Investigation of the Living Cationic Ring-Opening Polymerization of 2-Methyl-, 2-Ethyl-, 2-Nonyl-, and 2-Phenyl-2-oxazoline in a Single-Mode Microwave Reactor†

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ABSTRACT: The living cationic ring-opening polymerizations of 2-methyl-, 2-ethyl-, 2-nonyl-, and 2-phenyl-2-oxazoline were performed in acetonitrile at high temperatures of up to 200 °C in a single-mode microwave reactor. Upon enhancing the reaction rates by factors of up to 400 in the range from 80 to 200 °C, the first-order kinetics of the monomer consumption and the livingness of the polymerization were maintained. As a consequence of the fast, direct, and noncontact heating by the microwave irradiation, the polymerizations could be carried out in highly concentrated solutions or even from bulk conditions, yielding well-defined polymers (PDI < 1.20). Under the conditions applied in this study, a maximum number of 300 monomers (100 in the case of 2-methyl- and 2-nonyl-2-oxazoline) could be incorporated into the polymer chains under the premise that the average molecular weight distributions remained narrow (PDI < 1.20).

Introduction

The influence of microwave irradiation on chemical reactions is of great current interest in virtually every field of chemical synthesis. Prominent examples, particularly from organic and pharmaceutical research, have successfully shown that numerous reactions experience a significant acceleration, concomitant with an increased yield and an improved purity of the targeted product(s).[1−5] However, hazardous explosions or fires are likely to accompany chemical reactions when they are performed in domestic microwave ovens. This is in particular true for exothermic reactions as well as reactions with an increasing volume (formation of gaseous byproducts). These safety uncertainties have been overcome by microwave reactors specially designed for chemical synthesis.[6,7] This new class of reactors is additionally equipped with measuring tools for temperature and pressure inside the capped reaction vessels and thereby allows for an accurate control of the corresponding reactions. Utilizing capped vials, high-pressure and high-temperature syntheses are facilitated. Furthermore, the precise knowledge of the reaction parameters allows for a careful evaluation of the existence or absence of (nonthermal) microwave effects;[1−5] for the vast majority of reactions, it was shown that these microwave effects do not occur.[8]

Consequently, research activities in the field of microwave-assisted synthesis (MAS) attract a broad audience these days. A careful analysis of the publications describing microwave-assisted polymerizations, on the other hand, shows that controlled polymerizations have been investigated only sporadically.[8] This is notably deplorable as the control over these polymerizations often results from equilibria that significantly decrease the reaction rates. Under microwave irradiation, concomitant with the high temperatures and pressures accessible, these reactions might experience a significant acceleration. Previous studies concerning the microwave assistance on controlled or living polymerizations, however, solely considered controlled-radical polymerization reactions.[8] To investigate the effects of microwave irradiation (in combination with a high-pressure and high-temperature synthesis provided by the single-mode microwave reactor) on a living ionic polymerization, we have recently investigated the living cationic ring-opening polymerization of 2-ethyl-2-oxazoline in acetonitrile, initiated by methyl tosylate (Scheme 1).[9] The investigation of the polymerization of the 2-oxazolines has begun already in 1966.[10,11] Because of the large number of differently substituted monomers available[12,13] and the potential applications of the corresponding polymers in micellar catalysis, drug delivery, or hydrogels,[13−20] numerous strategies to decrease the reaction times, which are normally in the range of 10−20 h, have been tried.[13] However, no real breakthrough and consequently no widespread industrial applications have been achieved so far. Under microwave irradiation, we found that the reaction time for the polymerization of 2-ethyl-2-oxazoline in acetonitrile could be decreased from 6 h under standard conditions (conventional heating; reflux at 82 °C) down to less than 1 min under microwave irradiation (at 200 °C), which yields an acceleration factor of 400.[9] Furthermore, side reactions were reduced to a minimum at 140 °C, which was found to be the optimum temperature for the polymerization. The polymerization maintained its livingness over the whole range of temperatures investigated (80−200 °C). The average molecular weight distributions were found to be narrow (PDI < 1.20).

Inspired by these promising first results, we performed a detailed study of the microwave-assisted polymerization of 2-oxazolines using four representative congeners, namely 2-methyl-, 2-nonyl-, and 2-phenyl-2-oxazoline in addition to the initially investigated 2-ethyl-2-oxazoline. Our investigations were subjected

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† Dedicated to Prof. Dr. Horst Kessler on the occasion of his 65th birthday.

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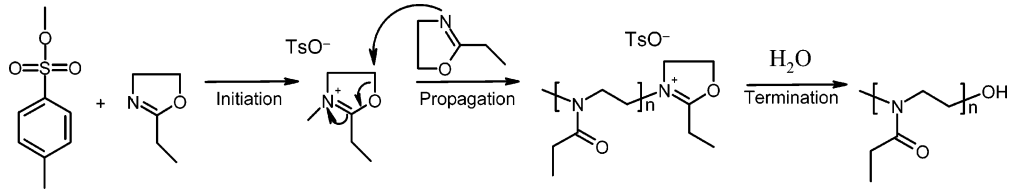
Scheme 1. Living Cationic Ring-Opening Polymerization of 2-Substituted 2-Oxazolines, Initiated by Methyl Tosylate



to the following incentives: (i) verification of the maintenance of the first-order kinetics of the monomer consumption and the livingness of the polymerization over the whole range of temperatures investigated; (ii) determination of the Arrhenius parameters (activation energy and frequency factor) for the polymerization reactions of the different monomers; (iii) identification of the maximum concentration up to which the polymers maintain narrow average molecular weight distributions; and (iv) determination of the maximum number of monomers that can be incorporated into the polymer chains (under the premise that the PDI values stay below 1.20).

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 polymerization reactions were performed in capped reaction vials specially designed for the single-mode microwave system Emrys Liberator (Biotage, formerly Personal Chemistry). These vials were heated, allowed to cool to room temperature, and filled with argon prior to use. All experiments were performed on 1 mL solutions; the specific polymerization reactions were terminated by quenching the reaction mixtures at the favored times with water. Poly(2-nonyl-2-oxazoline) was found to be insoluble in acetonitrile and was therefore dissolved in *o*-dichlorobenzene after the quenching procedure to allow a straightforward preparation of the samples.

GC measurements were performed utilizing an Interscience Trace GC with a Trace Column RTX-5 connected to a PAL autosampler. For the injection of polymerization mixtures, a special Interscience liner with additional glass wool was used. 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) at a flow rate of 0.5 mL min^{-1} at 50 °C (PEG or PMMA calibration).

Matrices and inorganic salts for the MALDI experiments were purchased from Sigma Aldrich. Analytical-grade solvents were purchased from Biosolve Ltd. The experiments were performed on a STR Biospectrometry Workstation (Applied Biosystems, Foster City, CA) time-of-flight mass spectrometer using linear mode for operation. All spectra were obtained in positive ion mode. Ionization was performed with a 337 nm pulsed nitrogen laser. All data were processed with the Data Explorer software package (Applied Biosystems). Samples were prepared using a multiple-layer spotting approach. Generally, the different layers (polymer, matrix, and salt additive) were applied to the MALDI sample target on top of the previous layer after complete drying of the previous spots (at least 90 s), according to a procedure previously reported.[21,22]

Microwave-Assisted Polymerizations of the 2-Oxazolines. Unless indicated otherwise, solutions with the hereinafter cited initial concentration of the initiator and monomers were used: $[2\text{-methyl-2-oxazoline}]_0 = [2\text{-ethyl-2-oxazoline}]_0 = 4$ M, $[2\text{-nonyl-2-oxazoline}]_0 = 2$ M, and $[2\text{-phenyl-2-oxazoline}]_0 = 3$ M. These different initial concentrations were utilized in order to provide comparable (weight) amounts of the monomers in the corresponding reaction solutions (see below). The polymerizations were initiated by methyl tosylate; ratio [monomer]:[initiator] = 60:1. Consequently, a typical stock solution with a volume of 25 mL contained the following quantities of monomer/initiator/solvent (all entries in grams), respectively: 8.511/0.3104/12.994 (2-methyl-2-oxazoline, 4 M), 9.914/0.3104/11.707 (2-ethyl-2-oxazoline, 4 M), 9.866/0.1552/11.895 (2-nonyl-2-oxazoline, 2 M), and 11.039/0.2328/11.889 (2-phenyl-2-oxazoline, 3 M). These stock solutions were divided over the different reaction vials. For each monomer, the polymerization reactions were carried out at six different temperatures (five in the case of 2-methyl- and 2-nonyl-2-oxazoline); for every investigated temperature, six polymerizations were performed with different reaction times.

For the concentration series, the ratio [monomer]:[initiator] was kept at a value of 60; only the amount of solvent was varied. For the experiments that aimed at the preparation of polymers with high average molecular weights, on the other hand, the ratio [monomer]:[solvent] was kept at the herein above-mentioned values, but the amount of initiator was varied. The solutions for both series were prepared in a Chemspeed synthesizer robot.[23]

Results and Discussion

Kinetic Investigation. The first set of investigations was performed in order to prove the first-order kinetics of the monomer consumption and the livingness of the polymerization for the three different 2-oxazolines, 2-methyl-, 2-nonyl-, and 2-phenyl-2-oxazoline, in addition to the experiments already performed for 2-ethyl-2-oxazoline.[9] For this purpose, stock solutions containing the monomer, the initiator methyl tosylate, and the solvent acetonitrile were prepared. The initial [monomer]:[initiator] ratio was kept at a value of 60 independently of the monomer, while the concentration of the monomer was varied according to its molecular weight (4 M for 2-methyl- and 2-ethyl-, 2 M for 2-nonyl-, and 3 M for 2-phenyl-2-oxazoline). The conversion was monitored for five different temperatures (six in the case of 2-ethyl- and 2-phenyl-2-oxazoline). For each temperature, six samples with different reaction times for the polymerization were prepared by quenching the reaction mixtures at the favored times with water. The amount of unreacted monomer, represented by $\ln([M_0]/[M_t])$, was subsequently determined by means of GC (Figure 1). For the fast polymerization of the methyl, ethyl, and nonyl derivatives, reaction temperatures up to 180 °C allowed for reliable kinetic measurements (reaction time for full conversion less than 1 min); for the comparably slower polymerizations involving the phenyl congener, results from reactions performed at temperatures up to 200 °C could be utilized for calculating the kinetic parameters. One peculiarity occurred in the course of

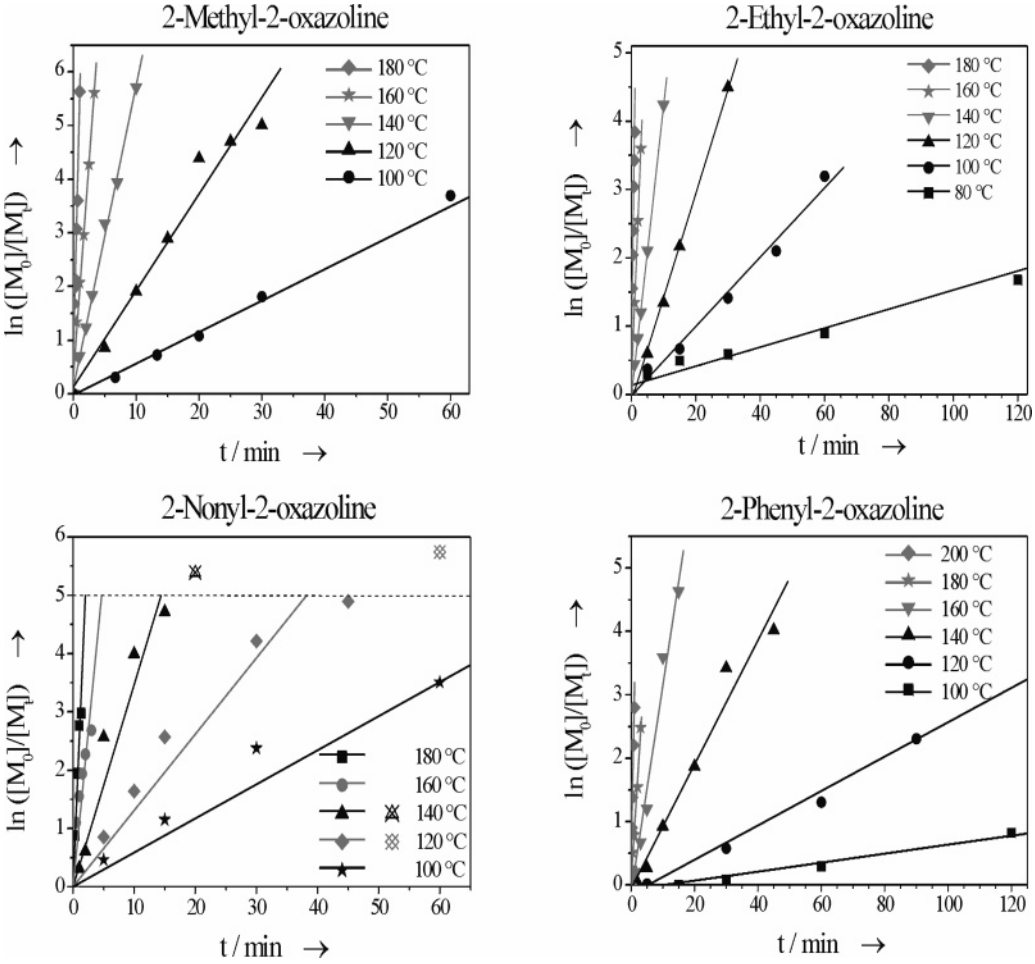


Figure 1. Monomer conversion, represented by the ratio $\ln\{[M_0]/[M_t]\}$, of the different congeners of the 2-oxazolines, plotted against time for five (six in the case of 2-ethyl- and 2-phenyl-2-oxazoline) temperatures (ratio [monomer]:[initiator] = 60).

the polymerization of 2-nonyl-2-oxazoline: Because of the low solubility of poly(2-nonyl-2-oxazoline) in acetonitrile, precipitation of the polymer was observed in the reaction solution after cooling to room temperature. Details of the polymer's solubility in the course of the polymerization and the applied conditions (high temperature, high pressure), however, are unknown due to the opaqueness of the reaction chamber. The recovery of this polymer from the reaction solution, on the other hand, does not require an additional step—it can simply be collected by filtration of the reaction mixture. The corresponding plots for 2-nonyl-2-oxazoline (Figure 1) exhibit severe distortions from the overall linear dependence on time for $\ln([M_0]/[M_t])$ values larger than 5. For the two highest temperatures, a bending of the corresponding curves became observable even for $\ln([M_0]/[M_t])$ values larger than 3. Control experiments in dichloromethane exhibit the same characteristics.[23] However, $\ln([M_0]/[M_t])$ values larger than 5 (3) already represent conversions higher than 99% (95%). For the subsequent calculations of the activation energies and frequency factors, only the data for $\ln([M_0]/[M_t])$ values below 5 (3) were taken into account.

Determination of the Arrhenius Parameters. The livingness of the polymerizations can be proven by a combination of the linear first-order kinetics and a linear increase of the number-average molecular weight against conversion. This was successfully demonstrated for the investigated monomers by plotting the number-average molecular weights (determined by means of GPC) against the conversion (Figure 2). Poly(2-methyl-2-oxazoline) showed strong interactions with the conventional column material (cross-linked polystyrene) in the case of the GPC system with $CHCl_3$ as eluent and therefore could only be measured on a system with *N*,*N*-dimethylformamide as eluent. Poly(2-nonyl-2-oxazoline), on the other hand, was measured exclusively on the system operated with $CHCl_3$ due to its insolubility in *N*,*N*-dimethylformamide. The other polymers investigated, poly(2-ethyl-2-oxazoline) and poly(2-phenyl-2-oxazoline), were suited for an analysis on both systems; the corresponding data points in Figure 2 result from measurements on the GPC system with $CHCl_3$ as eluent. For all polymers, the average molecular weight distributions were found to be narrow, indicated by PDI values well below 1.20.

In general, the four plots exhibit a good agreement among theoretical and experimental data. Deviations from the overall linearity (Figure 2) are comparably pronounced in the case of 2-nonyl-2-oxazoline for the low reaction temperatures that represent long reaction times. The polymerization at 140 °C, however, exhibits an almost perfect agreement with the theoretical values, revealing this temperature as the optimum one. Consequently, the assumption that the concentration of growing polymer chains [P*] is equal to the initial concentration of initiators $[I_0]$ is justified and may be considered for integrating the rate of polymerization (eq 1) to give the velocity equation (eq 2). Consequently, the slopes of the regression lines in Figure 2 (divided by $[I_0]$)

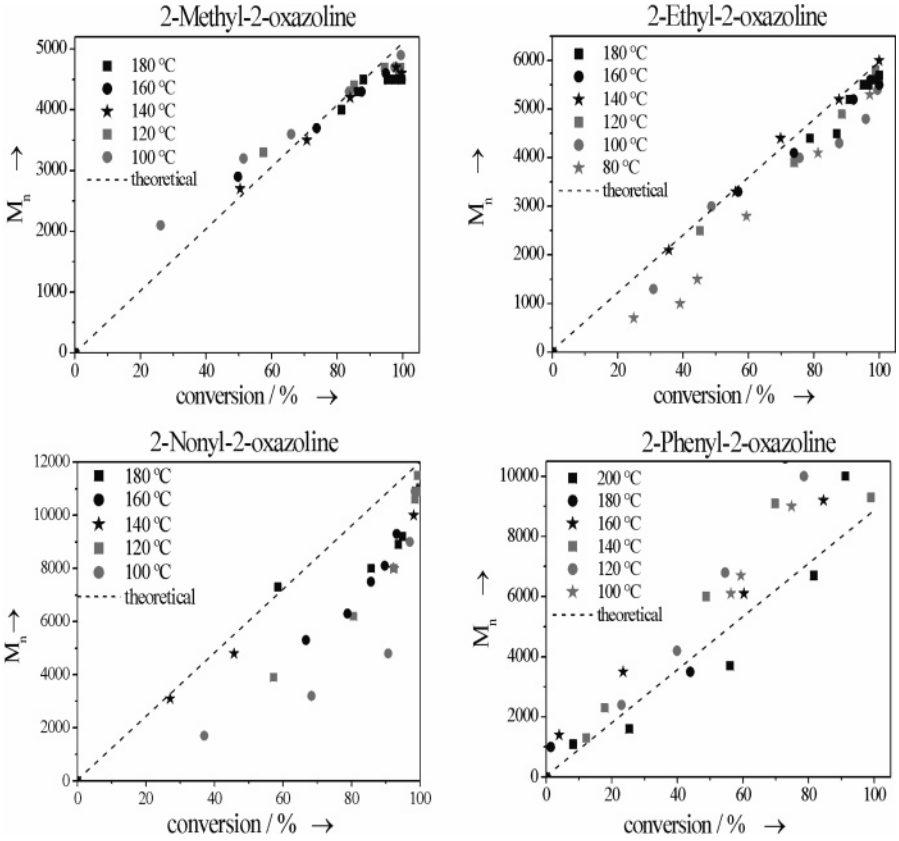


Figure 2. Number-average molecular weights (M_n) plotted against the conversion for the different 2-oxazolines (ratio [monomer]:[initiator] = 60).

are equal to k_p, the logarithms of which depend linearly on the inverse absolute temperature as indicated by the Arrhenius equation (eq 3).

$$-\frac{d[M]}{dt} = k_p[P^*][M] \quad (1)$$

$$\ln\left(\frac{[M_0]}{[M_t]}\right) = k_p[I_0]t \quad (2)$$

$$k_p = Ae^{-E_A/RT} \quad (3)$$

The Arrhenius plots for the polymerizations of the four monomers are shown in Figure 3. From the corresponding regression lines, the activation energies and frequency factors may be conveniently calculated, the results of which are summarized in Table 1 (including the corresponding values for 2-ethyl-2-oxazoline).[9] The polymerizations of 2-methyl-, 2-ethyl-, and 2-nonyl-2-oxazoline exhibit comparable activation energies and frequency factors. The polymerization of the phenyl congener shows the highest activation energy of this series. This is due to the resonance stabilization of the propagating species: The arene moiety at the charged end of the growing polymer chain partially compensates the positive charge (+M effect) and thereby decreases the reactivity of this polymer chain (relative to those of the other three 2-oxazolines investigated in the present study) (cf. Scheme 1). The frequency factor for the polymerization of 2-phenyl-2-oxazoline, however, lies in the range of the herein above-mentioned 2-oxazolines.

Previously, activation energies determined under conventional heating have been reported for the systems EtOx/BzBr/DMA (68.7 kJ mol^{-1}),[24] MeOx/MeI/CH_3CN (72.9 kJ mol^{-1}),[25] MeOx/TsOMe/CH_3CN (80.0 kJ mol^{-1}),[26] and PheOx/TsOMe/DMAc (81.3 kJ mol^{-1});[27] frequency factors have been cited for the herein above-mentioned systems MeOx/MeI/CH_3CN (1.7×10^8 L mol^{-1} s^{-1})[25] and MeOx/TsOMe/CH_3CN (1.9×10^9 L mol^{-1} s^{-1})[26] [BzBr: benzyl bromide; MeI: methyl iodide; TsOMe: methyl tosylate; DMA: *N*,*N*-dimethylacetamide]. The values for the herein presented systems perfectly fit in that range of literature data, evincing that the microwave irradiation affects the reaction speed of the polymerizations only as a fast and efficient heating device. In the literature, on the other hand, a controversial discussion has arisen whether the increase in reaction speed and the improved purity of the products upon exposition to microwave irradiation originate not only from the fast and direct heating of the reactants even beyond their boiling points but also from so-called microwave effects.[1–5] Further proof to the hypothesis that nonthermal microwave effects are *not* responsible for the increase in reaction speed (in this particular case) has been collected in the course of our study of the microwave-assisted polymerization of 2-ethyl-2-oxazoline by control experiments in a capped high-pressure NMR tube at 140 °C.[9] It was found that the conversion rates of 2-ethyl-2-oxazoline were independent of the heating

Table 1. Activation Energies E_A and Frequency Factors A for the Polymerizations of 2-Methyl-, 2-Ethyl-, 2-Phenyl-, and 2-Nonyl-2-oxazoline

monomer	frequency factor A, 10^8 L mol^{-1} s^{-1}	activation energy E_A, kJ mol^{-1}
2-methyl-2-oxazoline	5.00 ± 1.20	75.4 ± 0.5
2-ethyl-2-oxazoline[9]	1.99 ± 0.85	73.4 ± 0.5
2-phenyl-2-oxazoline	14.9 ± 2.8	84.4 ± 0.5
2-nonyl-2-oxazoline	7.58 ± 1.15	76.3 ± 0.5

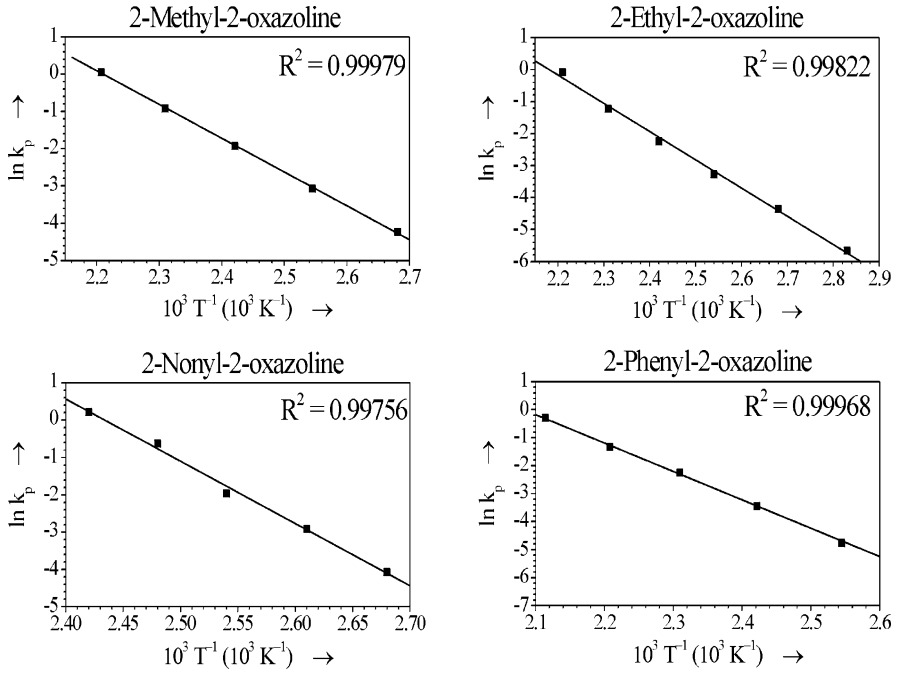


Figure 3. Arrhenius plots for the polymerizations of 2-methyl-, 2-nonyl-, and 2-phenyl-2-oxazoline in acetonitrile, initiated by methyl tosylate.

device (microwave irradiation vs conventional heating). Unfortunately, pronounced effects that might result from the direct (and exclusive) microwave absorption by the monomer could not be investigated since the cationic ring-opening polymerization of 2-oxazolines only proceeds in polar solvents which absorb microwave irradiation as well. Conclusively, compared to standard experiments in the laboratory, where the reaction temperature is limited by the boiling point of acetonitrile (82 °C), the polymerizations are accelerated under microwave irradiation by factors of up to 400 (6 h → less than 1 min) (cf. ref 9), still maintaining livingness and narrow molecular weight distributions (PDI < 1.20).

Bulk Polymerizations. Further investigations aimed at performing the polymerization reactions in reduced solvent amounts. In addition to the use of a halogen-free low-boiling solvent in an energy-saving process (the latter as a consequence of the good absorbance of the microwave irradiation by the solvent and the monomers), also this part of the study contributed to aspects of *green chemistry*. A series of solutions with an increasing concentration of the monomer (and a constant [monomer]:[initiator] ratio of 60) were subjected to polymerizations at 140 °C. The highest concentrations represent bulk polymerizations (Figure 4). The reaction times for completion could be calculated according to eq 2; the molecular weights were determined by GPC (cf. section above). The formation of polymers with the desired number-average molecular weights was observable for all samples. The PDI values, on the other hand, increased with the concentration of the monomer to a maximum for the bulk situation, representing a border case of a living polymerization in the case of 2-nonyl-2-oxazoline and 2-ethyl-2-oxazoline[9] and deviations from living behavior for the methyl and phenyl congener. A broadening of the corresponding GPC signals causes the increase in PDI values; furthermore, several peaks show the formation of shoulders (Figure 5), which might be generated from chain transfer reactions and subsequent chain coupling.[28] (For a more detailed discussion of these side reactions, cf. the section High Molecular Weight Polymers hereinafter.) Similar effects have been observed in the course of a concentrations series for the polymerization of 2-ethyl-2-oxazoline in *N*,*N*-dimethylacetamide (initiated by benzyl bromide) under conventional heating; the bulk polymerization itself, however, has not been performed.[29] We strongly assume that our success in going to bulk polymerization concomitant with (comparably) low PDI values is a direct effect of the fast, selective, and noncontact heating by the microwave irradiation, reducing side reactions to a minimum.

High Molecular Weight Polymers. The advantages of microwave assistance for this type of polymerization were also investigated in terms of accessible higher average molecular weights by a series of polymerizations with varying [monomer]:[initiator] ratios. The reaction times for completion could be calculated according to eq 2; the molecular weights were determined with GPC (cf. section above). The concentration of the monomers was kept at the values that had proven success in the course of the kinetic analysis (4 M for 2-methyl- and 2-ethyl-, 2 M for 2-nonyl-, and 3 M for 2-phenyl-2-oxazoline). All reactions were carried out at 140 °C. A reasonable agreement between the expected number molecular weights and those obtained from GPC analysis, concomitant with low PDI values, was found for all polymers for chain lengths below 300 monomer units (100 in the case of 2-methyl- and 2-nonyl-2-oxazoline) (Figure 6). The synthesis of even longer polymers with narrow average molecular weight distributions failed as the corresponding molecular weight distributions started to broaden and began to exhibit shoulders (indicative of chain transfer reactions and subsequent chain coupling) (Figure 7). In the literature,[28] this type of side reaction has been ascribed to originate from the abstraction of a α-proton of the positively charged growing polymer chain by an unreacted monomer. Consequently, an inactive (olefinic) polymer species and a positively charged monomer cation are formed (cf. Scheme 1). The positively charged

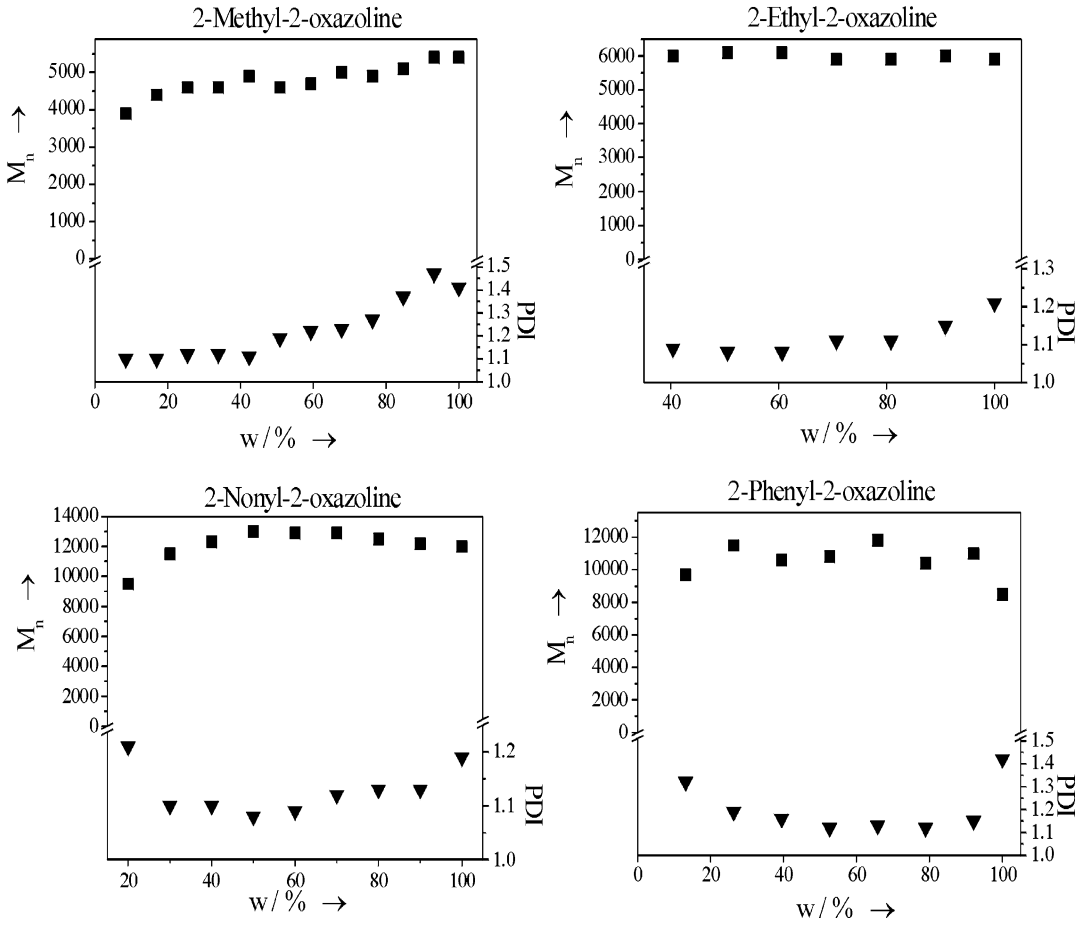


Figure 4. Number-average molecular weights (M_n) and PDI values (obtained by GPC) observed in the polymerization concentration series of the four differently substituted 2-oxazolines (ratio [monomer]:[initiator] = 60).

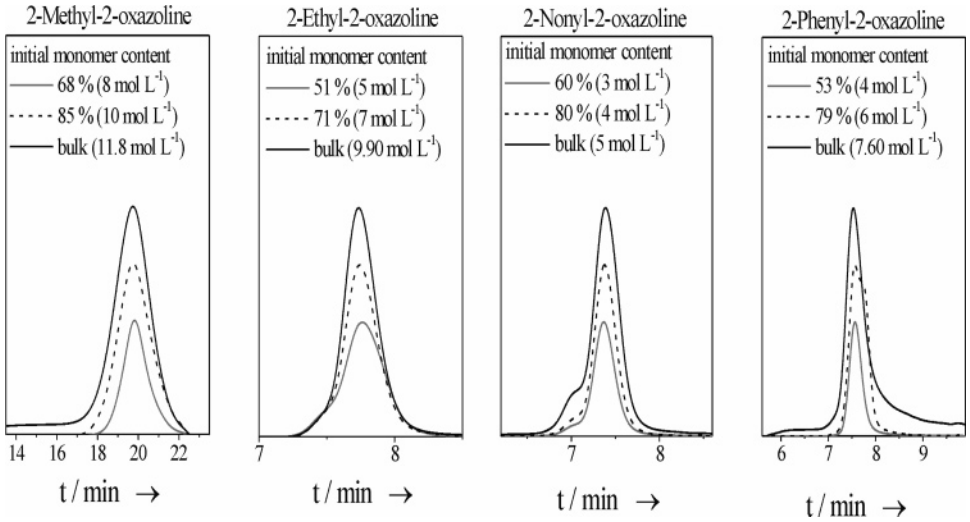


Figure 5. GPC traces of selected samples from the polymerization concentration series of the four different 2-oxazolines (ratio [monomer]:[initiator] = 60).

monomer cation may initiate the growth of a new polymer chain (with a finally relatively low molecular weight, compared to the polymer chains that started growing at the beginning of the polymerization); the olefinic polymer chain, on the other hand, may couple to a growing polymer chain to form a high molecular weight growing polymer chain (relative to the polymer chains that started growing at the beginning of the polymerization). For the polymers presented in this study, the formation of a high and low molecular weight polymer fraction, indicative of this type of side reactions, could be identified in the GPC traces by the presence of shoulders/tailing at low and high retention times (representing the high and low molecular weights, respectively). Concise examples of this phenomenon are those of poly(2-ethyl-2-oxazoline) ($[M]/[I_0] = 300$) or poly(2-nonyl-2-oxazoline) ($[M]/[I_0] = 152, 507$) (Figure 7, cf. also Figure 5). Despite the occurrence of these side reactions, well-defined polymers with number-average molecular weights up to 60 kDa [poly(2-ethyl-2-oxazoline)] could be prepared in a straightforward manner in comparably short reaction times (less than 2 h).

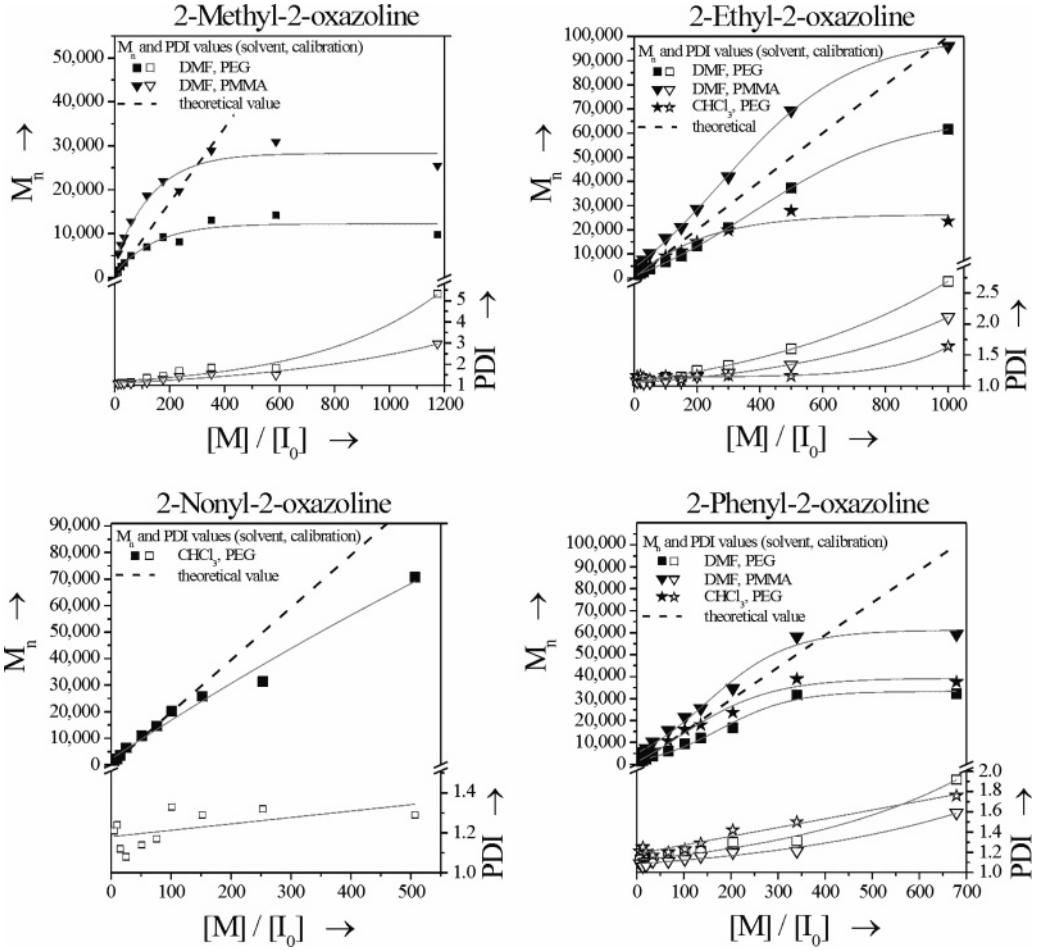


Figure 6. Dependence of the number-average molecular weights (M_n) and PDI values on the initial [monomer]:[initiator] ratios for polymers derived from 2-methyl-, 2-ethyl-, 2-nonyl-, and 2-phenyl-2-oxazoline (analysis by GPC).

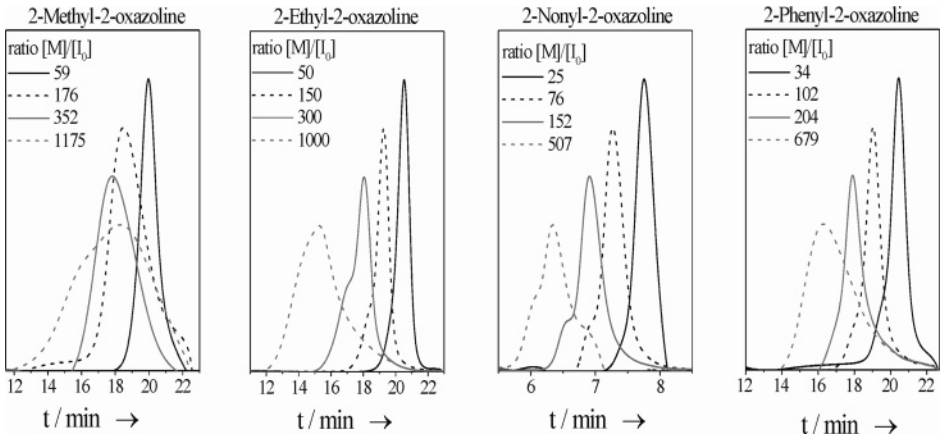


Figure 7. GPC traces of selected samples from the series with varying initial [monomer]:[initiator] ratios.

To unambiguously prove the successful synthesis of polymers with the targeted number-average molecular weights, we analyzed the well-defined poly(2-oxazoline)s (PDI < 1.30) by a previously developed MALDI multisample screening method (Figure 8).[21,22] Because of the optimized sample preparation, we were able to investigate poly(2-oxazoline)s with relatively high number-average molecular weights by MALDI−TOF mass spectrometry. The number-average molecular weights obtained by this technique showed a perfect agreement between theoretical and experimental data. This very good alignment can mainly be attributed to the fact that MALDI−TOFMS is an absolute analytical technique, whereas GPC is a relative one that requires calibration with well-suited polymer standards (that are not available for all polymers) and, in addition, is rather sensitive to nonspecific analyte/column interactions. Therefore, the data points shown in Figure 8 fit better to the expected values than the corresponding points in Figure 6. However, the samples that could be analyzed by MALDI−TOF mass spectrometry were limited by the number-average molecular weights (M_n < 30 kDa) and average molecular weight distributions (PDI < 1.30). In general, all mass spectra showed the expected signal spacings for the respective monomers of the investigated poly(2-oxazoline)s (85 Da for 2-methyl-, 99 Da for 2-ethyl-, 147 Da for 2-phenyl-, and 197 Da for 2-nonyl-2-oxazoline). The corresponding spectra of the poly(2-

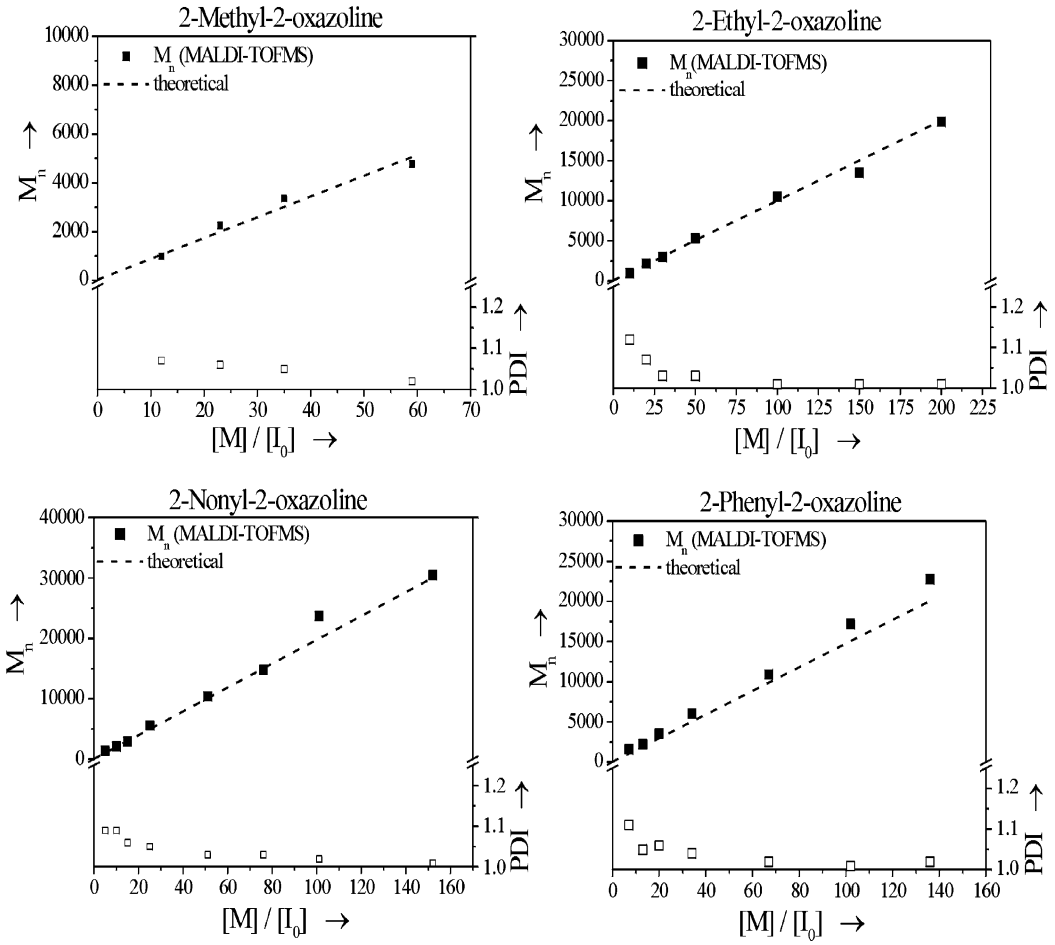


Figure 8. Dependence of the number-average molecular weights (M_n) and PDI values on the initial [monomer]:[initiator] ratios for polymers derived from 2-methyl-, 2-ethyl-, 2-nonyl-, and 2-phenyl-2-oxazoline (analysis by MALDI−TOF mass spectrometry).

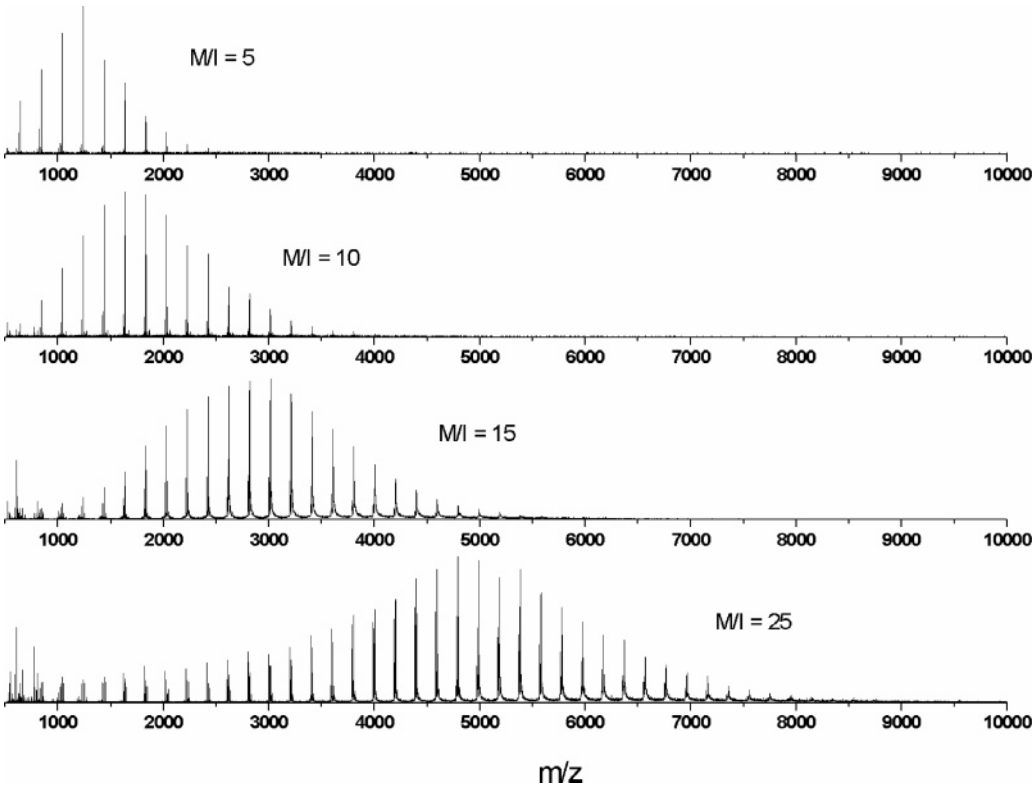


Figure 9. Mass spectra (obtained by MALDI−TOF) for poly(2-nonyl-2-oxazoline)s composed of 5, 10, 15, and 25 monomers.

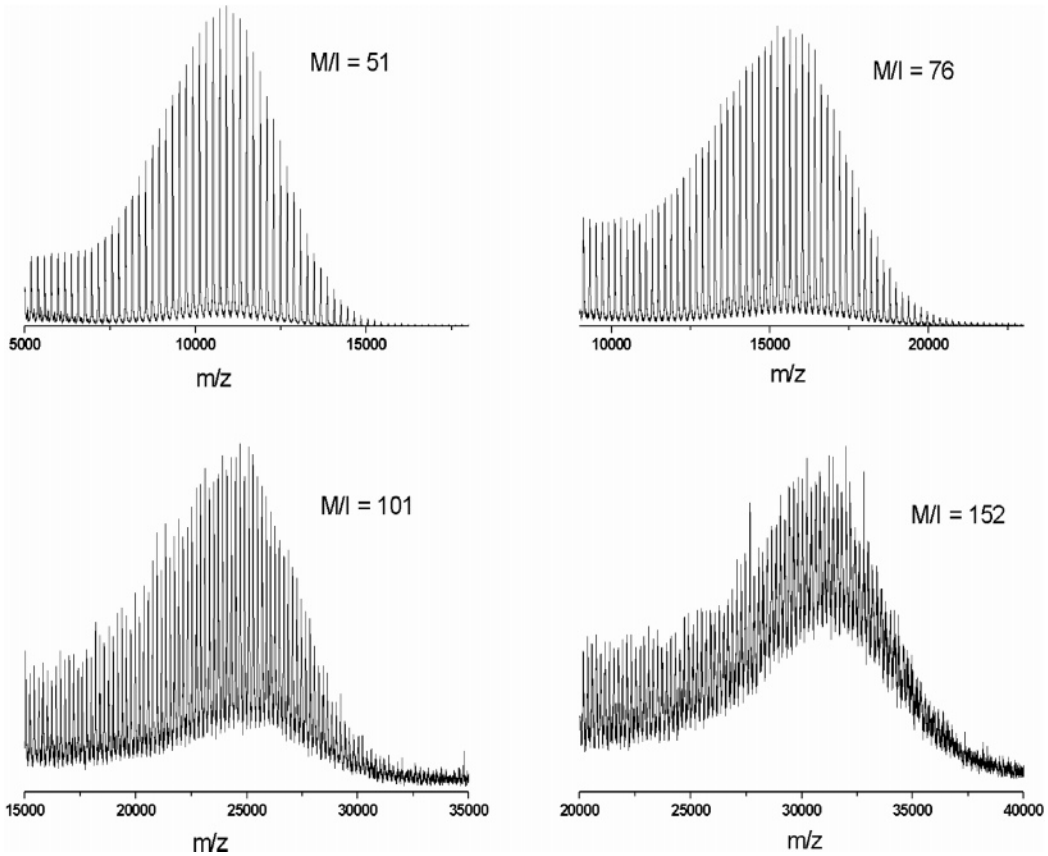


Figure 10. Mass spectra (obtained by MALDI−TOF) for poly(2-nonyl-2-oxazoline)s composed of 51, 76, 101, and 152 monomers.

nonyl-2-oxazoline)s may be depicted from Figures 9 and 10, showing the good resolution even up to high molar masses.

Conclusions and Outlook

The living cationic ring-opening polymerizations of four representative 2-oxazolines, namely 2-methyl-, 2-ethyl-, 2-nonyl-, and 2-phenyl-2-oxazoline, experienced significant enhancements of the reaction rates by factors of up to 400 in a single-mode microwave reactor. First-order kinetics of the monomer consumption and the livingness of the polymerization were maintained over the whole range of temperatures investigated in the course of this study (80−200 °C). Thus, the poly(2-oxazolines) exhibited narrow average molecular weight distributions, indicated by PDI values well below 1.20. As a consequence of the facilitated access to high-temperature and high-pressure syntheses in the single-mode microwave reactor, the halogen-free and low-boiling solvent acetonitrile could be used in this energy-saving synthetic strategy (good absorbance of the microwave irradiation by the monomers, the solvent, and the intermediates), meeting important criteria of green chemistry. In the case of 2-nonyl-2-oxazoline, the use of acetonitrile provided an easy workup of the poly(2-nonyl-2-oxazoline) as the polymer, in contrast to the well-soluble monomer, is not soluble in acetonitrile.

The activation energies for the polymerizations of the four 2-oxazolines were determined from the corresponding Arrhenius plots and found to be in the range of values obtained with conventional heating, indicating that solely temperature effects are responsible for the tremendous increase in reaction speed; nonthermal microwave effects are not discernible. A comparison of the four activation energies showed that 2-methyl-, 2-ethyl-, and 2-nonyl-2-oxazoline had similar activation energies, while that of 2-phenyl-2-oxazoline is significantly higher because of the +M stabilization of the propagating species (Scheme 1).

Because of the fast, selective, and noncontact heating by the microwave irradiation, the polymerizations could be carried out in highly concentrated solutions while the average molecular weight distributions remained narrow; for 2-ethyl- and 2-nonyl-2-oxazoline, this was even true for bulk polymerization. An inspection of the maximum number of monomers that can be incorporated into well-defined polymers (PDI < 1.20) revealed that 300 monomers designated the border case (100 in the case of 2-methyl- and 2-nonyl-2-oxazoline); attempts to synthesize longer well-defined polymer chains in a living way failed as the average molecular weight distributions broadened for polymerization degrees higher than 300 (100).

Future investigations will focus on the synthesis of di- and triblock copolymers with special attention to the preparation of amphiphilic compounds.

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