The white product was further purified by recrystallization from dioxane (96 °C, 25 g/l). The product X$_p$TX$_p$-diamine is a white solid. The yield was 37% and the purity as determined by ^{1}H NMR was $>98\%$. A mixture of X$_p$TX$_p$-diamine (11.8 g, 0.039 mol) and DPT (95 g, 0.30 mol), previously dissolved in 500 ml NMP, was stirred at 120 °C for 8 h in a 1000 ml flask equipped with magnetic stirrer, condenser, calcium chloride tube and nitrogen inlet. A homogeneous mixture was formed. The product was precipitated in *m*-xylene and the precipitate was collected on a glass filter (pore size 4). Subsequently, the product was washed three times with hot *m*-xylene (120 °C). The material was dried in vacuum at 70 °C overnight before use. The yield was 58%.

2.8. Synthesis of uniform tetra-amide T6T6T-diphenyl ($x=2$)

The synthesis was similar to the synthesis of TX$_p$TX$_p$T-diphenyl using 1,6-diamino hexane instead of *p*-xylylene diamine. The yield was 54%.

2.9. Synthesis of uniform hexa-amide IX$_m$IX$_m$IX$_m$I-diphenyl ($x=3$)

A mixture of IX$_m$I-diphenyl (14.9 g, 0.025 mol) and *m*-xylylene diamine (126 g, 0.93 mol) was heated to 120 °C in a 500 ml flask equipped with nitrogen inlet, calcium chloride tube, condenser and magnetic stirrer (no solvent). The reaction mixture was stirred at 120 °C for 24 h. A homogeneous mixture was formed. After precipitation in diethylether the product was collected on a glass filter (pore size 4). The product was subsequently washed three times with hot chloroform (50 °C). The yield was 37%. The purity as determined by ^{1}H NMR was $>95\%$. The product $X_mIX_mIX_m$-diamine (25.9 g, 0.039 mol) was added to DPI (150 g, 0.47 mol) dissolved in 300 ml NMP. The mixture was stirred at 120 °C for 24 h, after which it was precipitated in diethylether. The precipitate was collected on a glass filter (pores size 4) and subsequently the product was washed three times with hot chloroform (50 °C) to remove the excess DPI. The yield was 49%.

2.10. Synthesis of uniform hexa-amide T6T6T6T-diphenyl ($x=3$)

To an excess of 1,6-diaminohexane (85.0 g, 0.73 mol), previously dissolved in 300 ml NMP, T6T-diphenyl (20.0 g, 34.2 mmol) was added under a nitrogen atmosphere. The reaction mixture was stirred for 4 h. After cooling to room temperature a suspension was formed. The precipitated product was collected on a glass filter (pore size 4) and subsequently the product was washed three times with hot chloroform (50 °C). The yield of the product 6T6T6 was 68%. The purity as determined by ^{1}H NMR was $>90\%$. 6T6T6 (19.0 g, 30.1 mmol) was added to an excess of DPT (127.0 g, 0.40 mol) previously dissolved in 700 ml NMP. The reaction mixture was stirred at 160 °C for 8 h. Thereafter, the reaction product was precipitated in diethylether and collected on a glass filter (pore size 4). The white residue was washed three times with hot *m*-xylene (120 °C) and subsequently dried at 70 °C in vacuum overnight before use. The yield was 72%.

2.11. One pot synthesis of bisester-oligoamides

For example the synthesis of random $IX_mIX_mIX_mI$-diphenyl (average length $x=3$) is given. To a solution of DPI (20.0 g, 62.8 mmol) in NMP (200 ml) placed in a round-bottomed flask *m*-xylylene diamine (6.42 g, 47.1 mmol) was added. The molar ratio of DPI and *m*-xylylene diamine was 4:3. The flask was equipped with a reflux condenser, $CaCl_2$ tube, nitrogen inlet and magnetic stirrer. The reaction was performed at 120 °C for 4 h. The reaction mixture was directly used for characterization.

2.12. Copolymerization with poly(propylene oxide) (PPO-2300)

An example is given in case of a polyether(ester-amide) with tetra-amide segments of uniform length. A 250 ml reactor (a stainless steel cylindrical flange flask type cmd 075) was equipped with nitrogen inlet, condenser and a stirring device with magnetic coupling was charged with PPO-2300 (20.0 g, 8.69 mmol), T6T6T-diphenyl (7.39 g, 8.05 mmol), 100 ml NMP and 1 wt% Irganox 1330 (based on PPO) under nitrogen flow (the magnetic coupled stirring device was important to obtain high vacuum conditions). The reaction mixture was stirred under N_2-flow and heated to a temperature of 120 °C in 1 h and kept for 2 h at 120 °C. The reaction mixture was then slowly heated to 250 °C in 1 h and 2.0 ml catalyst (0.05 M $Ti(OC_3H_7)_4$ in *m*-xylene) was added when the temperature was at 150 °C. Before vacuum was applied the temperature was raised to 280 °C. Low vacuum (10–1 mbar) was applied for 1 h to remove most of the solvent. Thereafter, the temperature was reduced to 250 °C and finally the melt polycondensation step at high vacuum (0.1–0.08 mbar) was carried out for 2 h. The product was cooled to room temperature whilst maintaining a vacuum. Before us, the polymer was dried in vacuum at 70 °C overnight.

2.13. Hydrolysis of polyether(ester-amide)s

A polyether(ester-amide) (1 g) and NMP (25 ml) were placed in a reaction tube of 50 ml. The mixture was heated to 150 °C and after dissolution the temperature was set to 120 °C. Then 10 ml of 1 M NaOH solution in water was added. The reaction was performed for 8 h under a nitrogen atmosphere. Thereafter, the reaction mixture was precipitated in diethylether and subsequently washed three times with acetone. The hydrolysis product was dried in vacuum at 70 °C overnight before analysis.

2.14. ^{1}H NMR

^{1}H NMR spectra of bisester-oligoamides, the block copolymers and the hydrolysis products were recorded on a Bruker AC 300 spectrometer at 300.1 MHz. Deuterated trifluoro acetic acid (TFA-d) was used as the solvent.

2.15. MALDI-TOF (matrix assisted laser desorption ionization time-of-flight)

Mass spectrometry was performed using a Voyager-DE-RP MALDI-TOF mass spectrometer (Applied Biosystems/PerSeptive Biosystems, Inc., Framingham, MA, USA) equipped with delayed extraction. A 337 nm UV Nitrogen laser producing 3 ns pulses was used and mass spectra were obtained in the linear and reflection mode. Samples were dissolved in 10 μl of trifluoro acetic acid and added to 30 μl acetonitrile/water solution (50/50 molar) with 1.0 mg/l 2,5-dihydroxy-benzoic acid (DHB) as the matrix. One microlitre of solution was loaded on a gold-sample plate, after which the solvent was evaporated and the sample transferred to the mass spectrometer for analysis. It is assumed that the ionization efficiency of each oligoamide segment is similar and that the peak intensities of the MALDI-TOF spectra can be related to the number of molecules of a particular molecular weight. However, it should be mentioned that the MALDI-TOF spectra is semi-quantitative at best. The intensities were used to calculate the mol fractions of segments with a desired length (i.e. defined as the uniformity of an oligoamide segment).

2.16. Dsc

DSC spectra were recorded on a Perkin Elmer DSC7 apparatus, equipped with a PE7700 computer and TAS-7 software. A sample of 5–10 mg was heated at a rate of 20 °C/min. The first heating scan was used to determine the melting temperature of the bisester-oligoamides. The melting temperature (T_m) was taken as the temperature at the maximum of the endotherm.

3. Results and discussion

Bisester-oligoamide segments of uniform length were synthesized in steps. These segments can be used as starting materials in the synthesis of segmented blockcopolymers.

The synthesized bisester-diamide segments were not recrystallized. The yield of these segments was 72–76%. The synthesis of uniform bisester-(tetra-amide) segments required two steps [16], of which the extended XTX-diamine (Eq. (2)) was synthesized with low yields (30–50%). The overall yield of bisester-(tetra-amide) segments is, therefore, low. Uniform bisester-(hexa-amide) segments were synthesized in three steps. The overall yield of these segments was low due to low yields of the second step, the synthesis of the XTXTX-diamine.

Characterizing the length distribution of bisester-oligoamide segments in a multi-component mixture of segments (e.g. a multi-block copolymer) by NMR is difficult as only the average length of the amide segments can be determined. The use of MALDI-TOF techniques can help in evaluating the length distribution of the amide segments and thus the uniformity of these segments. In the MALDI-TOF measurement a mild ionization is used and fragmentation of the amide segments is thereby prevented [18].

3.1. ^{1}H NMR

The composition of bisester-amides was characterized by using the integral of peaks of the aromatic protons (6–9 ppm). The ^{1}H NMR spectra of the bisester-(tetra-amides) IX_mIX_mI, TX_pT X_pT and T6T6T (Fig. 2) are typical spectra for bisester-amides used. The structures of these bisester-(tetra-amides) are shown in Fig. 3 and their peak assignments are given in Table 1.

The mid terepthalamide group in 6T6 and T6T6T are at the same chemical shifts. As a measure of the composition, the amide:ester ratio in the bisester-oligoamide is determined. For IX_mIX_mI-diphenyl (and other $I(X_mI)_n$), with isophthalic and *m*-xylylene groups, the amide:ester ratio is equivalent to the sum of the integrals of peaks *c* and b' ($I_c+I_{b'}$, peak at 8.3 + 8.1 ppm, Fig. 2A) divided by the integral of peak *a* (I_a, peak at 8.8 ppm, Fig. 2A) as calculated by Eq. (1):

$$\text{amide : ester} = \frac{I_c + I_{b'}}{I_a} \quad (1)$$

With TX_pTX_pT-diphenyl and T6T6T-diphenyl (and other derived oligo-amides), based on terephthalic and *p*-xylylene or hexamethylene groups, the amide:ester ratio was calculated from the integral of peak $b+b'$ ($I_{b+b'}$, peaks at 8.0–8.1 ppm, Fig. 2B and C) divided by the integral of peak *a* (I_a, peak at 8.5 ppm, Fig. 2B and C) as calculated by Eq. (2):

$$\text{amide : ester} = \frac{I_{b+b'}}{I_a} \quad (2)$$

The amide:ester ratios of all the bisester-oligoamides (by ^{1}H NMR), which are directly related to the amide segment length (*x*), are summarized in Table 2.

The amide:ester ratios are for all three systems slightly higher than expected based upon the ratio in the monomer feed. This higher ratio suggests that the average amide length of the segments is slightly higher than aimed for. This is due to the presence of segments of higher molecular weight. These segments were more difficult to remove completely than shorter segments by the purification method used.

3.2. MALDI-TOF

The composition of the segments is very relevant for these amide blocks and were also studied by MALTI-TOF. In the analysis of the MALDI-TOF results it is assumed that the ionization efficiency of each oligoamide segment is similar and that the peak intensities of the MALDI-TOF spectra can be related to the number of molecules of a particular molecular weight. However, it should be

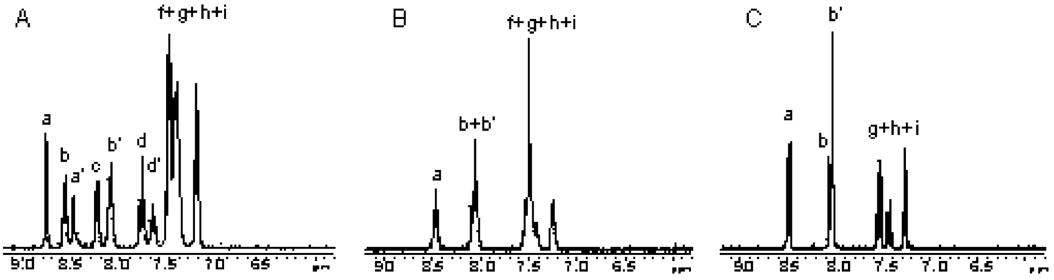


Fig. 2. ^{1}H NMR of bisester-(tetra-amide)s. Type: A, IX_mIX_mI-diphenyl; B, TX_pTX_pT-diphenyl; C, T6T6T-diphenyl.

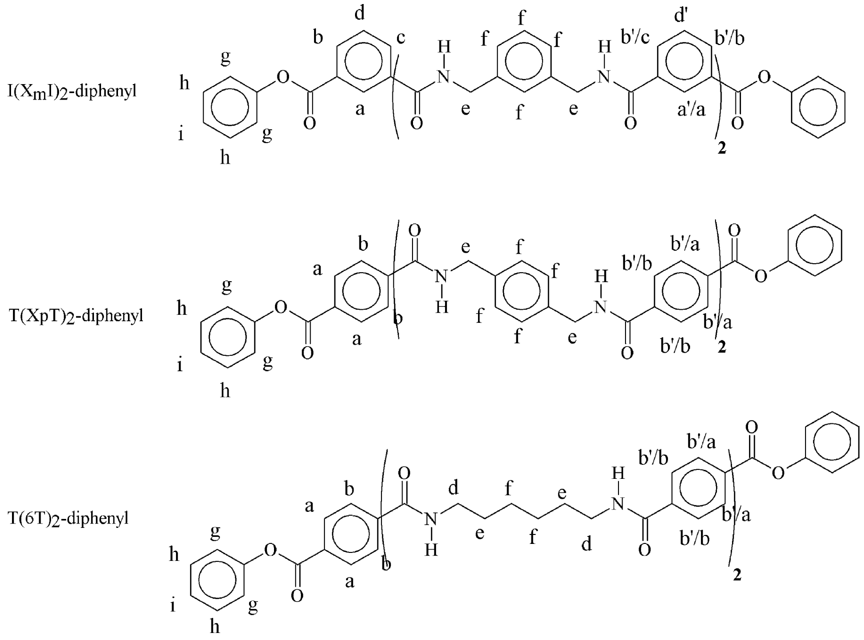


Fig. 3. Structure and proton assignment of the bisester-(tetra-amide)s ($x=2$).

mentioned that the MALDI-TOF spectra is semi-quantitative at best.

The uniformity of the amide segments was estimated as the sum of the intensities of peaks of the segment with the desired length divided by the sum of the intensities of all the peaks of the MALDI-TOF spectrum. The mol fraction of the major contaminant was derived by the dividing the intensity of the peak of the major contaminant by the sum of the intensities of all peaks. As an example the MALDI-TOF spectrum of the tetra-amide T6T6T-diphenyl is presented (Fig. 4).

The peak assignments obtained from the MALDI-TOF spectrum are given in Table 3. The analyzed molecules may contain a proton (H^+) or a metal ion (here Na^+). Thus, z equals unity ($z=1$) and the quantity m/z is considered to be equal to the molecular weight of the molecule either with or without H^+(+1 g/mol) or Na^+ (+22.7 g/mol).

The bisester-(tetra-amide) segment T6T6T-diphenyl contains very small amounts of 6T6-diamine, T6T-diphenyl ($x=1$) and somewhat larger amounts of octa-amide (T6T6T6T6T-diphenyl). Earlier it was suggested that synthesized uniform tetra-amide segments contain small

Table 1
Chemical shifts (δ) and peak assignment of bisester-(tetra-amide)s (7.0–9.0 ppm)

	Peak	δ (ppm)	Type[a]	Description[b]
I($X_mI)_2$-diphenyl	*a*	8.8	s	Isophthalic H, EA, ester side
	b	8.6	d	Isophthalic H, EA, ester side
	a'	8.5	s	Isophtalic H, AA, amide side
	c	8.3	d	Isophthalic H, EA, amide side
	b'	8.1	d	Isophthalic H, EA, amide side
	d	7.8	t	Isophthalic H, EA
	d'	7.7	t	Isophthalic H, EA
	f	7.5–7.2	m	H-aromatic *m*-xylylene group
	g+*h*+*i*	7.5–7.2	m	H-aromatic phenolic group
T($X_pT)_2$-diphenyl	*a*	8.5	d	Terephthalic H, EA, ester side
	b	8.1	d	Terephthalic H, EA, amide side
	b'	8.0	s	Terephthalic H, AA, amide side
	f	7.5–7.2	m	H-aromatic *p*-xylylene group
	g+*h*+*i*	7.5–7.2	m	H-aromatic phenolic group
T(6T)$_2$-diphenyl	*a*	8.5		Terephthalic H, EA, ester side
	b	8.1		Terephthalic H, EA, amide side
	b'	8.0		Terephthalic H, AA, amide side
	g+*h*+*i*	7.5–7.2		H-aromatic phenolic group
6T6-diamine	*a*	7.98		Terephthalic H, AA

[a] s = singlet, d = doublet, t = triplet and m = multiplet.

[b] EA: ester-amide substituted aromatic group; AA: amide-amide substituted aromatic group.

Table 2
Amide:ester ratio and uniformity of the bisester-oligoamides as determined by ^{1}H NMR and MALDI-TOF. (Ester is normalized to 1 per segment)

	X (exp.)	Amide:ester (exp.)	Amide:ester (^{1}H NMR)	Contaminant(s) (MALDI-TOF)[a]	Amide:ester (calc.)[b]	Uniformity (mol%) (calc.)[c]
IX_mI	1	1	1.09	$x=2$ (12%)	1.12	88
$I(X_mI)_2$	2	2	2.15	$x=3$ (3%), 4 (5%)	2.13	92
$I(X_mI)_3$	3	3	3.27	$x=2$ (5%), 4 (7%), 5 (9%)	3.20	79
TX_pT	1	1	1.09	$x=2$ (10%)	1.10	90
$T(X_pT)_2$	2	2	2.10	$x=4$ (4%)	2.08	96
T6T	1	1	1.02	$x=2$ (7%)	1.07	93
$T(6T)_2$	2	2	2.15	$x=1$ (2%), $x=4$ (16%)	2.26	80
$T(6T)_3$	3	3	3.29	$x=2$(6%),4(7%),5(5%)	3.11	82

[a] The % intensity contaminant is calculated from MALDI-TOF spectra relative to the expected bisester-oligoamide, which has 100% intensity.

[b] Calculated amide:ester ratio based on data from MALDI-TOF.

[c] Calculated uniformity from MALDI-TOF spectra (defined as the mole fraction of the segments with a desired amide segment length x).

amounts of longer amide segments [16]. T6T-diphenyl is formed by the reaction of DPT and 1,6-diaminohexane, which is probably a contaminant in the precursor 6T6-diamine. Another contaminant may be the amine-6T6T-methyl. This contaminant may have reacted with DPT and 1,6-diaminohexane to methyl-T6T6T6T-phenyl, which was also detected by MALDI-TOF. The major contaminant, T6T6T6T6T-diphenyl, is formed by the reaction of 6T6 with T. From the results of the MALDI-TOF experiment the uniformity of the bisester-(tetra-amide) segment T6T6T-diphenyl ($x=2$) was calculated to be 80 mol% (the sum of percentage T6T6T-diphenyl divided by the total percentage).

The compositions of the other bisester-oligoamide segments were analyzed in a similar way and the results are given in Table 2. Very small peaks (<3% intensity) were not taken into account.

The amide:ester ratios as determined by MALDI-TOF were also slightly higher than ideal. The major side peaks were from the longer segments. Although MALDI-TOF is at best a semi-quantitive analysis, still the ester:amide ratios corresponds well with the ^{1}H NMR results. The concentration of the segments with the desired length, the uniformity, is also determined. The bisester-oligoamides with $x=1$ have a uniformity of 88 mol% or higher, while the bisester-oligoamides with $x=2$ have uniformities of 80 mol% or higher and with $x=3$ approximately 80 mol%.

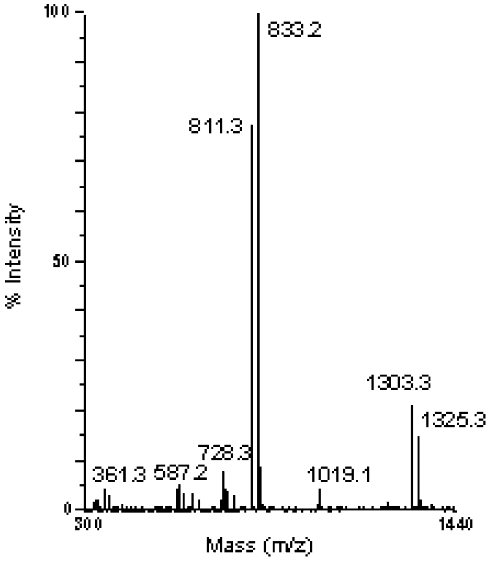


Fig. 4. MALDI-TOF spectrum of bisester-(tetra-amide) T6T6T-diphenyl.

Although MALDI-TOF is at best a semi-quantitative analysis, the ester:amide ratios correspond astonishing well with the ^{1}H NMR results. For all bisester-oligoamide segments the concentration of the segments with the desired length, the uniformity, has also been estimated. All oligoamides with $x=2$ seem to have uniformities of 80 mol% or higher, and those with $x=3$ around 80 mol%. However, it should be realized that all uniformity data in Table 2 should be taken with great care, in view of the non-quantitative character of the MALDI-TOF.

3.3. DSC

The thermal properties of bisester-oligoamide segments were characterized by DSC. The melting temperatures and enthalpies of these materials are shown in Table 4. The uniformity as determined by MALDI-TOF is also included.

The melting temperature of segments with a p-xylylene terephthalamide or a hexamethylene terephthalamide structure increases with increasing amide segment length x of the

Table 3
Peak assignment of the MALDI-TOF spectrum of T6T6T-diphenyl ($z=1$)

Mass (m/z) (g/mol)	Subscription	Relative intensity (%)
361.3	6T6-diamine	5
587.2	T6T-diphenyl (+Na)	5
728.3	–	7
811.3	T6T6T-diphenyl (+H)	68
833.2	T6T6T-diphenyl (+Na)	100
1019.1	Phenyl-T6T6T6T-methyl (+Na)	3
1303.3	T6T6T6T6T-diphenyl	20
1325.3	T6T6T6T6T-diphenyl (+Na)	13

Table 4
The melting temperature and enthalpy of the bisester-oligoamide segments as determined by DSC

	X	Uniformity (mol%)	T_m (°C)	ΔH_m (J/g)
IX_mI	1	88	166	59.4
$I(X_mI)_2$	2	92	206	53.6
$I(X_mI)_3$	3	79	137	29.1
TX_pT	1	90	290	180
$T(X_pT)_2$	2	96	334	175
T6T	1	93	264	125
$T(6T)_2$	2	80	313	141
$T(6T)_3$	3	82	346	40.9

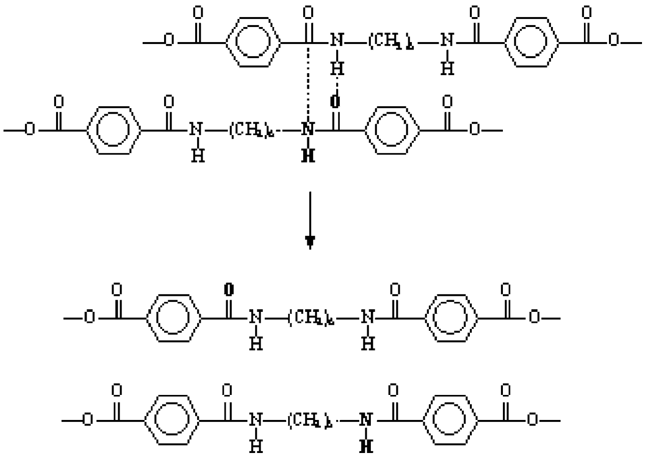


Fig. 5. Transamidation of bisester-diamide segments (T6T) without loss of uniform amide segment length.

segments. Segments based on *p*-xylylene terephthalamide have slightly higher melting temperatures as compared to segments based on hexamethylene terephthalamide. The length of the diamines, *p*-xylylene and hexametylene diamine, used is similar but the partial aromatic *p*-xylylene diamine is less flexible and thus is expected to have a lower melting entropy.

The melting temperature of the synthesized T6T6T-diphenyl (313 °C) agrees well with the literature value (316 °C) [16]. The melting enthalpy is, however, higher (141 vs. 129 J/g). $I(X_mI)_x$ bisester-oligoamides have appreciably lower melting temperatures and melting enthalpies as compared to $T(X_pT)_x$ bisester-oligoamides, which is due to the lower structure regularity of the $I(X_mI)_x$ segments (Fig. 1). The hexa-amide segments $I(X_mI)_3$ and $T(6T)_3$ ($x=3$) have lower melting temperatures and also lower melting enthalpies than corresponding shorter segments ($x=1$ or 2). This is unexpected as particular for longer segments higher melting temperatures are logical.

3.4. Amide segment uniformity in the block copolymers

During copolymerization of amide units with a telechelic polyether, interchange reactions like transamidation and ester-amide interchange, may occur. Transesterification of the bisester-oligoamide does not lead to loss of uniformity since the ester-groups are present only at the end of the amide segment. Also, transamidation in bisester-diamide segments ($x=1$) will not result in any loss of uniformity as the interchange of the amide groups results in the same segment, i.e. the amide groups have only changed place (Fig. 5). However, in bisester-(tetra-amide) segments ($x=2$) transamidation will result in loss of uniformity ester-amide interchange can also lead to loss of uniformity of the obtained segments. Consequently, randomization of bisester-(tetra-amide) leads to the formation of longer amide segments as well as to shorter segments (like the diamide segments).

The bisester-oligoamide segment length distribution in the block copolymer is difficult to study. With H NMR only an amide:ester ratio can be determined, which does not change if transreactions have taken place. If the oligoamide segments can be isolated from the block copolymer, analysis of these segments will be possible. In this study, block copolymers comprising bisester-(tetra-amide) segments and PPO-2300 were analyzed. The block copolymers were analyzed by ^{1}H NMR and the isolated bisester-(tetra-amide) segments, obtained from the hydrolysis of ester groups present in the block copolymer, by ^{1}H NMR and MALDI-TOF.

The ^{1}H NMR spectra of the polyether(ester-amide) with T6T6T segments and the product of hydrolysis are given in Fig. 6a and b.

In the hydrolysis product the polyether fragments were removed by washing with acetone and in the NMR spectrum the peaks of the polyether (at 1.4–4.0 ppm) have disappeared. The peaks in the range of 2.0–3.6 ppm in Fig. 6b are assigned to 1-methyl-2-pyrrolidone (NMP), which was used as a solvent for the hydrolysis of the segmented block copolymer. On these acquired materials the amide:ester rations were determined (Table 5). Compared to the starting materials the amide:ester ratio's have not changed. As ^{1}H NMR can only be used to determine the average compositions no conclusions can be drawn from Fig. 6a and b concerning a possible randomization that might have taken place during the synthesis of a block copolymer. However, the results suggests that the hydrolyzed amide segments are representative for the composition of the amide segments in the polymer.

From the MALDI-TOF spectra of the hydrolyzed material (Fig. 7b) it becomes obvious that the terephthalic ester groups in the polymer are converted into carboxylic acid end groups and are different from the phenyl ester groups of the starting bisester-amide (Fig. 7a). The peak at 833.2 (*m/z*) (Fig. 7a) is assigned to T6T6T-diphenyl + Na, while the peak at 680.9 (*m/z*) (Fig. 7b) is from T6T6T-$(COOH)_2$ + Na.

The composition of the amide segments as detected by

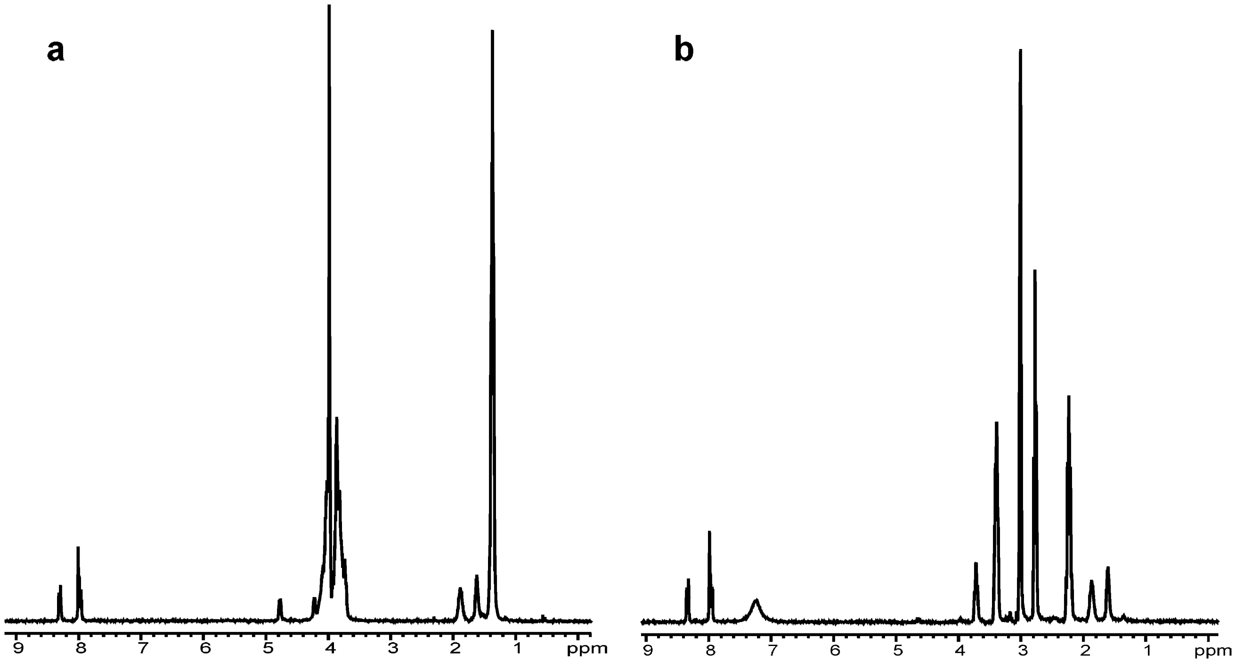


Fig. 6. ^{1}H NMR spectra of polyether(ester-amide) synthesized from T6T6T-diphenyl and PPO: a, blockcopolymer; b, after hydrolysis.

MALDI-TOF was obtained from the peak intensities as described above.

The results of the NMR and the MALDI-TOF analysis suggest that during melt-synthesis of block copolymers with uniform tetra-amide segments the concentration of the diamide segments has not increased and that the concentration of the higher length amides has increased only slightly.

It is, therefore, concluded that during the high temperature melt polymerization the uniformity of the segments is mainly preserved, i.e. no randomization of the amide segment length has taken place during the melt polymerization.

3.5. Distribution of amide segments in a one pot synthesis

The bisester-oligoamides synthesized in steps and purified are considered to have a nearly uniform length (Table 3). It is also of interest to study the length distribution of amide segments, which have been synthesized in one pot and whereby the segments have probably a random segment length distribution and this in absence of the polyether. A random distribution can be described by the most probable distribution function of Flory [19]. In this theory, it is assumed that end groups have equal reactivity during the reaction. In the case of A–A–B–B copolymer and whereby the molar ratio of the components A–A and B–B is not stoichiometric ($r\neq 1$), the following species are expected to be present:

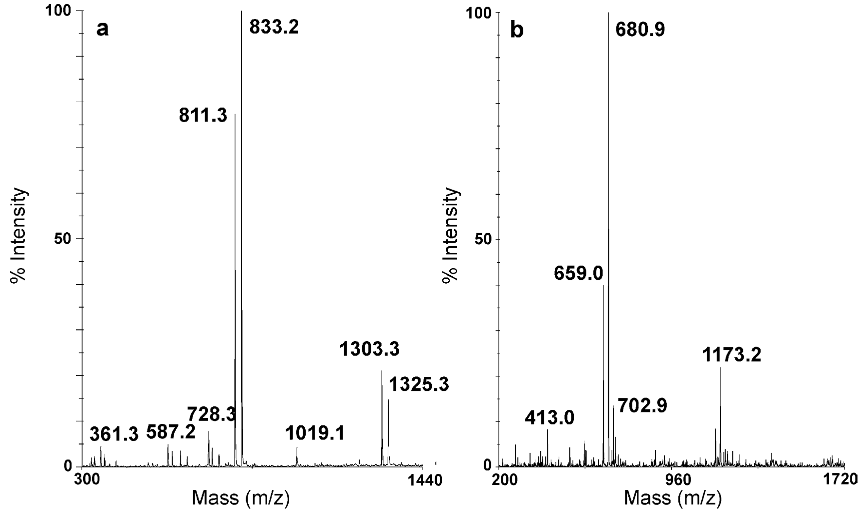
- (A–AB–B)$_{n/2}$ (even type).
- (A–AB–B)$_{(n-1)/2}$A–A (odd type).
- B–B(A–AB–B)$_{(n-1)/2}$ (odd type).

Of course, when $r\neq 1$ the concentration of the 'even type' sequences is negligible, especially when the conversion (p) is high. In the case $r\neq 1$ and $p=1$, the average weight distribution function is described by Flory (Eq. (3)).

Table 5
The amide:ester ratio of bisester-(tetra-amide) segments by ^{1}H-NMR and the contaminants in the bisester-(tetra-amide) segments as determined by MALDI-TOF.

	Amide:ester ratio by ^{1}H NMR			MALDI-TOF	
	Oliglomer	Blockcopolymer (before hydr.)	Hydrolysis product	Contaminants (before)[a]	Contaminants (after)[b]
IX$_m$IX$_m$I	2.15	2.20	2.22	$x=3$ (3%), $=4$ (5%)	$x=3$ (6%), $=4$ (5%)
TX$_p$TX$_p$T	2.10	2.08	2.06	$x=3$ (2%), $=4$ (4%)	$x=4$ (9%)
T6T6T	2.15	2.12	2.17	$x=4$ (16%)	$x=4$ (13%)

[a] MALDI-TOF of the bisester-(tetra-amide) (monomer).
[b] MALDI-TOF of the hydrolysis product.



T6T6T-diphenyl

Hydrolysis product

Fig. 7. MALDI-TOF spectra of synthesized T6T6T-diphenyl and hydrolyzed PEEA with T6T6T segments. a, synthesized T6T6T-diphenyl; b, hydrolysis product.

The quantity n is restricted to odd integral values [19].

$$w_{\mathrm{n}} = nr^{(n-1)/2}(1-r)^2/(1+r) \tag{3}$$

w_n, weight fraction of n-mer with n = odd numbers (1,3,5 etc.).

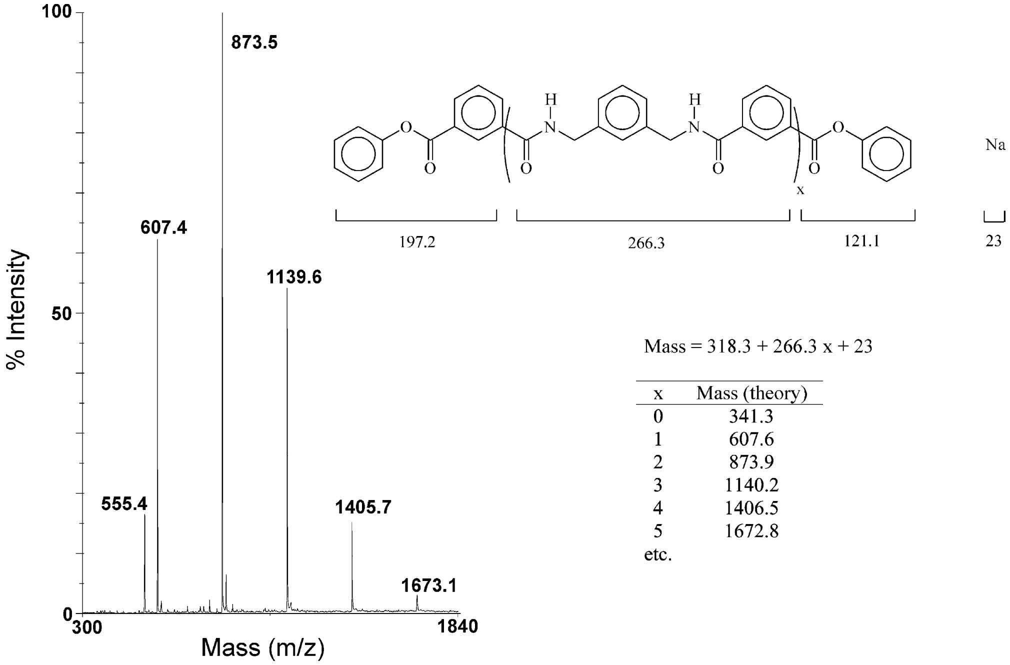
n, the n-mer (n is odd numbered, referring to the odd typed specimens).

r, the stoichiometric balance.

From W_n the N_n, the number fraction can be calculated with (4)

$$N_n = \frac{W_n}{n} = r^{(n-1)/2}(1-r)^2/(1+r) \tag{4}$$

With Eq. (4) the theoretical distribution of segment length can be calculated. In the case of an average random amide segment length $x=2$ ($n=5$) the calculated number fraction



Mass = 318.3 + 266.3 x + 23

x	Mass (theory)
0	341.3
1	607.6
2	873.9
3	1140.2
4	1406.5
5	1672.8
etc.	

Fig. 8. MALDI-TOF spectra of a bisester-oligoamide ($I(X_mI)_x$) with random amide segments; expected amide segment length $x=2$ (mass: 873.6 g/mol), ($r=2/3$).

of $x=2$ is 15% and for and $x=5$ ($n=11$) the calculated number fraction $x=5$ is 6.7 wt%.

The synthesis of $I(X_mI)_x$-diphenyl in one pot occurred in a NMP-solution and the reaction mixture appeared to be homogeneous throughout the reaction. The reaction mixtures in NMP were analyzed by means of MALDI-TOF. The MALDI-TOF spectrum of bisester-oligoamides with an expected random length of $x=2$, which is based on the molar ratio of diamine:diester monomers (2:3), is given in Fig. 8.

Next to segments with $x=2$ more fractions with other segment lengths can be detected and these fractions have higher peak intensities than in the uniform segments. With an average length of $x=2$ the highest concentration was for $x=2$. Next to tetra-amide sequences other sequences are present: $x=1$ (607.4, IX_mI-diphenyl + Na), $x=3$ (1139.6, $I(X_mI)_3$-diphenyl + Na), $x=4$ (1405.7, $I(X_mI)_4$-diphenyl + Na) and $x=5$ (1673.1, $I(X_mI)_5$-diphenyl + Na).

This spectrum is much broader than the spectrum of the purified $x=2$ (Fig. 4). A DSC of the one pot synthesized $I(X_mI)_3$-diphenyl did not give a clear melting temperature.

In order to get a semi-quantitative approximation of whether this one pot synthesis results in a random distribution of the amide segments next to the relative intensities from MALDI-TOF also the calculated Flory number distribution (4) was plotted (Fig. 9a). In a similar way was this done for $x=5$ (Fig. 9b). In comparing the MALDI-TOF intensities with the Flory distribution for $x=2$ and $x=5$ (black bars) it is clear that the MALDI-TOF intensities (open bars) are very low for the low molecular weight species and also lower at the higher molecular weights. A possible reason is the higher reactivity of the first ester group over the second ester group. In other words, it seems as if the one pot synthesis of making amide segments has a broader distribution than the multi-step synthesis products of T6T6T (Fig. 4) but a narrower distribution than the theoretical random distributions (Fig. 9). However, as MALDI-TOF is only semi-quantitative these results should be looked at with great caution.

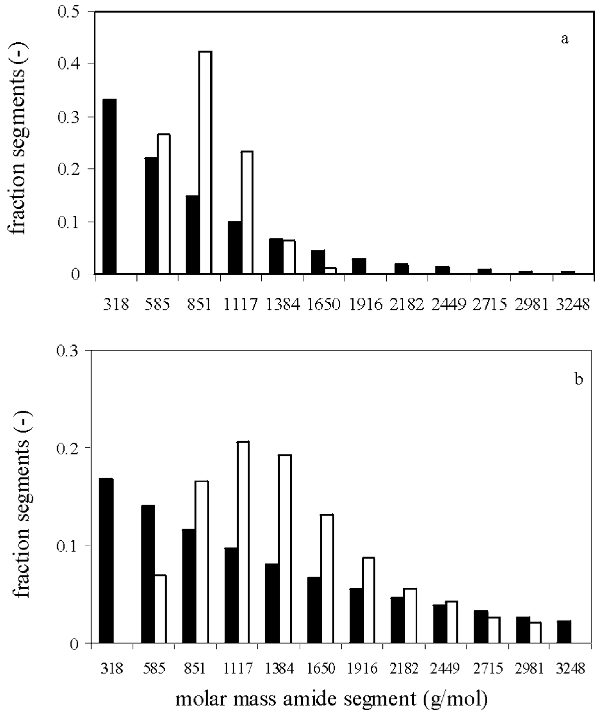


Fig. 9. Intensities of amide segments $I(X_mI)_x$ (open bars) synthesized in one pot derived from MALDI-TOF for ester-amide ratios of: a, 3/2 ($x=2$); b, 6/5 ($x=5$). (Closed bars: distribution function by Flory Eq. (4)).

4. Conclusions

Bisester-oligoamide segments with amide segment length (x) and phenolic ester end groups were synthesized with high uniformity and relatively high yields. The segments with $x=1$ and $x=2$ have, respectively, a uniformity of 88 and 80 mol% or higher. The major contaminants are the longer amide segments with twice the desired length, i.e. tetra-amide segments ($x=2$) in case of $x=1$ and octa-amides ($x=4$) for $x=2$. Bisester-(hexa-amide) segments were obtained with 79–82 mol% of the desired length ($x=3$), still sufficiently uniform for polymerization. The majority of the contaminants appeared to be longer amide sequences ($x=4$ and $x=5$).

The amide:ester ratio, which is related to the amide segment length x, in the bisester-oligoamide segments as studied by ^1H NMR was in agreement with the values obtained by MALDI-TOF. The uniformity of the amide segments was also studied after melt polymerization and it was found that randomization reactions during melt polymerization are insignificant. The uniformity of the synthesized segments is, therefore, preserved in the corresponding block copolymer.

Synthesizing the amide segments in a one-pot reaction resulted in a significant broadening of the distribution but did not results in a fully random distribution of the amide segment length, this probably due to the higher reactivity of the first ester group over the second ester group.

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References

[1] Holden G, Legge NR, Schroeder HE, editors. Thermoplastic elastomers: a comprehensive review. 1st ed. Munich: Hanser Publishers; 1987.

[2] O'Sickey MJ, Lawrey BD, Wilkes GL. J Appl Polym Sci 2002;84: 229.

[3] Bayer AG (Germany). Private communication.

[4] Bonte GIM, Weremeus Buning GH, Dijkstra K, Warnier JMM. WO 00/24803; 1998.

[5] Van der Schuur JM, Feijen J, Gaymans RJ. Polymer 2005;46:327.

[6] Harrell LL. Macromolecules 1969;2:607.

[7] Ng HN, Allegrezza AE, Seymour RW, Cooper SL. Polymer 1974;14: 255.

[8] Eisenbach CD, Baumgartner M, Gunter G. Advances. In: Jal J, Marks JE, editors. Elastomers and rubber elasticity. New York: Plenum Press; 1985. p. 51.

[9] Krijgsman J, Husken D, Gaymans RJ. Polymer 2003;44:7573.

[10] Gaymans RJ, de Haan JL. Polymer 1993;34:4360.

[11] Niesten MCEJ, Feijen J, Gaymans RJ. Polymer 2000;41:8487.

[12] Kaczmarczyl B, Sek D. Polymer 1995;36:5019.

[13] Rabani G, Rosair GM, Kraft A. J Polym Sci, Part A 2004;42:1449.

[14] Kotliar AM. J Polym Sci, Macromol Rev 1981;16:367.

[15] Serrano PJM, Van Bennekom ACM, Gaymans RJ. Polymer 1998;39: 5773.

[16] Krijgsman J, Husken D, Gaymans RJ. Polymer 2003;44:7043.

[17] Naskar SS. US Patent 3,705,186; 1972.

[18] Nielen MWF. Mass Spectrom Rev 1999;18:309.

[19] Flory PJ. Principles of polymer chemistry. 4th ed. Cornell University Press: Wisconsin; 1964. p. 322.