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Synthesis and Characterization of Polyesteramides Derived from an Oxazoline-Functional Alcohol and Dicarboxylic Acid Anhydrides

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ABSTRACT: Novel polyesteramides were synthesized by copolymerization in bulk of 5-(4,5-dihydro-1,3-oxazol-2-yl)-1-pentanol and various cyclic dicarboxylic acid anhydrides at temperatures varying between 120 and 200°C. The polymers resulting from polycondensation were characterized by means of ¹H-NMR, FTIR, MALDI-TOF-MS, SEC, and DSC. The glass transition temperatures, T_g , of the copolymers were varied between -28 and +31°C as a function of the anhydride type. Molecular weights, M_w , were dependent on reaction temperature, reaction time, and anhydride type. Spectroscopic investigation of reaction products and esteramide model compounds provided evidence for imide by-product formation, which accounts for the low degree of polymerization. © 1999 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 37: 3367–3376, 1999

Keywords: oxazoline; polyesteramide; polycondensation; MALDI-TOF-MS

INTRODUCTION

1,3-Oxazolines are versatile intermediates in polymer chemistry. They can readily react via electrophilic attack at the nitrogen atom or via nucleophilic attack at the carbon atom in 5-position. Cationic ring-opening polymerization of 1,3-oxazolines affords poly(*N*-acethyleneimine)s.¹ Moreover, 1,3-oxazolines can be copolymerized together with electrophiles such as anhydrides.² Polymerization of 2-substituted 1,3-oxazolines with cyclic anhydrides, displayed in Figure 1, is believed to proceed via zwitterions (pathway a).³ However, in view of the known grafting reactions of oxazolines onto anhydride functional copolymers, e.g., poly(styrene-*co*-maleic anhydride), SMA, an alternative mechanism was proposed

involving a bicyclic adduct of oxazoline and anhydride (Fig. 1, pathway b).⁴

Another possibility to obtain oxazoline-based polymers is the reaction of bis(oxazoline)s with difunctional nucleophiles such as bis(phenol)s, dithiols, *sec*-diamines or dicarboxylic acids.^{1,5} For example, bis(oxazoline)s were applied as chain extenders⁶ for α,ω -dicarboxylic acids to produce higher molecular weight polyesteramides. Another route to synthesize polyesteramides is represented by the copolymerization of cyclic dicarboxylic acid anhydrides, bis(oxazoline)s, and diols. Po et al. were the first to demonstrate that the bulk reaction of these three components leads to polyesteramides.⁷ In this ternary system, the α,ω -dicarboxylic acids are generated *in situ* by conversion of two equivalents of cyclic anhydride with one equivalent diol. Subsequently, these *in situ*-formed α,ω -dicarboxylic acids can react with bis(oxazoline)s forming polyesteramides via chain extension. Since soluble polymers were obtained,

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Figure 1. Reaction mechanism of 1,3-oxazolines with cyclic dicarboxylic acid anhydrides involving zwitterionic intermediates (pathway a) or bicyclic intermediates (pathway b).

it was concluded that the well-known reaction of anhydrides with oxazolines (see Fig. 1) can be neglected, because this reaction would cause crosslinking. Obviously, in the presence of an alcohol, the reaction of alcohol with cyclic anhydrides is favored with respect to that of cyclic anhydrides with 1,3-oxazolines. Also, secondary amines were used as nucleophiles to generate dicarboxylic acids *in situ*.⁸ These ternary systems require accurate control of stoichiometry and investigation of kinetics is also crucial. Due to the polyaddition mechanism, even a small deviation from the stoichiometric molar ratio can account for the severely reduced degree of polymerization. Therefore, an objective of this research was to develop binary systems that are composed of cyclic anhydride and dual-functional 2-hydroxyalkyl-functionalized 1,3-oxazolines. It was expected that the use of α -oxazoline- ω -alcohols could provide better control of stoichiometry and afford a higher degree of polymerization. The key intermediate was 5-(4,5-dihydro-1,3-oxazol-2-yl)-1-pentanol, OXA-OH, prepared by the method of Hölderle et al. from ϵ -caprolactone and 2-aminoethanol.⁹ OXA-OH was examined as a dual-functional comonomer in polyesteramide synthesis as depicted in Figure 2.

EXPERIMENTAL

Materials. 2-Undecyl-4,5-dihydro-1,3-oxazoline, C11OXA, was obtained from Henkel AG (Düsseldorf, Germany) and distilled prior to use. 1-Octanol, C8OH; succinic anhydride, S; phthalic anhydride, P; 2-octen-1-yl succinic anhydride, OS; 1,2-cyclohexanedicarboxylic anhydride, HP, and *cis*-5-norbornene-endo-2,3-dicarboxylic anhydride, N, were purchased from Aldrich (Deisenhofen, Germany) and purified by sublimation (liquid C8OH and OS were distilled). 5-(4,5-dihydro-1,3-oxazol-2-yl)-1-pentanol, OXA-OH, was synthesized from ϵ -caprolactone and 2-aminoethanol according to Hölderle.⁹

Model Reactions. The model reactions were carried out in dried glass flasks under inert gas atmosphere at 160°C. In model reaction I (Fig. 3), representing a two step reaction, S was heated with C8OH for 1 h and the obtained hemiester, HE, was cooled down to room temperature. In the second step, the equivalent molar amount of C11OXA was added and the mixture heated again at 160°C for 1 h to produce the esteresteramide 1-[2-(dodecanoylamino)ethyl] 4-octyl succinate,

Figure 2. Copolymerization of the binary system OXA–OH/cyclic anhydrides affords polyesteramides.

EEA. In model reaction II (Fig. 3), which is a one-pot reaction, S, C8OH, and C11OXA were mixed equimolarly and heated together for 2 h to yield EEA.

Polyaddition. All polyaddition runs were performed under the same reaction conditions. Temperature was varied between 120, 160, and 200°C (see Table I); 3 g OXA–OH (19.2 mmol) was heated together with the stoichiometric amount of anhydride (19.2 mmol) in a dried glass flask under inert gas atmosphere using magnetic stirring. For the solid anhydrides S, P, HP, and N, a homogenous melt was formed within 60 s. Due to sublimation of anhydride, a small amount of condensed anhydride needles was visible at the neck of the flask. After cooling down to room temperature, the reaction products were analyzed without further purification. Additionally, in some polyaddition runs samples for NMR and GPC analysis were recovered in argon countercurrent.

Characterization

Size Exclusion Chromatography (SEC). Molecular weights were determined by means of a

Knauer–Mikrogelset A14 (Berlin, Germany) in CHCl₃ solution calibrated with PS standards.

Differential Scanning Calorimetry (DSC). Glass transition temperatures were recorded with a Perkin–Elmer DSC-7 (Norwalk, Connecticut) using a heating rate of 10K/min (second heating run).

Nuclear Magnetic Resonance Spectroscopy (NMR). The ¹H–NMR spectra were recorded in CDCl₃ on a Bruker ARX-300 (Karlsruhe, Germany) at 300 MHz. TMS was utilized as the internal standard.

Matrix Assisted Laser Desorption/Ionization–Time of Flight–Mass Spectroscopy (MALDI–TOF–MS). MALDI–TOF–MS analyses were carried out in reflector mode on a Reflex II System from Bruker–Franzen Analytik GmbH (Bremen, Germany). Spectroscopic grade THF was used as solvent for the matrix 2,5-dihydroxybenzoic acid (20 mg/ml) and the copolymers P200-2 (8.26 mg/ml) and P200-60 (8.67 mg/ml). Mixtures of matrix and samples were prepared in the volume ratio 3 : 1 and 3 : 2. A 1-μL aliquot of these mixtures was taken and allowed to dry on the target under

Figure 3. Scheme of the preparation of model compound EEA in two separate steps (model reaction I). The identical product EEA is received in a one-pot reaction (model reaction II).

atmospheric pressure. Voltages were 20 kV for UIs1, 16 kV for UIs2, 21.5 kV for URefl, and 7.3 kV for ULens. At least 200 scans were accumulated to obtain each spectra. All data were calibrated by means of polystyrene standards.

Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra were recorded on a Bruker IFS 88 spectrometer (Karlsruhe, Germany) with MIR-DTGS-detector and KRS-5 polarizator.

RESULTS AND DISCUSSION

Model Compounds

In order to assign ^1H -NMR and FTIR signals of the polyesteresteramides, the esteresteramide model compound EEA was synthesized as depicted in Figure 3. In model reaction I, S was esterified with C8OH to afford the ester carboxylic acid, HE (hemi-ester-4-(octyloxy)-4-oxobu-

Table I. Preparation Conditions and Physical Properties of Polyesteramides

Copolymer ^a	Anhydride	Temperature (°C)	M_w^b (kg/mol)	M_n^b (kg/mol)	M_w/M_n^b	T_g^c (°C)
S120-60	succinic	120	7.8	4.4	1.8	-4
S160-60	succinic	160	13.2	8.0	1.6	-4
S200-60	succinic	200	10.6	4.7	2.3	-4
P120-60	phthalic	120	—	—	—	—
P160-60	phthalic	160	3.9	2.2	1.8	17
P200-60	phthalic	200	5.6	4.1	1.4	17
OS120-60	octenyl succinic	120	8.5	5.5	1.5	-27
OS160-60	octenyl succinic	160	27.6	16.1	1.7	-28
OS200-60	octenyl succinic	200	19.0	10.7	1.8	-25
HP120-60	hexahydrophthalic	120	6.1	4.5	1.4	17
HP160-60	hexahydrophthalic	160	6.1	4.5	1.4	17
HP200-60	hexahydrophthalic	200	6.0	4.2	1.4	19
N120-60	norbornylene dicarboxylic	120	3.8	1.8	2.1	28
N160-60	norbornylene dicarboxylic	160	9.7	6.6	1.5	31
N200-60	norbornylene dicarboxylic	200	9.3	6.2	1.5	31

^a Time of reaction = 60 min.^b Determined by SEC.^c Determined by DSC.

tanoic acid). In a separate second step, HE was heated with C11OXA to give the esteresteramide, EEA (1-[2-(dodecanoylamino)ethyl] 4-octyl succinate). In order to verify that the presence of an alcohol suppresses the reaction of oxazoline with anhydride, the identical three educts are heated together in one pot under the same conditions (model reaction II, Fig. 3). The ¹H-NMR-spectra of the reaction products of both model reactions are shown in Figure 4. In both model reactions EEA is formed exclusively, indicating that no side products of the reaction between C11OXA and S are formed. These observations confirm the result of Po et al. that the equimolar reaction of an oxazoline, an anhydride, and an alcohol leads to esteramide formation without by-products.⁷ In the case that zwitterion formation (see Fig. 1) occurs, the intermediate may be followed by the interception of this intermediate by the alcohol, thus preventing zwitterionic polymerization. In other words, the oxazoline could be functioning as an acylation catalyst. Figure 4 shows the characteristic ¹H-NMR signals and Table IV summarizes the FTIR signals of HE and EEA.

Polymerization

Linear polyesteramides are prepared by means of bulk polymerization of OXA-OH and cyclic anhydrides such as succinic (S), phthalic (P), octenyl-

succinic (OS), hexahydrophthalic (HP), and norbornyldicarboxylic acid anhydride (N). Table I summarizes the properties of the resulting polyesteramides. The sample code of the copolymers (e.g., S160-60) represents the type of anhydride (S for succinic anhydride), the reaction temperature (160°C), and the total reaction time (60 min). The

Figure 4. ¹H-NMR of the model compound EEA exhibiting a similar esteresteramide structure as the copolymers.

Figure 5. ^1H -NMR of the copolymers N160-60, OS160-60, HP160-60, P160-60, and S160-60 after 60 min.

temperature during polyaddition is varied between 120, 160, and 200°C. The total reaction time is 1 h. All polymers are pale yellow or yellow in color.

All polymerization runs yield polymers, except for P120-60, because phthalic anhydride does not dissolve completely in the melt. For all aliphatic anhydrides, the highest molecular weight is obtained at 160°C. The highest molecular weight of $M_w = 27.6$ kg/mol is achieved with OS160-60; however, for copolymers based on N and HP, M_w is constant at all polymerization temperatures. The glass transition temperatures, T_g , of the copolymers depend upon anhydride type and vary between -4°C for OXA-OH/S and $+31^\circ\text{C}$ for

OXA-OH/N. Increasing T_g of the polyesteramides is paralleled by increasing chain stiffness of the anhydrides side groups: $\text{N} > \text{P} \cong \text{HP} > \text{S}$. Copolymers containing OS exhibit the lowest T_g ($= -27^\circ\text{C}$) due to the presence of the very flexible octenyl side group of OS.

^1H -NMR Characterization

The ^1H -NMR spectra of the copolymers polymerized at 160°C (60 min) are displayed in Figure 5. The peak assignment of the ^1H -NMR signals of the methylene groups within the esteresteramide structure of EEA, S160-60, and P160-60 are listed in Table II. For comparison, the ^1H -NMR signals of the used anhydrides are listed in Table III. For S160-60, the triplet of the methylene group adjacent to the OH-group appears at 3.37 ppm in the monomer OXA-OH and at 4.05 ppm (*a*) in the polymers, thus indicating the complete esterification of the alcohol functionality. The triplets of the methylene groups in the monomeric oxazoline ring at 3.68 and 4.15 ppm shift to 3.50 (*f*) and 4.14 ppm (*g*) in the esteramide structure of the copolymer. These chemical shifts are in accordance with those of the model compound EEA and confirm the presence of the proposed esteresteramide backbone of the polymer. For P160-60, the corresponding signals of its esteresteramide backbone are slightly shifted to higher ppm values, due to the vicinity of the phenyl ring of phthalic anhydride. The ^1H -NMR signals of the hydrogens of phthalic anhydride appear from 7.8 to 8.0 ppm in the monomer and from 7.4 to 7.9 ppm in the polyesteramide. Additional signals at 7.83, 4.55, 3.95, and 2.28 ppm are observed and cannot be attributed to the esteresteramide structure, indicating the formation of unexpected by-products.

The ^1H -NMR spectra of the other polymers N160-60, OS160-60, and HP160-60 are more complex. The signals of the esteresteramide backbone overlap in the range from 3.8 to 4.3 ppm. Moreover, the signals of the olefinic hydrogens of N

Table II. ^1H -NMR Assignment of Model Compounds HE, EEA, and Copolymers S160-60 and P160-60

	<i>h,i</i>	R1, R2	<i>a</i>	<i>b,c,d</i>	<i>e</i>	<i>f</i>	<i>g</i>	N-H
HE	2.65, m	—	4.05, t	1.40, m/1.65, m	2.25, t	—	—	—
EEA	2.65, m	—	4.05, t	1.40, m/1.65, m	2.15, t	3.55, t	4.10, t	5.9–6.1, broad
S160-60	2.61, m	—	4.05, t	1.35, m/1.62, m	2.20, t	3.50, t	4.14, t	6.3–6.7, broad
P160-60	—	7.4–7.9, m	4.28, t	1.2–1.9, m	2.05–2.40, m	3.64, t	4.42, b. s	6.4–6.9, broad

Table III. ^1H -NMR Assignment of Anhydrides Used

Anhydride	h,i	R1, R2
S	3.00	—
P	—	7.8–8.0, m
OS	3.00, m/3.18, m	0.85, t/1.2–1.43, m/2.02, q/2.75, m/2.50, m/5.30, m/5.01, m
HP	3.12, m	1.48, m/1.72–1.98, m
N	3.49, s	1.58, d/1.78, d/3.59, s/6.30, s

(6.1–6.4, m) and OS (5.0–5.3, m) remain unchanged during polymerization.

FTIR Characterization

The FTIR signals of model compounds (HE and EEA) and copolymers, analyzed without further purification, are summarized in Table IV. No residual anhydride signals at $1860/1780\text{ cm}^{-1}$ and oxazoline signals at 1664 cm^{-1} are detected in all copolymers. The FTIR spectra are in accordance with the esteresteramide structure. For all copolymers, the bands of the ester carbonyl are detected at 1730 cm^{-1} and the amide I/amide II bands are identified, respectively, at 1650 and 1550 cm^{-1} . However, an additional signal at 1778 cm^{-1} is also detected, which may indicate the formation of cyclic imides. Literature reports IR signals of succinic imide and phthalic imide at 1784 and 1778 cm^{-1} , respectively.¹⁰ Unfortunately, a mechanistic pathway based on the presented polymer structure (Fig. 2), which would produce a succinimide or phthalimide structure, cannot be presented.

Table IV. Characteristic FTIR Signals of Educts and Copolymers in cm^{-1}

Educt	Anhydride	Oxazoline
OXA-OH	—	1664
S, P, HP, N, OS	1860, 1780	—
Product	Ester	Amide I/II
HE	1729	1712 ^a
EEA	1729	1643, 1553
S160-60	1726	1634, 1537
P160-60	1724	1651, 1546
HP160-60	1730	1649, 1546
N160-60	1750	1644, 1539
OS160-60	1736	1654, 1552

^a Signal of carboxylic acid.

Influence of Reaction Time

In order to study the polyaddition kinetics, samples are recovered during the copolymerization run P200- t after $t = 3, 10$, and 60 min. The ^1H -NMR spectra are presented in Figure 6. The signals obtained are in agreement with the formation of an esteresteramide backbone. The reaction of the oxazoline with the *in situ*-generated carboxylic acid is already completed within 3 min. Besides the assigned signals, additional signals at 7.80, 4.48, 3.95, and 2.28 ppm (the same signals are found for P160-60) increase with longer reaction times. The intensities of the unassigned signals are very small after 3 min. This implies that the formation of side products occurs during polymerization, but is much slower with respect to the

Figure 6. ^1H -NMR of phthalic anhydride, OXA-OH and copolymer P200- t after different reaction times of $t = 2, 12$, and 60 min.

Figure 7. Molecular weight of copolymers S200-t and P200-t decrease with increasing reaction time $t = 2, 10, 20$, and 60 min.

esteresteramide formation. The appearance of the signal at 7.80 ppm corresponds to the aromatic hydrogens of phthalic anhydride and indicates that the ester groups are involved in this side reaction. From the literature, ^1H -NMR signals of the aromatic hydrogens of β -hydroxyphthalimides are reported at 7.80 ppm.¹¹ The signals of the methylene groups adjacent to the imide nitrogen have a chemical shift of 4.30 and 3.70 ppm. These signals of β -hydroxyphthalimides from the literature are very similar to the unassigned signals of P200-60. This supports the suggested imide formation.

Figure 7 and Table V show the molecular weight of the polyesteramides versus reaction time for S200-t and P200-t. The molecular weight is decreasing with longer reaction periods. Most

Table V. Molecular Weight Determined by Means of SEC of Polyesteramides After Different Reaction Time

Copolymer	Time (min)	M_w^a (kg/mol)	M_n^a (kg/mol)	M_w/M_n^a
S200-10	10	16.1	9.2	1.8
S200-20	20	12.2	8.0	1.5
S200-60	60	10.6	4.7	2.3
P200b-2 ^b	2	10.2	7.2	1.4
P200-10	10	10.1	6.9	1.5
P200-20	20	8.4	5.8	1.4
P200-60	60	5.6	4.1	1.4

^a Determined by means of SEC.

^b P200b-2 was prepared by a separate polymerization run.

Figure 8. MALDI-TOF traces of P200-t after 2 min (a) and 60 min (b), respectively.

likely, this is a consequence of the suggested imide formation.

MALDI-TOF-MS Characterization

Figure 8 depicts the MALDI-TOF-MS spectra of P200-t, with $t = 2$ (a) and $t = 60$ min (b). Both spectra show main signals that are accompanied by signals with lower intensity. The main signals of both spectra can be attributed to the molecular weight of protonated copolymers, assuming that the cations have a charge of $z = 1$. These species are designated as OxAy-H^+ , where the copolymer composition is indicated with $x =$ the number of OXA-OH units and $y =$ the number of P units within the polymer. The intensity ratio of the lower signals compared to that of corresponding main signals is larger for P200-60 (Fig. 8b) than for P200-2 (Fig. 8a) and will be discussed in more detail in the next section. Table VI summarizes the assignment of the main signals of both spectra. All combinations of OXA-OH and P, except O8A7-H^+ , are detected and their measured m/z

Table VI. Assignment of MALDI-TOF-MS Main Signals of the Copolymers P200-2 and P200-60

Signal ^a	Calculated Mass ^b (g/mol)	Measured Mass (<i>m/z</i>)
O2A2	611.3	611.2
O2A3	759.3	759.2
O3A2	768.4	768.4
O3A3	916.4	916.5
O3A4	1064.4	1064.4
O4A3	1073.5	1073.5
O4A4	1221.5	1221.5
O4A5	1369.5	1369.6
O5A4	1378.6	1378.6
O5A5	1526.6	1526.7
O5A6	1674.7	1674.8
O6A5	1683.7	1683.9
O6A6	1831.8	1831.9
O6A7	1979.8	1980.0
O7A6	1988.9	1989.0
O7A7	2136.9	2137.0
O7A8	2284.9	2285.0
O8A7	2294.0	—
O8A8	2442.0	2442.3
O8A9	2590.0	2590.3
O9A8	2599.1	2599.3
O9A9	2747.1	2747.4
O9A10	2895.2	2895.3
O10A9	2904.3	2905.7
O10A10	3052.3	3052.6
O10A11	3200.3	3200.5
O11A10	3209.4	3210.8
O11A11	3357.4	3357.9

^a The signals are referred to the samples and reflect copolymer composition.

^b Mass of single charged protonated species calculated with isotopes ¹²C, ¹H, ¹⁶O, and ¹⁴N.

ratios are in good agreement with their calculated masses. For P200-60, the relative intensities of all main signals are strongly decreasing with increasing *m/z*, i.e., molecular weight. This is expected for polymers resulting from the polyaddition mechanism. For P200-2 (Fig. 8a), on the other hand, the relative intensity of the symmetric species OxAx (consisting of an equal number of OXA-OH and P) is larger in comparison to its adjacent asymmetric copolymers OxA(*x* + 1).

Figure 9 shows detailed spectra of P200-2 (Fig. 9a) and P200-60 (Fig. 9b) in the range between *m/z* = 1520 and 1590. The main signal at *m/z* = 1526.7 of both spectra originates from the protonated species O5A5-H⁺. Its measured isotopic pattern agrees very well with the calculated pattern as summarized in Table VII. In addition to

Figure 9. Detailed MALDI-TOF spectra of P200-t after 2 min (a) and 60 min (b), respectively.

the main signal of O5A5-H⁺, additional isotopic patterns with minor intensity are detectable. These can be assigned to adducts consisting of the copolymeric species with water (H₂O-H⁺), so-

Table VII. Isotopic Pattern of MALDI-TOF Signal O3A3-H⁺ (Calculated as ¹²C₄₈¹H₅₈¹⁶O₁₅¹⁴N₃⁺) and O5A5-H⁺ (Calculated as ¹²C₈₀¹H₉₆¹⁶O₂₅¹⁴N₅⁺) of P200-2

<i>m/z</i>	Intensity Calculated ^a (%)	Intensity Found ^b (%)	Integration Interval (<i>m/z</i>)
916	100.0	100.0	916.0–917.0
917	54.2	56.2	917.0–918.0
918	17.3	19.5	918.0–919.0
919	4.2	1.7	919.0–920.1
920	0.8	—	920.1–921.1
1526	100.0	100.0	1526.1–1527.2
1527	90.4	90.1	1527.2–1528.2
1528	45.4	44.9	1528.2–1529.3
1529	16.4	18.6	1529.3–1530.3
1530	4.6	6.9	1530.3–1531.3

^a Calculated with program *chempute* (Universität Tübingen).

^b Signal intensity integrated with program *X-TOF* (Bruker-Software).

dium (Na^+), or potassium (K^+): $m/z = 1544.6$: $\text{O5A5-H}_2\text{O-H}^+$; $m/z = 1548.6$: O5A5-Na^+ ; $m/z = 1564.5$: O5A5-K^+ ; $m/z = 1566.7$: $\text{O5A5-H}_2\text{O-Na}^+$, and $m/z = 1582.6$: $\text{O5A5-H}_2\text{O-K}^+$. The minor signals of P200-2 at $m/z = 1553.8$ and 1569.6 and for P200-60 at $m/z = 1551.8$, 1570.7 , and 1586.8 might indicate unidentified by-products during the polyaddition procedure. Careful analysis of the whole spectrum shows similar results, i.e., main signals (see Table VI) including isotopic patterns and minor signals of adducts as described for Figure 9. The molecular weight distribution of the copolymers could not be calculated. Obviously, MALDI-TOF-MS analysis of the investigated polyesteramides with a SEC polydispersity of about 2 (see Table I) does not detect high molecular weight polymers and thus leads to smaller M_n and M_w . MALDI-TOF-MS spectra support the formation of polyadducts of OXA-OH and P, which are expected as main products according to the mechanism in Figure 2. The multiple minor signals are attributed to adducts with sodium, potassium, and water. However, several other small signals, for example, in the range O5A5 at $m/z = 1552$, 1566 , 1569 , and 1586 indicate the formation of by-products.

CONCLUSIONS

Novel polyesteramides were prepared via copolymerization of α -oxazoline- ω -alcohol, OXA-OH, and various anhydrides. Copolymers were formed within a few minutes. The glass transition temperatures of the polymers correlate with the structure of the anhydride used. Crosslinking due to the reaction of oxazoline with anhydride was not detected. The resulting polyesteramides had molecular weights approaching $M_w = 28,000$ g/mol as determined by SEC. The backbone of the copolymers exhibits an esteresteramide structure, which was confirmed by $^1\text{H-NMR}$, FTIR, and MALDI-TOF-MS measurements, including studies of an esteresteramide model compound. Molecular weight decreased with increasing reaction times. According to $^1\text{H-NMR}$ and FTIR spectroscopy, a side reaction appears involving the formation of imides. This undesirable side reaction does not permit the synthesis of high molec-

ular weight polyesteramides. However, oligoesteramides represent interesting intermediates to produce thermosets using multifunctional monomers such as trisoxazolines.

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