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Microwave-Assisted Synthesis of a 4^2-Membered Library of Diblock Copoly(2-oxazoline)s and Chain-Extended Homo Poly(2-oxazoline)s and Their Thermal Characterization

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ABSTRACT: A library of 4 chain-extended homo- and 12 diblock copoly(2-oxazoline)s was prepared from 2-methyl-, 2-ethyl-, 2-nonyl-, and 2-phenyl-2-oxazoline within less than a day (total net reaction time). The living cationic ring-opening polymerization was initiated by methyl tosylate and performed in acetonitrile at 140 °C in a single-mode microwave reactor. A total number of 100 (50 + 50) monomer units was incorporated into the respective polymer chains; the thus-obtained 16 polymers exhibited narrow average molecular weight distributions (PDI < 1.30). All compounds were stable up to temperatures of (at least) 300 °C. The subsequent determination of the glass-transition temperatures and the specific heats revealed a significant influence of the type of substituents attached to the polymers' backbones: the glass-transition temperature as well as the corresponding specific heat increased with an increasing rigidity of the substituents in the polymer (phenyl/methyl vs nonyl/ethyl).

Introduction

The living cationic ring-opening polymerization of 2-oxazolines represents one key strategy for the preparation of well-defined polymers with narrow average molecular weight distributions.[1−4] A large number of differently substituted 2-oxazolines can be conveniently synthesized by the reaction of 2-aminoethanol with nitriles,[5,6] and, consequently, the properties of the corresponding polymers can be fine-tuned by the selection of an appropriately substituted monomer. Furthermore, by a combination of a hydrophilic block [like poly(2-ethyl-2-oxazoline)] and a hydrophobic block [like poly(2-nonyl-2-oxazoline)], also amphiphilic block copoly(2-oxazoline)s can be obtained (Scheme 1).[4,7,8] In aqueous solution, these block copolymers will aggregate into micelles which may be utilized in applications as diverse as micellar catalysis, drug delivery, or hydrogels.[9−16]

Widespread industrial applications of poly(2-oxazoline)s, however, have not been realized so far, as the polymerizations normally require reaction times in the range from several hours up to several days. Recently, we were able to successfully perform the living cationic ring-opening polymerization of four differently substituted 2-oxazolines, namely 2-methyl-, 2-ethyl-, 2-nonyl-, and 2-phenyl-2-oxazoline,[17−20] in a single-mode microwave reactor (Emrys Liberator, Biotage).[21] As a consequence of the facilitated access to high-temperature and high-pressure syntheses (compared to reactors that are operated with conventional heating), concomitant with the uniform and noncontact heating provided by the microwave irradiation, the polymerizations were accelerated by factors of up to 400 (compared to conventional reflux conditions), while the livingness of the polymerization and the first-order kinetics of the monomer consumption were maintained. Side reactions, like chain-transfer and subsequent chain-coupling reactions that often occur upon the polymerization of 2-oxazolines,[22] were found to be kept at a minimum if the polymerization was performed in acetonitrile at 140 °C (superheated conditions); the average molecular weight distributions of the corresponding polymers were very narrow (indicated by polydispersity indices well below 1.20). These observations, however, might not be ascribed to so-called (nonthermal) microwave effects[21] but to the fact that the polymerizations were performed at (relatively) high temperatures; reference experiments with conductive heating in acetonitrile (in pressurized reactors)[17] or in high-boiling solvents (like γ-butyrolactone)[22] exhibited similar reaction kinetics.

Like the homo poly(2-oxazoline)s, also block copoly(2-oxazoline)s and block copolymers containing poly(2-oxazoline) segments have been in the focus of many investigations.[23−29] In the present study, we have expanded the microwave-assisted polymerization of 2-oxazolines to the preparation of chain-extended homo poly(2-oxazoline)s and diblock copoly(2-oxazolines) (composed of 50 + 50 monomers), utilizing the abovementioned four monomers 2-methyl-, 2-ethyl-, 2-nonyl-, and 2-phenyl-2-oxazoline (Table 1). The thus-obtained collection of compounds is the first example of a library of polymers that were prepared under microwave irradiation and, from this point of view, proves the feasibility of using nonconductive heating for the synthesis of a systematically varied set of polymers with narrow average molecular weight distributions (a publication describing the preparation of (exclusively) amphiphilic diblock copoly(2-oxazoline)s with conventional heating in pressurized reactors is currently in preparation).[30] The $4^2 = 16$-membered library was subsequently characterized by means of GPC, NMR, TGA, and DSC. The measurement of contact angles (for the calculation of surface energies) of spin-coated films of these 16 polymers has been recently described as part of a publication

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Scheme 1. Mechanism for the Stepwise Preparation of the $Et_{50}Non_{50}$ Block Copolymer from the Cationic Ring-Opening Polymerization of 2-Ethyl- and 2-Nonyl-2-oxazoline, Initiated by Methyl Tosylate

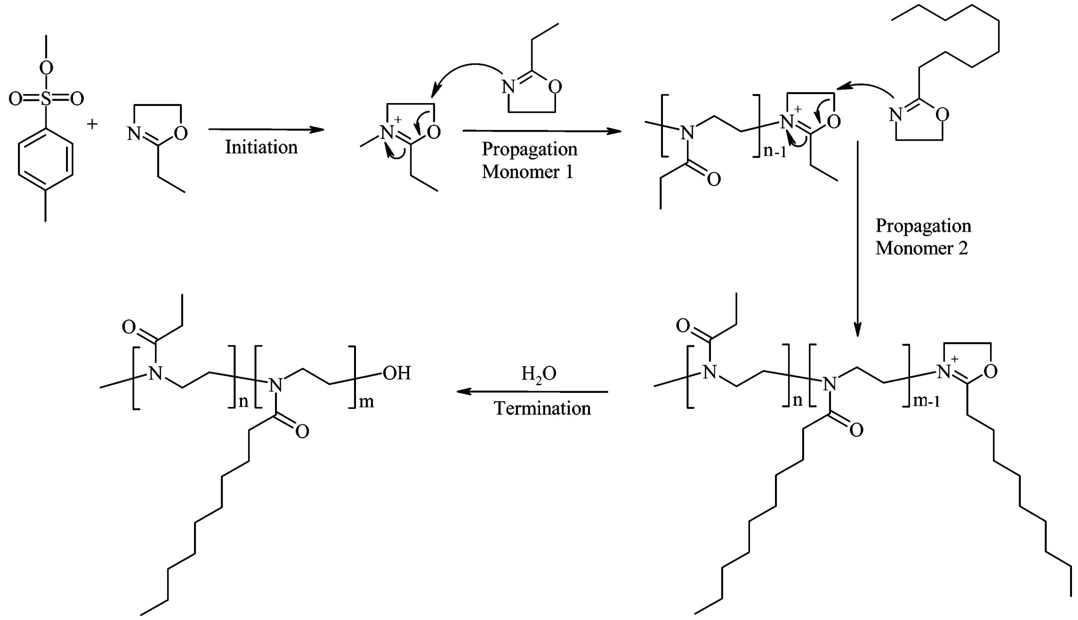
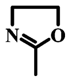
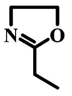
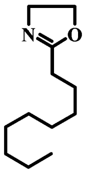
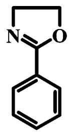


Table 1. Overview of the Four Monomers Used for the Synthesis of a 16-Membered Library of 12 Diblock Copolymers and Four Chain-Extended Homopolymers[a]

				
Name	2-methyl-2-oxazoline	2-ethyl-2-oxazoline	2-nonyl-2-oxazoline	2-phenyl-2-oxazoline
Abbreviation	Me	Et	Non	Phe
M [g mol^{-1}]	85.11	99.14	197.32	147.18
E_A [kJ mol^{-1}]	75.4 ± 0.5	73.4 ± 0.5	76.3 ± 0.5	84.4 ± 0.5
f [10^8 L mol^{-1} s^{-1}]	5.00 ± 1.20	1.99 ± 0.85	7.58 ± 1.15	14.9 ± 2.8

[a] For the activation energies and frequency factors, cf. ref 19. M: molar mass. E_A: activation energy. *f*: frequency factor.

on the automated determination of surface energies (for the surface energies of poly(2-oxazoline)s, see also refs 24–27).[20]

Results and Discussion

Synthesis of the Chain-Extended Homopolymers and Diblock Copolymers. For the synthesis of the 16-membered library of chain-extended poly(2-oxazoline)s and diblock copoly(2-oxazoline)s from the four monomers 2-methyl-, 2-ethyl-, 2-nonyl- and 2-phenyl-2-oxazoline (Table 1), several findings from precedent studies were taken into account:[17,19] (i) The microwave-assisted polymerizations were performed in acetonitrile at 140 °C, as these conditions had proven to provide polymers with low polydispersity indices. (ii) To ensure a comparable weight percentage of the (first) monomer in solution, the initial concentrations of the (first) monomers were adapted to the corresponding molar masses (Table 1): $[\text{2-methyl-2-oxazoline}]_0 = [\text{2-ethyl-2-oxazoline}]_0 = 4$ M; $[\text{2-nonyl-2-oxazoline}]_0 = 2$ M, and $[\text{2-phenyl-2-oxazoline}]_0 = 3$ M. (iii) In the case of 2-methyl- and 2-nonyl-2-oxazoline, the number of 100 monomer units per polymer chain had turned out to be the upper limit for the preparation of polymers with polydispersity indices below 1.20 (2-ethyl- and 2-phenyl-2-oxazoline: upper limit of 300 monomers per polymer chain). Consequently, we prepared polymer blocks that were composed of 50 monomers, and, in final consequence, synthesized chain-extended polymers and diblock copolymers (composed of 100 monomers each) that still exhibited low polydispersity indices.

For the living cationic ring-opening polymerizations themselves, stock solutions containing the first monomer, the initiator methyl tosylate (monomer:initiator

Table 2. Reaction Times for the Preparation of the Diblock Copoly(2-oxazoline)s[a]

	second monomer			
first monomer	2-methyl-2-oxazoline	2-ethyl-2-oxazoline	2-nonyl-2-oxazoline	2-phenyl-2-oxazoline
2-methyl-2-oxazoline	4 M 400 s + 400 s	4 M 400 s + 500 s	4 M 400 s + 400 s	4 M 400 s + 1800 s
2-ethyl-2-oxazoline	4 M 500 s + 400 s	4 M 500 s + 500 s	4 M 500 s + 400 s	4 M 500 s + 1800 s
2-nonyl-2-oxazoline	2M 800 s + 800 s	2M 800 s + 1000 s	2 M 800 s + 800 s	2 M 800 s + 3600 s
2-phenyl-2-oxazoline	3 M 2400 s + 600 s	3 M 2400 s + 800 s	3 M 2400 s + 600 s	3 M 2400 s + 2400 s

[a] In each cell, the corresponding entries indicate the initial concentration of the first monomer (first line), and the reaction times for the polymerization of the first and the second monomer, respectively (second line). For the reaction times, see ref 19.

Table 3. Number-Average Molecular Weights and Polydispersity Indices for the Mono Block and Chain-Extended Poly(2-oxazoline)s

polymer	M_n (kDa) [theoretical value after 100% conversion][a]	M_n (kDa) [measured GPC values][a]	PDI
Me$_{50}$[b]	4.3	4.0	1.10
Me$_{50}$Me$_{50}$[b]	8.5	6.3	1.16
Et$_{50}$[c]	5.0	4.8	1.08
Et$_{50}$Et$_{50}$[c]	10.0	9.5	1.12
Non$_{50}$[c]	9.9	9.2	1.10
Non$_{50}$Non$_{50}$[c]	19.8	16.1	1.14
Phe$_{50}$[c]	7.4	7.2	1.13
Phe$_{50}$Phe$_{50}$[c]	14.7	12.0	1.27

[a] In a precedent kinetic study, it has been shown by MALDI−TOF−MS comparison experiments that the selected calibrations indicated too low molecular weights for higher polymerization degrees.[19] [b] Measurements utilizing a *N*,*N*-dimethylformamide solution (with 5×10^{-3} M NH_4PF_6) as eluent (PEG or PMMA calibration). [c] Measurements using a chloroform:triethylamine:2-propanol (94:4:2) mixture as eluent (PS calibration).

ratio of 50:1) and the solvent acetonitrile were prepared. Each of the stock solutions was divided over six vials (two vials for a reproducibility test of the synthesis of the first block, and four vials for the synthesis of the corresponding chain-extended polymers and diblock copolymers) and irradiated at 140 °C for the appropriate times (Table 2). [The reaction times for completion of the polymerization (as indicated in Table 2) were calculated from the reaction rate constants that were determined in a precedent kinetic study).[19]] The vials were subsequently retransferred to an inert atmosphere of argon. The second monomer was added (without any additional solvent), and the vials were irradiated for the second time (cf. Table 2). This procedure was also followed for the diblock copolymers that contained a poly(2-nonyl-2-oxazoline) block as first block, despite of the insolubility of that polymer in acetonitrile at room temperature.[19]

The total (net) reaction times (Table 2) depend on the initial concentration of the initiator and the type of monomer to be polymerized;[19] they span the range of 13.3 min (for the combinations Me$_{50}$Me$_{50}$ and Me$_{50}$Non$_{50}$) to 80 min (for the chain-extended Phe$_{50}$Phe$_{50}$). In fact, reaction times of less than 30 min are required for any polymer that does not contain a poly(2-phenyl-2-oxazoline) block, whereas the polymers that contain a poly(2-phenyl-2-oxazoline) block require reaction times of more than 30 min in general. This is due to the +M-stabilization of the propagating species in the case of 2-phenyl-2-oxazoline that renders this monomer less active than the other three congeners and therefore requires longer reaction times for the completion of the polymerization. Nevertheless, compared to conventional heating, the polymerizations were significantly accelerated by factors of up to 40 under the applied conditions (compared to reflux conditions with conventional heating), and the synthesis of the whole library of compounds takes less than 1 day (20.4 h of net polymerization time). Depending on the respective monomers' molar masses, the molecular weights of the diblock copolymers span a range from 8.5 kDa (Me$_{50}$Me$_{50}$) to 19.7 kDa (Non$_{50}$Non$_{50}$).

Analysis by Means of GPC and NMR. For the analysis of the polymers by means of GPC, in principle two systems (operating with chloroform or *N*,*N*-dimethylformamide as eluents) were available. However, polymers that contained a poly(2-methyl-2-oxazoline) block showed strong interactions with the conventional column material (cross-linked polystyrene) in the case of the GPC system with chloroform as eluent and therefore could only be measured on a system with *N*,*N*-dimethylformamide as eluent. Polymers that contained a poly(2-nonyl-2-oxazoline) block, on the other hand, were measured exclusively on the system operated with chloroform due to their insolubility in *N*,*N*-dimethylformamide. Consequently, the polymers Me$_{50}$Non$_{50}$ and Non$_{50}$Me$_{50}$ could not be measured reliably on either of the systems; also measurements in THF were not possible as a consequence of the insolubility of these two diblock copolymers in that solvent. To obtain some information on the distribution of the average molecular weights of these two diblock copolymers, they were remeasured with a solvent mixture of chloroform:triethylamine:2-propanol = 80:10:10. Using this solvent mixture, interactions of the poly(2-methyl-2-oxazoline) block with the column material were kept at a minimum, and the PDI values could be estimated to be approximately 1.10 for Me$_{50}$Non$_{50}$ and approximately 1.60 for Non$_{50}$Me$_{50}$, respectively. Thus, the Non/Me combinations showed the same characteristics like the Non/Et combinations (see below).

The polymers that did not contain a poly(2-nonyl-) or a poly(2-methyl-2-oxazoline) block were suited for an analysis on both systems. By means of GPC, the molecular weights could be determined reliably only for the monoblock and chain-extended poly(2-oxazoline)s; the corresponding values are summarized in Table 3. The thus-obtained number-average molecular weights for the chain-extended poly(2-oxazoline)s, however, were found to be too low in general. This observation had been already reported in a precedent kinetic study,[19] in which it had been shown by MALDI−TOF−MS comparison experiments, that the as-synthesized polymers revealed the targeted molecular weights, despite of the too low molecular weights that were obtained from GPC measurements. The synthesis of the first block could be performed with good reproducibility in the case of the four monomers (Table 3, Figure 1). For

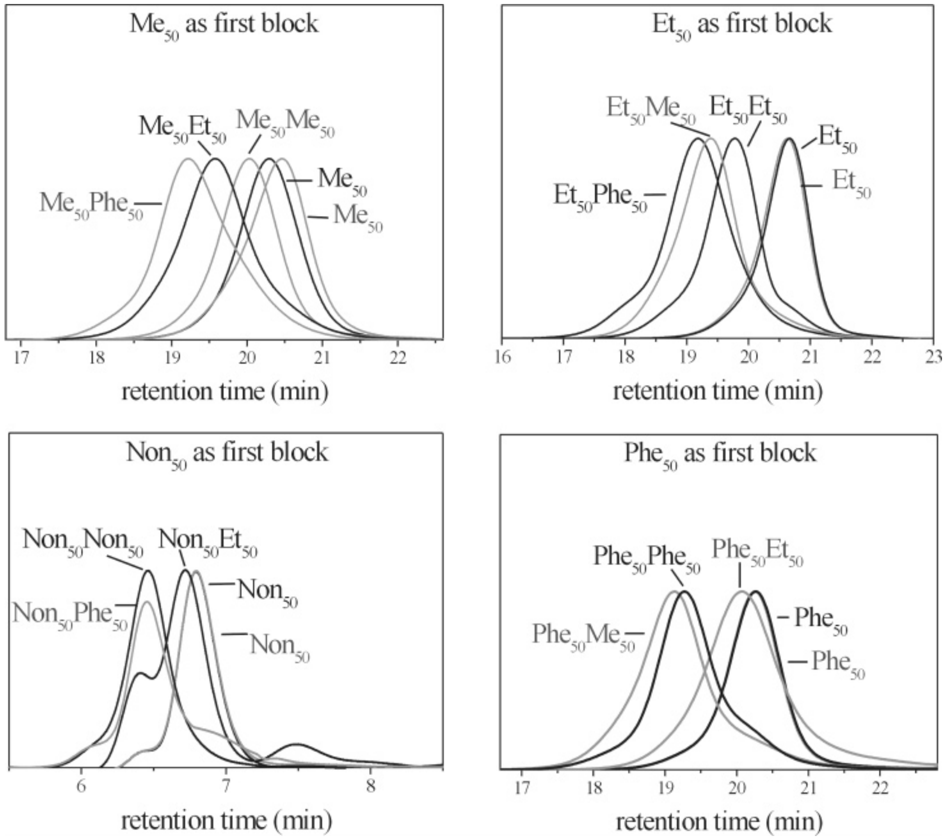


Figure 1. Selected GPC traces of the set of 16 chain-extended and diblock copoly(2-oxazoline)s, obtained from measurements in *N*,*N*-dimethylformamide (except for the ones with Non_{50} as first block: measurements in chloroform). The compounds $Et_{50}Non_{50}$ and $Phe_{50}Non_{50}$ could be measured solely in chloroform (not shown; cf. Table 4). $Me_{50}Non_{50}$ and $Non_{50}Me_{50}$ could not be measured in either of the systems available (cf. text). For the trace of the polymer $Non_{50}Et_{50}$, cf. text.

Table 4. (Theoretical) Number-Average Molecular Weights (M_n^{th}) and Polydispersity Indices for the Four Chain-Extended and the 12 Diblock Copoly(2-oxazoline)s[a]

	second monomer			
first monomer	2-methyl-2-oxazoline	2-ethyl-2-oxazoline	2-nonyl-2-oxazoline	2-phenyl-2-oxazoline
2-methyl-2-oxazoline	M_n^{th} = 8.5 kDa PDI: - - -/1.16	M_n^{th} = 9.2 kDa PDI: - - -/1.17	M_n^{th} = 14.2 kDa PDI: - - -/- - -	M_n^{th} = 11.6 kDa PDI: - - -/1.25
2-ethyl-2-oxazoline	M_n^{th} = 9.2 kDa PDI: - - -/1.18	M_n^{th} = 9.9 kDa PDI: 1.12/1.16	M_n^{th} = 14.8 kDa PDI: 1.15/- - -	M_n^{th} = 12.3 kDa PDI: 1.27/1.19
2-nonyl-2-oxazoline	M_n^{th} = 14.2 kDa PDI: - - -/- - -	M_n^{th} = 14.8 kDa PDI: 1.64/- - -	M_n^{th} = 19.7 kDa PDI: 1.14/- - -	M_n^{th} = 17.2 kDa PDI: 1.24/- - -
2-phenyl-2-oxazoline	M_n^{th} = 11.6 kDa PDI: - - -/1.18	M_n^{th} = 12.3 kDa PDI: 1.35/1.19	M_n^{th} = 17.2 kDa PDI: 1.28/- - -	M_n^{th} = 14.7 kDa PDI: 1.27/1.16

[a] In each cell, the first (second) entry for the polydispersity indices results from measurements in chloroform (*N*,*N*-dimethylformamide).

the diblock copoly(2-oxazoline)s, on the other hand, the calibrations available (PMMA, PS, PEG) were found to be inaccurate in terms of determining the average molecular weights. Moreover, the folding behavior of the different diblock copolymers significantly influenced the hydrodynamic volume and, consequently, the observed average molecular weights. The polydispersity indices calculated from the corresponding traces, however, were regarded as a measure for the narrowness of the average molecular weight distributions (Table 4). With the exception of $Non_{50}Et_{50}$ (and $Non_{50}Me_{50}$), they were found to be lower than 1.30. So, 10 of the 16 polymers exhibited polydispersity indices well below 1.20, indicative of the desired narrow average molecular weight distributions. However, these (low) values still show some deviation from polydispersity indices very close to 1.00 which have been reported for poly(2-isobutyloxazoline)s that were prepared utilizing a specially synthesized initiator.[31] This might refer to the fact that, for the polymerizations presented herein, the polymerization rate constant might be larger than the initiation rate constant.[32,33] In fact, it has been shown for the polymerizations of 2-methyl- and 2-phenyl-2-oxazoline that the polymerization rate constant increases faster than the initiation rate constant if the reaction temperature is sufficiently high.[34,35] For the polymerization of 2-phenyl-2-oxazoline, for example, it could be shown that the polymerization rate constant is lower/higher than the initiation rate constant if the polymerization is performed at temperatures lower/higher than 100 °C.[35]

The number of monomer units incorporated into the diblock copoly(2-oxazoline)s could be obtained only from the calculation of the ratios of the two types of monomers in the polymer chain (determined by ^1H NMR spectroscopy), concomitant with the knowledge that the first block was composed of 50 monomer units (determined by GPC) (Table 5); the initiating methyl group

Table 5. Ratios of the Different Monomers in the 12 Diblock Copoly(2-oxazoline)s (Obtained by ^{1}H NMR Measurements)[a]

	second monomer			
first monomer	2-methyl-2-oxazoline	2-ethyl-2-oxazoline	2-nonyl-2-oxazoline	2-phenyl-2-oxazoline
2-methyl-2-oxazoline		50:49	50:52	50:52
2-ethyl-2-oxazoline	50:50		50:50	50:52
2-nonyl-2-oxazoline	50:50	50:46		50:45
2-phenyl-2-oxazoline	50:48	50:46	50:50	

[a] The value for the first monomer was set to 50 (cf. Table 3).

could not be reliably integrated in the respective ^{1}H NMR spectra due to the partial (or complete) overlap of that signal with the signals that represented the $=N-CH_2-$ groups of the polymers' backbones. By the combined GPC and ^{1}H NMR analyses, the polymers' chain lengths where shown to be in the range of 95 to 102 monomers, indicating only slight deviations from the desired number of 100 monomers per polymer chain.

A pronounced deviation from the narrow polydispersity indices became observable in the case of $Non_{50}Et_{50}$ (PDI = 1.64; Table 4) and $Non_{50}Me_{50}$ (see above). The formation of both, a shoulder of the corresponding GPC trace (see Figure 1) in the region of (comparably) short retention times (high-molecular weights) as well as the formation of a polymer with a longer retention time (a lower molecular weight) than the one for the first block (Non_{50}), were assumed to originate from chain-transfer reactions and subsequent chain-coupling (Scheme 2).[22] This side reaction is known to significantly increase the polydispersity indices of polymers that were synthesized under living conditions[36] (as it is known from impurities that turn growing polymer chains into so-called "dead ends").[37] Taking $Non_{50}Et_{50}$ as an example, this side reaction is initiated by the abstraction of a proton from the α-carbon atom of the propagating species, $\mathbf{P}_1{}^+$, by the nitrogen atom of a monomer, **Et**. Consequently, a positively charged monomer cation, $\mathbf{Et}^+$, and a noncharged polymer with a C=C double-bond, $\mathbf{P}_1{}^=$, is formed. The noncharged polymer, $\mathbf{P}_1{}^=$, subsequently reacts with the monomer cation, $\mathbf{Et}^+$, (reversible proton exchange) or with another growing polymer chain to form the positively charged polymer, $\mathbf{P}_{1-1}{}^+$. The three types of cations may act as propagating species in the polymerization, and, consequently, the intended preparation of a diblock copoly(2-oxazoline) (starting from $\mathbf{P}_1{}^+$) as well as the formation of a high- and a low-molecular weight polymer (starting from $\mathbf{P}_{1-1}{}^+$ and $\mathbf{Et}^+$, respectively) become observable.

Evidence for this hypothesis could be derived from the analysis of two different fractions, **F1** and **F2**, obtained from a GPC fractionation experiment of $Non_{50}Et_{50}$ (Figure 2). By means of ^{1}H NMR, it could be shown that the fraction **F1** [representing the intended preparation of a diblock copoly(2-oxazoline)] contained polymers with a 2-nonyl-2-oxazoline:2-ethyl-2-oxazoline ratio of 50:53. The low-molecular weight fraction **F2**, on the other hand, solely contained poly(2-ethyl-2-oxazoline), the chain-growth of which started from $\mathbf{Et}^+$ (admittedly, as a consequence of the partial overlap of the two fractions (cf. Figure 2), a 2-nonyl-2-oxazoline:2-ethyl-2-oxazoline ratio of 18:1 became discernible in the ^{1}H NMR spectra). The corresponding IR spectra confirm these findings and exhibit that the low-molecular weight fraction **F2** solely contains poly(2-ethyl-2-oxazoline), while the fraction **F1** contains a block copolymer that is composed of poly(2-nonyl-2-oxazoline) and poly(2-ethyl-2-oxazoline).

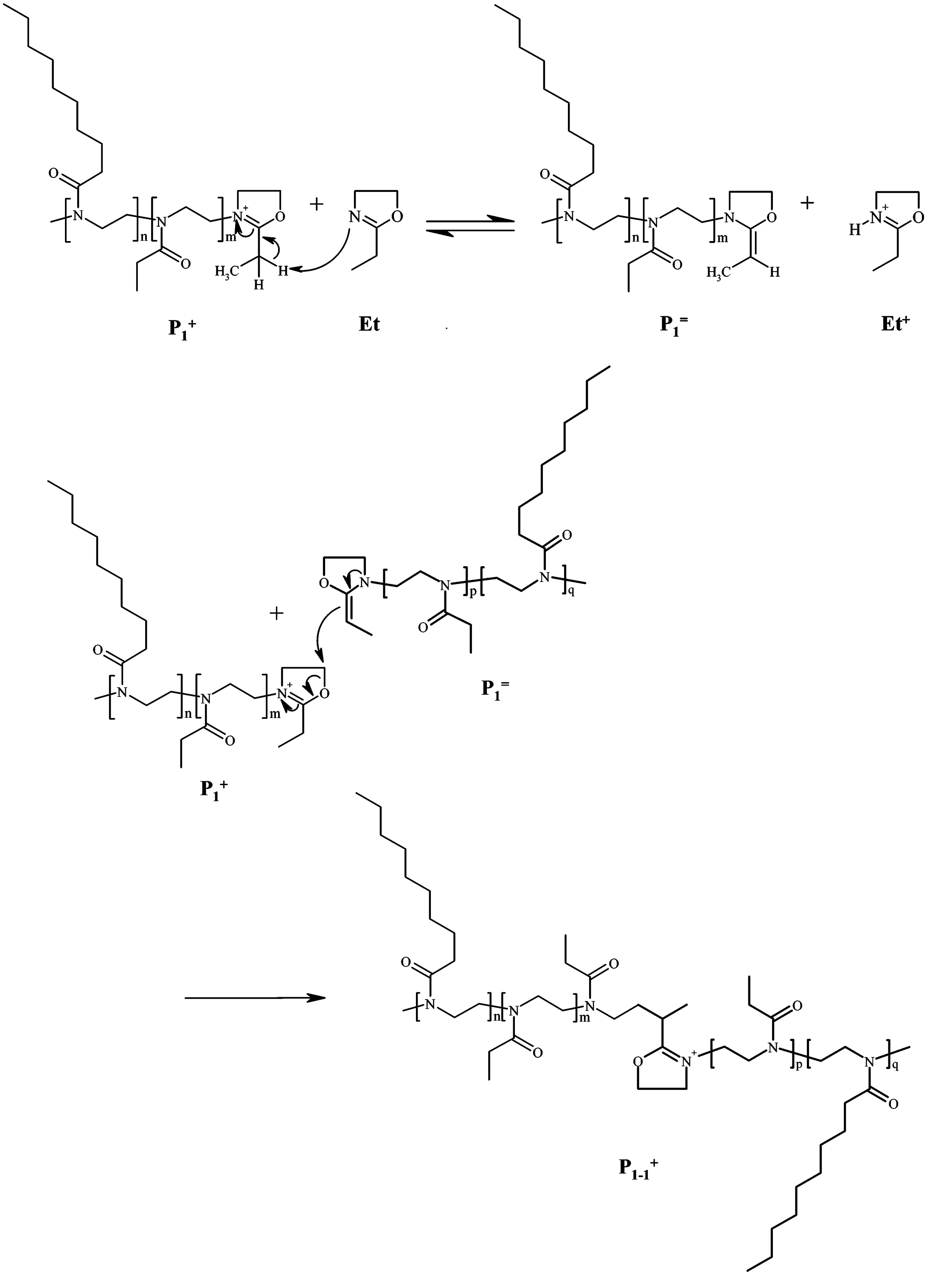
The occurrence of chain-transfer reactions and subsequent chain-coupling has been reported for a large number of 2-oxazolines. In the present study, we observed these side reactions to a high degree in the case of $Non_{50}Et_{50}$ and $Non_{50}Me_{50}$ and to a significantly lower degree in the case of $Et_{50}Et_{50}$ and $Non_{50}Phe_{50}$ (cf. Figure 1). The difficulties of the synthesis of $Non_{50}Et_{50}$ and $Non_{50}Me_{50}$ are still under investigation; we have found this side reaction to occur invariably upon the addition of 2-ethyl-2-oxazoline to the growing chain of poly(2-nonyl-2-oxazoline). However, the extent of the side reaction varies with the experimental parameters, like the shape of the reactor or the volume of the reaction liquor (Figure 3). The origin of this phenomenon is unknown; apart from the probability that the onset of the side reactions occurs rather randomly, we also assume that the different shapes of the reactors influence the velocity of the melting of the poly(2-nonyl-2-oxazoline) and thereby also contribute to the different extents of the occurrence of side reactions.

Thermal Analysis. The thermal stability of the set of chain-extended homo and diblock copoly(2-oxazoline)s was determined by thermogravimetric analysis in the range from 30 to 500 °C. The polymers that contained a hydrophilic block revealed a weight loss of approximately 10% at around 100 °C due to the loss of water; the polymers that contained a (hydrophobic) block of poly(2-nonyl-2-oxazoline) exhibited a weight loss of only approximately 1%. All polymers were stable up to temperatures of (at least) 300 °C (Figure 4). In fact, the temperatures after 5% of degradation span a relatively broad range from 308 to 371 °C. All polymers degraded in one step, and the temperatures at the inflection point ranged from 393 to 437 °C. The high thermal stability is notably worth mentioning as copolymers composed of blocks of poly(2-oxazoline)s and poly(β-methyl hydrogen itaconate) or poly(*N*-phenylmaleimide) were reported to undergo degradation at temperatures lower than 200 °C.[38−39]

The glass-transition temperature (T_g) is commonly considered as a measure for the chain mobility of a polymer: the higher the glass-transition temperature, the lower the chain mobility.[40] Consequently, for this set of 16 polymers, any differences in chain mobility and glass-transition temperatures originate from the different substituents attached to the $[-CH_2-CH_2-N(CO)-]$ backbone. A systematically varied set of diblock copoly(2-oxazoline)s has previously not been thermally characterized; in the literature, glass-transition temperatures have been reported only for three of the four homo polymers, namely poly(2-methyl-2-oxazoline) (82 and 80 °C, respectively),[41,42] poly(2-ethyl-2-oxazoline) (70 and 61 °C, respectively),[42,43] and poly(2-phenyl-2-oxazoline) (105 and 103 °C, respectively).[42,44] Poly(2-nonyl-2-oxazoline) has been reported not to show any glass-transition temperature.[44] A melting point has been determined (by means of DSC) only in the case of poly(2-nonyl-2-oxazoline) (151 °C).[44]

The findings in the course of the differential scanning calorimetry of the present library of 16 polymers were

Scheme 2. Mechanism of the Chain-Transfer Reaction and the Subsequent Chain Coupling That Occur during the Synthesis of the Diblock Copolymer Non$_{50}$Et$_{50}$[22] [a]



[a] The two cationic species Et$^+$ (from the chain-transfer reaction) and P$_{1-1}^+$ (from the chain-coupling reaction) may act as propagating species in the subsequently continued polymerization and cause the formation of a high- and a low-molecular weight fraction (cf. Figure 1), apart from the (desired) continued polymerization.

found to be in good agreement with the literature data for the four (chain-extended) homo polymers: poly(2-methyl-2-oxazoline) (T_g = 78.7 ± 2.1 °C), poly(2-ethyl-2-oxazoline) (T_g = 59.3 ± 1.6 °C), poly(2-phenyl-2-oxazoline) (T_g = 106.9 ± 2.1 °C), and poly(2-nonyl-2-oxazoline) (no T_g; T_m = 147.1 °C). In fact, all polymers that contained a poly(2-nonyl-2-oxazoline) block exhibited a melting point in the narrow range from 146 to 151 °C. The glass-transition temperatures and the corresponding specific heats were measured three times for each sample (after an initial first heating run that was not considered for the subsequent calculations) in order to enable the calculation of standard deviations, which were in the range of ±3% or lower (with a few exceptions only). Except for the diblock copolymers Phe$_{50}$Non$_{50}$ and Non$_{50}$Phe$_{50}$ (and Non$_{50}$Non$_{50}$), all poly-

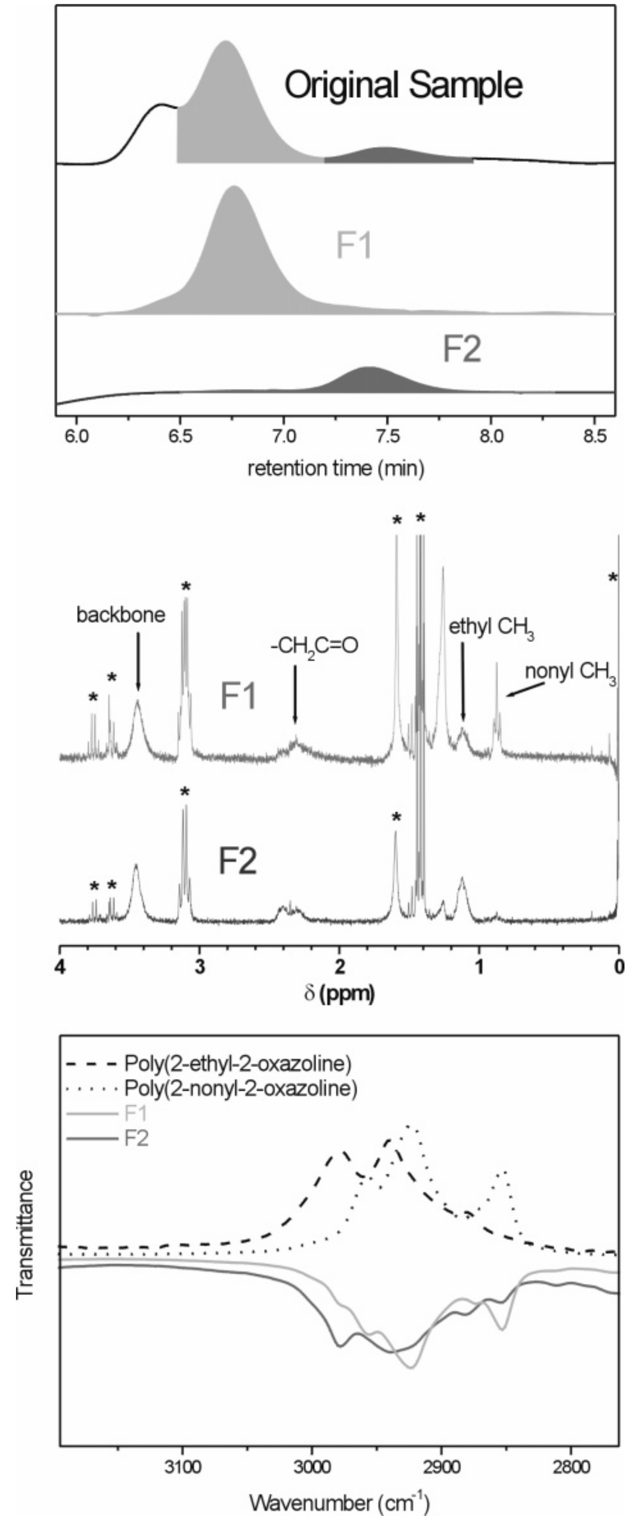


Figure 2. Fractionated GPC of the diblock copolymer $Non_{50}Et_{50}$, illustrating the molecular weight range of the two fractions **F1** and **F2** (top). Excerpts from the ^1H NMR (in $CDCl_3$; middle; the signals marked with an asterisk represent solvents from the synthesis and the subsequent GPC eluation) and IR spectra (bottom) of the two fractions, evincing that **F1** contains a polymer that is composed of 2-nonyl- and 2-ethyl-2-oxazoline in a 50:53 ratio (ratio of the signals in the ^1H NMR spectrum at 0.8 and 1.1 ppm, respectively) and that **F2** is a poly(2-ethyl-2-oxazoline) (cf. Scheme 2).

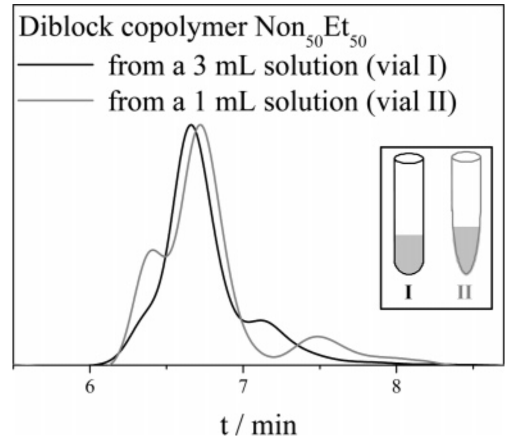


Figure 3. Influence of the volume of the reaction liquor and the shape of the reactor on the extent of side reactions during the synthesis of the diblock copolymer $Non_{50}Et_{50}$.

mers exhibited a small endotherm (glass-transition temperature); these were found to be equal (within the range of the standard deviation) for each of the pairs $X_{50}Y_{50}$ and $Y_{50}X_{50}$ (like $Me_{50}Et_{50}$ and $Et_{50}Me_{50}$) (Figure 5); even the combinations $Non_{50}Et_{50}$ and $Et_{50}Non_{50}$ as well as $Non_{50}Me_{50}$ and $Me_{50}Non_{50}$ followed this rule, despite the side reactions occurring during the synthesis of these diblock copoly(2-oxazoline)s (cf. above). A more detailed analysis of this set of 13 glass-transition temperatures showed that the five polymers that contained a poly(2-phenyl-2-oxazoline) block ($Phe_{50}Non_{50}$ and $Non_{50}Phe_{50}$ did not exhibit any glass-transition temperatures) and the chain-extended $Me_{50}Me_{50}$ homo polymer had glass-transition temperatures in the range from 80 to 110 °C, whereas the remaining seven entries (which did not contain a poly(2-phenyl-2-oxazoline) but a poly(2-ethyl-2-oxazoline) or/and a poly(2-nonyl-2-oxazoline) block) revealed glass-transition temperatures lower than 80 °C. The three combinations $Et_{50}Et_{50}$, $Non_{50}Et_{50}$, and $Et_{50}Non_{50}$, which were composed of monomers with (relatively) flexible substituents revealed the lowest glass-transition temperatures ($T_g \leq 60$ °C). Apparently, the kind of substituent greatly influences the glass-transition temperature, and rigid (flexible) substituents like phenyl or methyl (nonyl or ethyl) cause an increase (a decrease) of the glass-transition temperatures. Similar trends became observable by a careful analysis of the specific heat (Δc_p) of the glass-transition temperatures (Figure 6). The polymers that contained a poly(2-nonyl-2-oxazoline) block ($Non_{50}Non_{50}$, $Non_{50}Phe_{50}$ and $Phe_{50}Non_{50}$ did not exhibit any glass-transition temperature) had the lowest specific heats of this series ($\Delta c_p < 0.3\ J{\cdot}g^{-1}{\cdot}K^{-1}$), whereas the polymers that contained a poly(2-phenyl-2-oxazoline) block ($Non_{50}Phe_{50}$ and $Phe_{50}Non_{50}$ did not exhibit any glass-transition temperatures) revealed the highest specific heats of this series ($\Delta c_p > 0.3\ J{\cdot}g^{-1}{\cdot}K^{-1}$). To summarize, the glass-transition temperatures as well as their specific heats can be manipulated and fine-tuned by the selection of appropriately substituted monomers to be incorporated into the polymer chain.

Conclusions

Under microwave irradiation, a 16-membered library of four chain-extended homo- and 12 diblock copoly(2-oxazoline)s was prepared from four differently substituted monomers, namely 2-methyl-, 2-ethyl-, 2-nonyl-, and 2-phenyl-2-oxazoline within less than 1 day (total net reaction time). The living cationic ring-opening polymerizations were initiated by methyl tosylate and carried out under an inert atmosphere of argon in acetonitrile at 140 °C. The thus-obtained 16 compounds

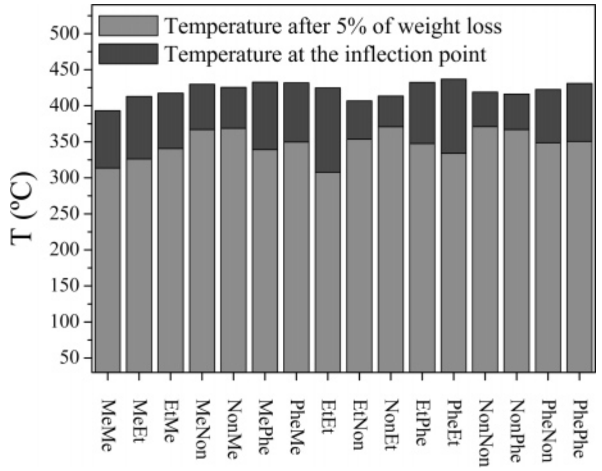


Figure 4. Thermal stability of the poly(2-oxazoline)s, determined by TGA.

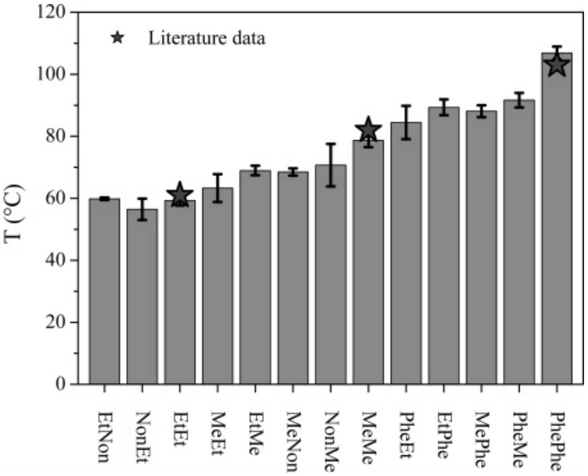


Figure 5. Glass-transition temperatures for the chain-extended and diblock copoly(2-oxazoline)s (the error bars represent the range of the standard deviation). $Non_{50}Non_{50}$, $Non_{50}Phe_{50}$ and $Phe_{50}Non_{50}$ did not exhibit a glass-transition temperature. The stars represent the literature values for $Me_{50}Me_{50}$, $Et_{50}Et_{50}$, and $Non_{50}Non_{50}$, respectively.[41-44]

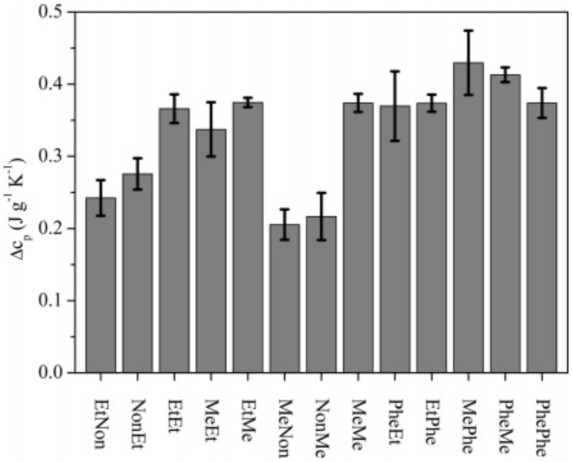


Figure 6. Specific heats of the glass-transition temperatures for the chain-extended and diblock copoly(2-oxazoline)s (the error bars represent the range of the standard deviation) (cf. Figure 5).

were composed of 100 (50 + 50) monomers; the required reaction times spanned the range from 13.3 to 80 min for the completion of the polymerization. The analysis by GPC and ^{1}H NMR revealed the successful incorporation of the desired number of monomers into well-defined polymer chains with narrow average molecular weight distributions (PDI < 1.30). Only in the case of $Non_{50}Et_{50}$ and $Non_{50}Me_{50}$ were chain-transfer reactions and subsequent chain-coupling observed as side reactions. The (selective) occurrence of this type of side reaction is still under investigation.

Thermogravimetric analysis showed that all polymers were stable up to temperatures of 300 °C (or even higher). The melting points and mobilities of the polymer chains were measured by DSC. All polymers that contained a poly(2-nonyl-2-oxazoline) block showed a melting point in the range from 146 to 151 °C. Except for $Non_{50}Non_{50}$, $Non_{50}Phe_{50}$, and $Phe_{50}Non_{50}$ (which did not show any glass-transition temperatures), the poly(2-oxazoline)s exhibited glass-transition temperatures in the range from 56.5 to 106.9 °C. The polymers that contained a poly(2-phenyl-2-oxazoline) block as well as the chain-extended $Me_{50}Me_{50}$ homo polymer had glass-transition temperatures higher than 80 °C, while the polymers that contained a poly(2-ethyl-2-oxazoline)- or/and a poly(2-nonyl-2-oxazoline) block) revealed glass-transition temperatures lower than 80 °C. Analogous observations were made concerning the specific heat (Δc_p) of the glass-transition temperatures. Thus, the properties of the well-defined polymers (with narrow average molecular weight distributions) can be designed by the selection of well-suited substituents to the corresponding 2-oxazoline heterocycle(s). The mechanical properties of these 16 compounds are currently investigated.

Experimental Part

Materials and Instrumentation. All chemicals, except for acetonitrile (Biosolve LTD), were purchased from Aldrich; 2-nonyl- and 2-phenyl-2-oxazoline were kind gifts from Henkel (Germany). Methyl tosylate and the 2-oxazolines were distilled prior to use (the latter over barium oxide) and stored under argon. Acetonitrile was dried over molecular sieves (3 Å).

The polymerizations were performed in capped reaction vials in the single-mode microwave reactor Emrys Liberator (Biotage), equipped with a noninvasive IR sensor (accuracy: ± 2%) for the measurement of the reaction temperatures. Prior to use, the vials were heated, allowed to cool to room temperature and filled with argon. The polymerizations were terminated by quenching the reaction mixtures with water after the incorporation of the second monomer into the polymer chain.

Gel permeation chromatography (GPC) was measured either on a Shimadzu system with a SCL-10A system controller, a LC-10AD pump, a RID-10A refractive index detector, and a PLgel 5 μm Mixed-D column using a chloroform:triethylamine: 2-propanol (94:4:2) mixture as eluent at a flow rate of 1 mL·min^{-1} at 50 °C (PS calibration) or on a Waters system with a 1515 pump, a 2414 refractive index detector, and a Waters Styragel HT4 column utilizing a *N*,*N*-dimethylformamide solution (with 5×10^{-3} M NH_4PF_6) with a flow rate of 0.5 mL·min^{-1} at 50 °C (PEG or PMMA calibration), respectively. ^{1}H NMR spectra were recorded on a Varian AM-400 spectrometer or a Varian Gemini 300 spectrometer from polymer solutions in d_3-chloroform (reference: TMS). For the differential scanning calorimetry and the thermogravimetric analyses, samples of approximately 10 mg were used for the corresponding measurements. The compounds were dried in a vacuum oven at 40 °C for 24 h prior to use. Thermogravimetric analyses were performed in a TG 209 F1 Iris by Netzsch under a nitrogen atmosphere in the range from 30 to 500 °C with a heating rate of 20 K·min^{-1}. Thermal transitions were determined on a DSC 204 F1 Phoenix by Netzsch under a nitrogen atmosphere with heating and cooling rates of 40 K·min^{-1} (three measurements per sample after an initial first heating run that was not considered for the subsequent calculations); melting points (in the case of the polymers that contained a poly(2-nonyl-2-oxazoline) block) were measured with a heating rate of 10 $K\cdot min^{-1}$ and a cooling rate of 40 $K\cdot min^{-1}$.

FT-IR spectra were recorded on a Bruker Tensor 37 with HTS-XT extension. Samples were prepared on silicone microtiter plates by solution drop-casting and subsequent solvent evaporation by an inert gas flow.

Microwave-Assisted Preparation of the Diblock Copoly(2-oxazoline)s. All polymerizations were carried out in acetonitrile at 140 °C. For the synthesis of the first block, solutions (2 mL) with the hereinafter cited initial concentration of the initiator and monomers were used: $[\text{2-methyl-2-oxazoline}]_0 = [\text{2-ethyl-2-oxazoline}]_0 = 4$ M; $[\text{2-nonyl-2-oxazoline}]_0 = 2$ M, and $[\text{2-phenyl-2-oxazoline}]_0 = 3$ M. The polymerizations were initiated by methyl tosylate, ratio [monomer]:[initiator] = 50:1. These abovementioned conditions had proven success in a precedent kinetic study.[17,19] After the polymerization of the first monomer (for the reaction times, see Table 2), the vials were retransferred to an inert atmosphere of argon, and the second monomer was added. The solution was again heated in the microwave reactor (for the reaction times, see Table 2), and quenched with water.

^{1}H NMR Measurements of the Block Copoly(2-oxazoline)s (in d_3-Chloroform/TMS). $Me_{50}Et_{50}$: $\delta = 1.1$ (s, br, 192 ($150 + x$) H, $=N-C(O)-CH_2-C\mathbf{H}_3$ and impurity); 1.9 (s, CH_3CN); 2.1 (s, br, 119 (100) H, $=N-C(O)-C\mathbf{H}_2-CH_3$); 2.3 (m, br, 153 (150) H, $=N-C(O)-C\mathbf{H}_3$); 3.5 (s, br, 400 (200+200) H, $=N-(C\mathbf{H}_2)_2-N=$); 7.26 (s, $C\mathbf{H}Cl_3$). $Me_{50}Non_{50}$: $\delta = 0.9$ (m, br, 166 (150) H, $=N-C(O)-CH_2-CH_2-(CH_2)_6-C\mathbf{H}_3$); 1.3 (s, br, 710 (600) H, $=N-C(O)-CH_2-CH_2-(C\mathbf{H}_2)_6-CH_3$); 1.6 (s, br, 92 (100) H, $=N-C(O)-CH_2-C\mathbf{H}_2-(CH_2)_6-CH_3$); 2.0−2.2 (m, br, 161 (150) H, $=N-C(O)-C\mathbf{H}_3$); 2.3 (m, br, 115 (100) H, $=N-C(O)-C\mathbf{H}_2-CH_2-(CH_2)_6-CH_3$); 3.5 (m, br, 400 (200+200) H, $=N-(C\mathbf{H}_2)_2-N=$); 7.26 (s, $C\mathbf{H}Cl_3$). $Me_{50}Phe_{50}$: $\delta = 1.8-2.4$ (m, br, 393 ($150 + x$) H, $=N-C(O)-C\mathbf{H}_3$, CH_3CN); 2.8−3.6 (s, br, 400 (200+200) H, $=N-(C\mathbf{H}_2)_2-N=$); 6.8−7.4 (m, br, 262 ($250 + x$), $=N-C(O)-C_6\mathbf{H}_5$ and $C\mathbf{H}Cl_3$). $Et_{50}Me_{50}$: $\delta = 1.1$ (s, br, 150 (150) H, $=N-C(O)-CH_2-C\mathbf{H}_3$); 1.75 (s, CH_3CN); 2.1 (m, br, 170 (150) H, $=N-C(O)-C\mathbf{H}_3$); 2.3 (s, br, 95 (100) H, $=N-C(O)-C\mathbf{H}_2-CH_3$); 3.5 (s, br, 400 (200+200) H, $=N-(C\mathbf{H}_2)_2-N=$); 7.26 (s, $C\mathbf{H}Cl_3$). $Et_{50}Non_{50}$: $\delta = 0.9$ (m, br, 150 (150) H, $=N-C(O)-CH_2-(CH_2)_7-C\mathbf{H}_3$); 1.1 (m, br, 149 (150) H, $=N-C(O)-CH_2-C\mathbf{H}_3$); 1.3 (s, br, 695 (700) H, $=N-C(O)-CH_2-(C\mathbf{H}_2)_7-CH_3$); 1.6 (s, CH_3CN); 2.3 (m, br, 192 (100+100) H, $=N-C(O)-C\mathbf{H}_2-(CH_2)_7-CH_3$ and $=N-C(O)-C\mathbf{H}_2-CH_3$); 3.5 (m, br, 400 (200+200) H, $=N-(C\mathbf{H}_2)_2-N=$). $Et_{50}Phe_{50}$: $\delta = 1.1$ (m, br, 133 (150) H, $=N-C(O)-CH_2-C\mathbf{H}_3$); 1.9 (s, CH_3CN); 2.3 (s, br, 95 (100) H, $=N-C(O)-C\mathbf{H}_2-CH_3$); 3.0−3.5 (s, br, 400 (200+200) H, $=N-(C\mathbf{H}_2)_2-N=$); 7.0−7.5 (m, br, 327 ($250 + x$), $=N-C(O)-C_6\mathbf{H}_5$ and $C\mathbf{H}Cl_3$). $Non_{50}Me_{50}$: $\delta = 0.9$ (m, br, 150 (150) H, $=N-C(O)-CH_2-CH_2-(CH_2)_6-C\mathbf{H}_3$); 1.3 (s, br, 600 (600) H, $=N-C(O)-CH_2-CH_2-(C\mathbf{H}_2)_6-CH_3$); 1.6 (s, br, 110 (100) H, $=N-C(O)-CH_2-C\mathbf{H}_2-(CH_2)_6-CH_3$); 2.0−2.3 (m, br, 262 (250) H, $=N-C(O)-C\mathbf{H}_3$, $=N-C(O)-C\mathbf{H}_2-CH_2-(CH_2)_6-CH_3$); 3.5 (m, br, 401 (200 + 200) H, $=N-(C\mathbf{H}_2)_2-N=$); 7.26 (s, $C\mathbf{H}Cl_3$). $Non_{50}Et_{50}$: $\delta = 0.9$ (m, br, 128 (150) H, $=N-C(O)-CH_2-(CH_2)_7-C\mathbf{H}_3$); 1.0−1.8 (m, br, 901 (850) H, $=N-C(O)-CH_2-C\mathbf{H}_3$, $=N-C(O)-CH_2-(C\mathbf{H}_2)_7-CH_3$); 2.3 (m, br, 223 (100 + 100) H, $=N-C(O)-C\mathbf{H}_2-(CH_2)_7-CH_3$ and $=N-C(O)-C\mathbf{H}_2-CH_3$); 3.5 (m, br, 400 (200+200) H, $=N-(C\mathbf{H}_2)_2-N=$). $Non_{50}Phe_{50}$: $\delta = 0.9$ (m, br, 150 (150) H, $=N-C(O)-CH_2-(CH_2)-C\mathbf{H}_3$); 1.3 (s, br, 615 (600) H, $=N-C(O)-CH_2-CH_2-(C\mathbf{H}_2)_6-CH_3$); 1.6 (s, br, 98 (100) H, $=N-C(O)-CH_2-C\mathbf{H}_2-(CH_2)_6-CH_3$); 2.3 (m, br, 124 (100) H, $=N-C(O)-C\mathbf{H}_2-CH_2-(CH_2)_6-CH_3$); 2.8−3.8 (m, br, 382 (200 + 200) H, $=N-(C\mathbf{H}_2)_2-N=$); 6.8−7.5 (m, br, 285 ($250 + x$), $=N-C(O)-C_6\mathbf{H}_5$ and $C\mathbf{H}Cl_3$). $Phe_{50}Me_{50}$: $\delta = 1.9$ (s, CH_3CN); 2.1 (m, br, 145 (150) H, $=N-C(O)-C\mathbf{H}_3$); 2.4−3.8 (m, br, 400 (200+200) H, $=N-(C\mathbf{H}_2)_2-N=$); 6.8−7.4 (m, br, 223 ($250 + x$), $=N-C(O)-C_6\mathbf{H}_5$ and $C\mathbf{H}Cl_3$). $Phe_{50}Et_{50}$: $\delta = 1.1$ (m, br, 191 (150) H, $=N-C(O)-CH_2-C\mathbf{H}_3$); 1.9 (s, CH_3CN); 2.0−2.6 (m, br, 146 (100) H, $=N-C(O)-C\mathbf{H}_2-CH_3$); 2.8−3.8 (m, br, 400 (200+200) H, $=N-(C\mathbf{H}_2)_2-N=$); 6.8−7.5 (m, br, 269 ($250 + x$), $=N-C(O)-C_6\mathbf{H}_5$ and $C\mathbf{H}Cl_3$). $Phe_{50}Non_{50}$: $\delta = 0.9$ (m, br, 159 (150) H, $=N-C(O)-CH_2-(CH_2)-C\mathbf{H}_3$); 1.3 (s, br, 622 (600) H, $=N-C(O)-CH_2-CH_2-(C\mathbf{H}_2)_6-CH_3$); 1.6 (s, br, 92 (100) H, $=N-C(O)-CH_2-C\mathbf{H}_2-(CH_2)_6-CH_3$); 2.0 (s, CH_3CN); 2.3 (m, br, 101 (100) H, $=N-C(O)-C\mathbf{H}_2-CH_2-(CH_2)_6-CH_3$); 2.8−3.8 (m, br, 400 (200+200) H, $=N-(C\mathbf{H}_2)_2-N=$); 6.8−7.5 (m, br, 286 ($250 + x$), $=N-C(O)-C_6\mathbf{H}_5$ and $C\mathbf{H}Cl_3$).

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