Full Paper

Acetyl Halide Initiator Screening for the Cationic Ring-Opening Polymerization of 2-Ethyl-2-Oxazoline

Renzo M. Paulus, C. Remzi Becer, Richard Hoogenboom, Ulrich S. Schubert*

Kinetic investigations on the cationic ring-opening polymerization of 2-ethyl-2-oxazoline were conducted using acetyl chloride, acetyl bromide, and acetyl iodide as initiators. Various polymerization temperatures ranging from 80 to 220 °C were applied under microwave irradiation. The resulting polymerization mixtures were characterized with GC and GPC for the determination of monomer conversion and molecular weight distribution, respectively. Well defined polymers with narrow molecular weight distributions ($\overline{M}_{\text{n,GPC}} = 6\,000$ Dalton, PDI ≈ 1.10) were obtained with all three initiators.
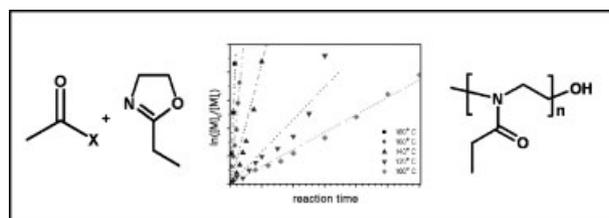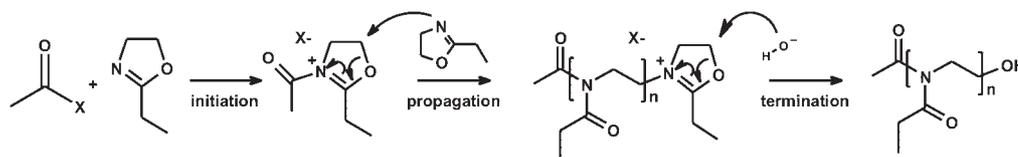
Introduction

The living cationic ring-opening polymerization (CROP) of 2-ethyl-2-oxazoline (EtOx) was first described in literature in 1966.[1–4] Ever since, the biocompatible and hydrophilic poly(2-ethyl-2-oxazoline)s have been used for a broad range of applications.[5,6] The living character of the polymerization provides easy access to block copolymers by sequential addition of different monomers and functional end-groups by using functional initiators or terminating agents.[7] By chain extending the hydrophilic poly(2-ethyl-2-oxazoline) [P(EtOx)] with a hydrophobic block, amphiphilic structures can be obtained.[8–12] The polymerization kinetics for the cationic ring-opening polymerization of 2-oxazolines with many initiators were

already investigated by a number of groups.[13–18] Most commonly, tosylate and triflate derivatives are used as initiators for the cationic ring-opening polymerization of oxazolines.[19] Moreover, some research groups focused on using bifunctional and multifunctional initiators in order to combine CROP of oxazolines with nitroxide mediated radical polymerization, anionic ring-opening polymerization or other living radical polymerization techniques.[20,21] The use of acetyl chloride and methacryloyl chloride as initiator for the CROP of 2-methyl-2-oxazoline and 2-phenyl-2-oxazoline was demonstrated with and without addition of silver triflate or potassium iodide to accelerate the polymerizations.[22] However, the use of different acetyl halides as initiators for the CROP of 2-oxazolines has not been reported to the best of our knowledge.

The acetyl halide initiated reaction mechanism for the cationic ring-opening polymerization of 2-ethyl-2-oxazoline is depicted in Scheme 1. The polymerization is initiated by the electrophilic acetyl halide forming the cationic oxazolinium ring. The C–O bond in the oxazolinium ring is weakened and the polymerization propagates by nucleophilic attack of the next monomer onto this carbon atom. Block copolymers can be potentially synthesized by adding a second monomer when all initial monomer is consumed

R. M. Paulus, C. R. Becer, R. Hoogenboom, U. S. Schubert
Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology and Dutch Polymer Institute (DPI), PO Box 513, 5600 MB Eindhoven, The Netherlands
Fax: +31 40 247 4186; E-mail: u.s.schubert@tue.nl
R. M. Paulus, C. R. Becer, U. S. Schubert
Laboratory of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena and Dutch Polymer Institute (DPI), Humboldtstr. 10, 07743 Jena, Germany

Acetyl Halide Initiator Screening for the Cationic Ring-Opening Polymerization . . .

Macromolecular
Chemistry and Physics

Scheme 1. Schematic representation of the mechanism of the living cationic ring-opening polymerization of 2-ethyl-2-oxazoline with acetyl halide as initiator (X = Cl, Br, I).

or the polymerization can be terminated by adding a nucleophile (terminating agent). If chain transfer and chain termination can be excluded, the polymerization proceeds in a living manner. In this case, the concentration of propagating species is constant and the polymerization should proceed via first order kinetics.

The rate of polymerization k_p (assuming all initiator molecules react instantaneously upon heating) can be expressed by Equation (1).

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

Integration of Equation (1) results in the velocity Equation (2) when it is assumed that the concentration of the propagating species is equal to the starting initiator concentration. The temperature dependence of the rate of polymerization is expressed in Equation (3) (Arrhenius equation).

$$\ln\frac{[M]_0}{[M]_t} = k_p[I]_0 \cdot t \tag{2}$$

$$k_p = A \cdot e^{-\frac{E_a}{RT}} \tag{3}$$

A major drawback of the cationic ring-opening polymerization of 2-oxazolines is the long reaction times from several hours up to several weeks.[23] However, it was shown in our previous reports that the required polymerization period can be reduced by performing the reaction in a closed vial under microwave irradiation.[24,25] Relatively high polymerization temperatures and pressure can be reached by using this type of reaction setup which results in acceleration for the synthesis of poly(2-oxazoline)s. Recently, we also reported up-scaling possibilities for the polymerization of oxazolines under microwave irradiation.[26,27]

In this contribution, we report kinetic investigations for the polymerization of 2-ethyl-2-oxazoline using three different acetyl halide initiators at various polymerization temperatures. The motivation for this kinetic study with acetyl halides as initiators was their commercial availability and their potential future application for the synthesis of functionalized polymers using various acetyl halides with functional groups as initiator. Moreover, the synthesis of high molecular weight poly(2-ethyl-2-oxazoline)s was investigated using these commercially available acetyl halide initiators.

Experimental Part

Materials and Instrumentation

Acetonitrile (Biosolve Ltd) was dried in the Pure Solv 400-4-MD solvent purification system (Innovative Technology Inc.). 2-Ethyl-2-oxazoline (Henkel) was distilled over barium oxide (Aldrich) and stored under argon. Acetyl chloride (Fluka), acetyl bromide (Aldrich) and acetyl iodide (TCI Europe nv) were used as received.

Gas chromatography (GC) measurements were performed on an Interscience Trace GC with a Trace Column RTX-5 and a PAL autosampler. Gel permeation chromatography (GPC) was measured on a Shimadzu system equipped with a SCL-A10 system controller, a LC-10AD pump, a RID-10A refractive index detector, a SPD-10A UV-detector at 254 nm and a PLgel 5 μm Mixed-D column at 50 °C utilizing chloroform: triethylamine: 2-propanol (94:4:2) mixture as eluent at a flow rate of 1 mL·min⁻¹. The molecular weights were calculated against polystyrene standards. Polymerizations were performed using the Emrys Liberator monomode microwave synthesizer (Biotage, formerly Personal-Chemistry) under temperature control utilizing an IR temperature sensor.

MALDI-TOFMS measurements were carried out on a Voyager-DE™ PRO Biospectrometry™ Workstation time-of-flight mass spectrometer using linear mode for operation. The spectra were obtained in the positive ion mode. Ionization was performed with a 337 nm pulsed nitrogen laser. Samples were prepared with dithranol as matrix and NaI as cationizing agent in a multiple-layer approach as described in literature.[28]

Typical Polymerization Procedure

In order to perform a kinetic study for each initiator at different temperatures, stock solutions were prepared with monomer, solvent and initiator (acetyl chloride, acetyl bromide or acetyl iodide) having a monomer to initiation ratio of 60 and an initial monomer concentration of 4 M. From these stock solutions, 1 mL aliquots were transferred into different microwave vials. Subsequently, 10 of these vials were heated with different predefined reaction times for each investigated temperature. All reactions were terminated by the automated addition of 100 μL
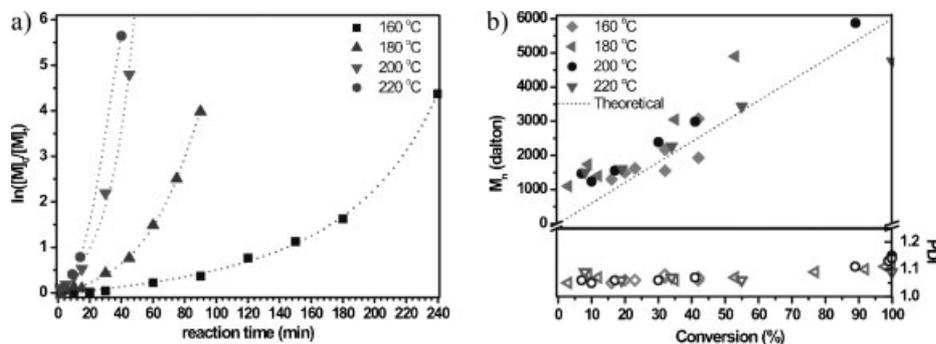
Figure 1. (a): First order kinetic plot for the acetyl chloride initiated cationic ring-opening polymerization of 2-ethyl-2-oxazoline in acetonitrile at different temperatures using 4 M monomer concentration and a monomer to initiator ratios of 60. The dotted lines are added to guide the eye. (b): $\overline{M}_{n,GPC}$ against monomer conversion and PDI values for the acetyl chloride initiated polymerization of 2-ethyl-2-oxazoline in acetonitrile at different temperatures.

water using the liquid handling system of the microwave synthesizer. Samples were taken from the microwave reactors and diluted (100 µL crude sample + 1 000 µL chloroform) for GC analysis and acetonitrile was used as internal standard to calculate the monomer conversions. A second sample was withdrawn from the reactors and diluted (100 µL crude sample + 1 000 µL chloroform: triethylamine: 2-propanol (94:4:2) mixture) for GPC analysis in order to calculate the molecular weights and polydispersity indices against polystyrene standards.

Results and Discussion

The polymerization of 2-ethyl-2-oxazoline in acetonitrile initiated with acetyl chloride, acetyl bromide and acetyl iodide was investigated at different temperatures (160, 180, 200 and 220 °C for acetyl chloride; 100, 120, 140, 160 and 180 °C for acetyl bromide; 80, 90, 100, 120, 140 and 160 °C for acetyl iodide) in closed reaction vials using

microwave irradiation as heating source. All polymerizations in this kinetic study were performed using a 4 M initial monomer concentration and a monomer to initiator ratio of 60.

The monomer conversions were calculated from GC measurements and the semi-logarithmic kinetic plot for the acetyl chloride initiated CROP of EtOx is shown in Figure 1(a). According to the polymerization kinetics, the polymerization rates (k_i is the initial slope of the fitted non-linear kinetic plot and k_p is the final slope of the fitted non-linear kinetic plot) increased in time at all investigated temperatures. This acceleration in k_p might be related to the increase in the concentration of cationic active centers in time: After fast initiation with the acetyl chloride, covalent chloride propagating species are formed that have a very low reactivity. With increasing reaction time, the equilibrium between the covalent and the more reactive cationic propagating species will be formed
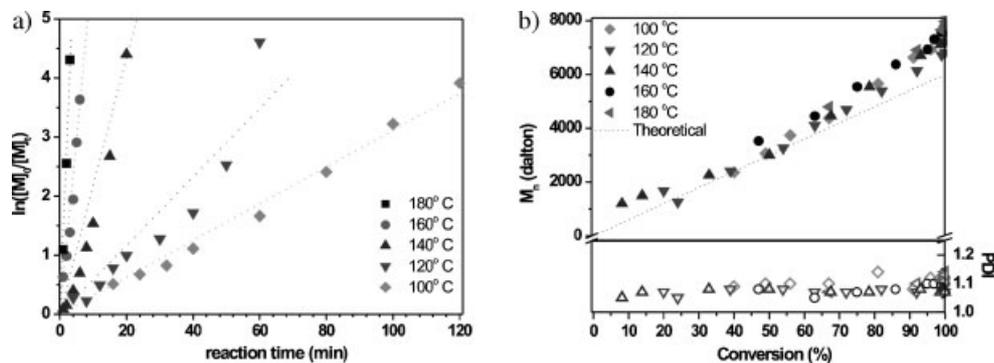

Figure 2. (a): First order kinetic plot for the acetyl bromide initiated cationic ring-opening polymerization of 2-ethyl-2-oxazoline in acetonitrile at different temperatures using 4 M monomer concentration and a monomer to initiator ratios of 60. The dotted lines are linear fits to the data. (b): $\overline{M}_{n,GPC}$ against monomer conversion and PDI values for the acetyl bromide initiated polymerization of 2-ethyl-2-oxazoline in acetonitrile at different temperatures.
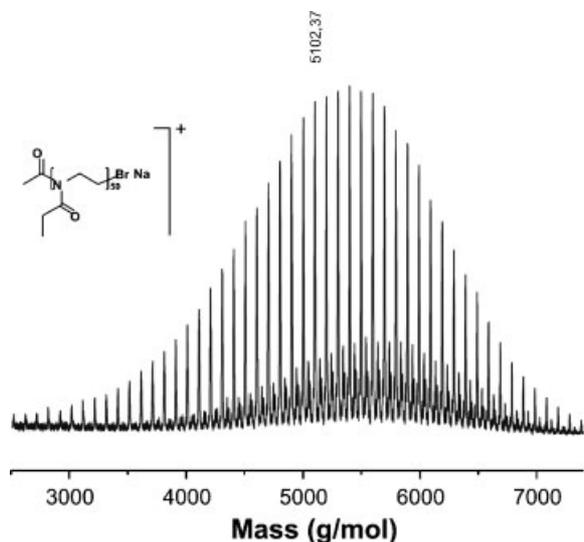
Acetyl Halide Initiator Screening for the Cationic Ring-Opening Polymerization . . .

Macromolecular
Chemistry and Physics

Figure 3. MALDI-TOF MS spectrum of the acetyl bromide initiated polymer of 2-ethyl-2-oxazoline with the corresponding peak assignment.

Figure 5. GPC traces obtained at different reaction times for the acetyl iodide initiated polymerization of 2-ethyl-2-oxazoline in acetonitrile at 140 °C (GPC with chloroform: triethylamine: 2-propanol (94:4:2) mixture).

resulting in higher polymerization rates. Similar observations have been previously made for the cationic ring-opening polymerization of 2-ethyl-2-oxazoline with benzyl bromide as initiator using *N,N*-dimethylacetamide as solvent.[29] The molecular weights and polydispersity indices of the synthesized polymers, determined by GPC, are plotted against monomer conversion in Figure 1(b). An increase in the molecular weight of the polymers was observed with increasing conversions and the polydispersity indices remained below 1.2 for all polymers and mostly below 1.10, which supports the proposed fast initiation followed by a slow polymerization rate. Nonetheless, it should be noted that, especially at low conversion, the molecular weight versus conversion plot is deviating from the theoretical molecular weight. The

reason for this non-linearity is not clear, but might be related to the used polystyrene calibration for the GPC and/or the occurrence of some minor side reactions.

The acetyl bromide initiated polymerization of EtOx was investigated at six different polymerization temperatures, namely 100, 120, 140, 160 and 180 °C. The resulting first order kinetic plots for these polymerizations (Figure 2(a)) revealed linear first order kinetics for all investigated polymerization temperatures indicating fast initiation and the absence of chain termination. Moreover, the apparent rate constants increased with increasing temperatures, as expected based on the higher energy input. Molecular weight and polydispersity index versus conversion plot is shown in Figure 2(b). The molecular weights obtained by measuring GPC were found to be close to the theoretical molecular weights proving the livingness of the polymerization, whereby the polydispersity indices remained
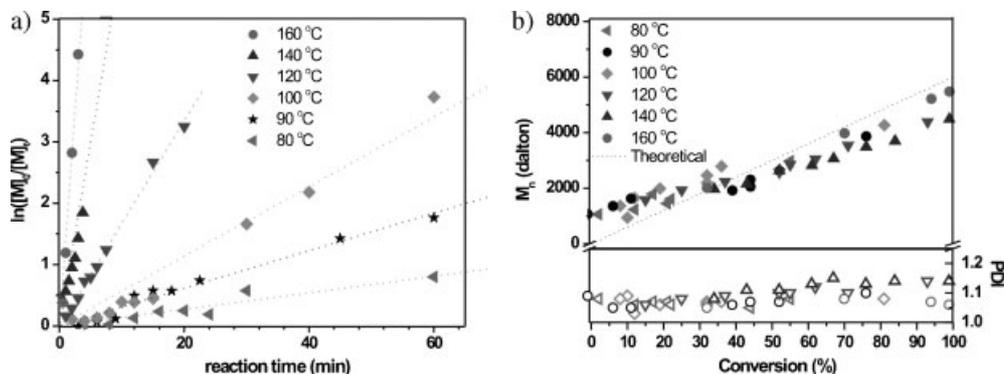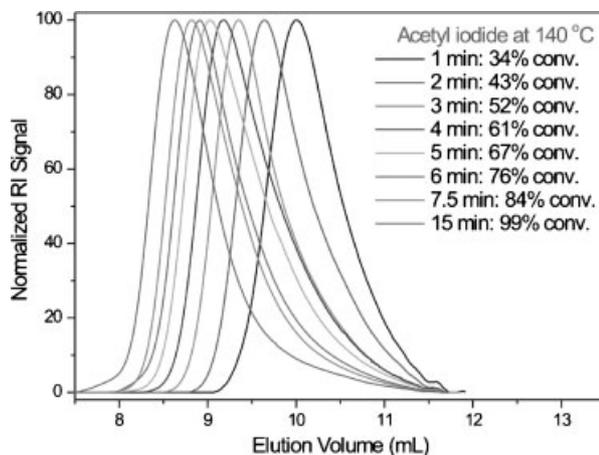

Figure 4. (a): First order kinetic plot for the acetyl iodide initiated cationic ring-opening polymerization of 2-ethyl-2-oxazoline in acetonitrile at different temperatures using 4 M monomer concentration and a monomer to initiator ratios of 60. The dotted lines are linear fits to the data. (b): $\overline{M}_{n,GPC}$ against monomer conversion and PDI values for the acetyl iodide initiated 2-ethyl-2-oxazoline polymerization in acetonitrile at different temperatures.

Table 1. Polymerization rates for the different initiators (in 10^{-3} L·mol^{-1}·s^{-1}) at different temperatures.

Initiator	80°C	90°C	100°C	120°C	140°C	160°C	180°C	200°C	220°C
Acetyl chloride (k_i)	–	–	–	–	–	1.8 ± 0.2	3.8 ± 0.3	8.3 ± 0.3	38 ± 5
Acetyl chloride (k_p)	–	–	–	–	–	11.4	47.4	111.3	126.79
Acetyl bromide	–	–	7.8 ± 0.1	15 ± 1	54 ± 4	149 ± 1	342 ± 18	–	–
Acetyl iodide	3.5 ± 0.3	7.7 ± 0.3	14.3 ± 0.1	42 ± 1	150 ± 9	351 ± 1	–	–	–

below 1.2. To further investigate our proposed initiation mechanism, a poly(2-ethyl-2-oxazoline) was prepared using acetyl bromide as initiator and a monomer to initiator ratio of 100. The polymerization was performed up to ≈50% to repress the possible occurrence of side reactions and the polymer was analyzed by MALDI-TOF MS. Figure 3 displays the MALDI-TOF MS spectrum with a peak spacing of 99.13 corresponding to the mass of one monomer unit. In addition, end-group analysis revealed that the major distribution corresponds to poly(2-ethyl-2-oxazoline) having the acetyl initiator group at one chain end and the bromide at the other chain end, whereby the polymer was charged by a sodium(I) ion, which proves the proposed polymerization mechanism.

The acetyl iodide is expected to result in the fastest polymerization amongst the three investigated acetyl halides. As shown in Figure 4(a), the acetyl iodide initiated polymerizations exhibited a linear relationship in the first order kinetic plots and increased polymerization rates were observed at elevated temperatures. Molecular weights of the resulting polymers increased linearly with the increasing conversion and the polydispersity indices remained below 1.2, as depicted in Figure 4(b). These results demonstrate that the polymerizations proceeded via a living polymerization mechanism with fast initiation. Nonetheless, the small deviations of the molecular weight from the theoretical molecular weight might be due to the used polystyrene standards for calibration and/ or the occurrence of minor side reactions like chain-transfer[30] or spontaneous initiation by small traces of impurities.[31,32] As a representative example of the monomodal distributions of the resulting polymers, GPC
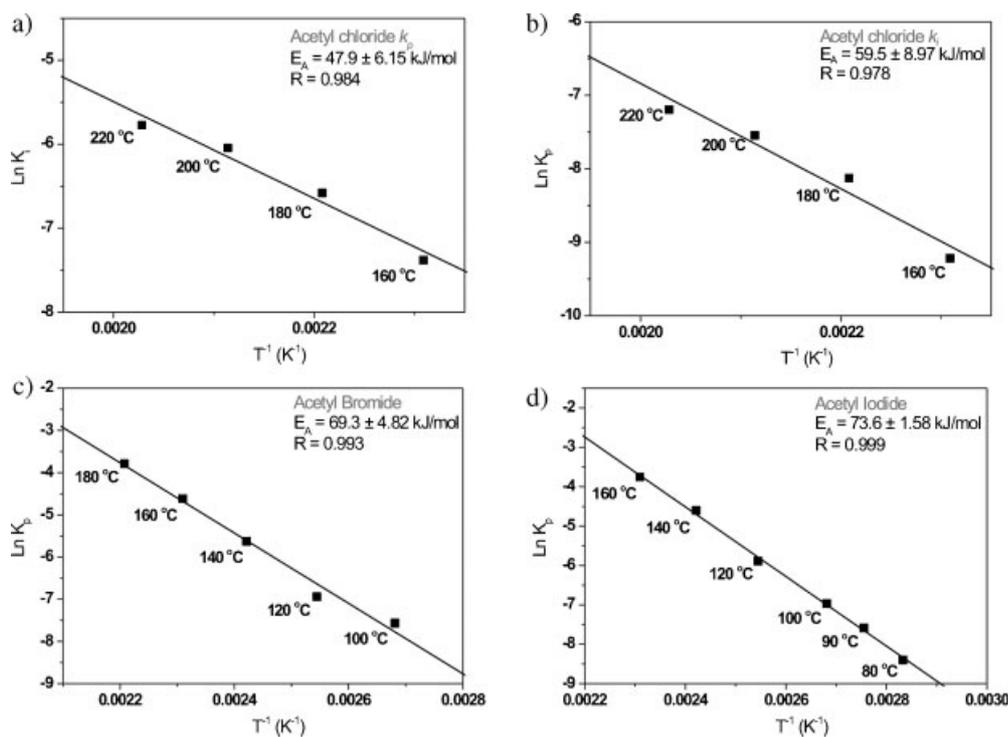

Figure 6. Arrhenius plots for the acetyl chloride (a: k_i, b: k_p), acetyl bromide (c) and acetyl iodide (d) initiated polymerizations of 2-ethyl-2-oxazoline in acetonitrile.

Acetyl Halide Initiator Screening for the Cationic Ring-Opening Polymerization . . .

Macromolecular
Chemistry and Physics

Table 2. Molecular weights of the polymers with higher monomer to initiator ([M]/[I]) ratios obtained from GPC analysis (chloroform: triethylamine: 2-propanol (94:4:2) mixture as eluent) calculated with polystyrene standards.

Sample	[M]/[I]	Temperature	Reaction time	$\overline{M}_{n,theo}$	$\overline{M}_{n,GPC}$	$\overline{M}_{w,GPC}$	PDI
		°C	min	Dalton	Dalton	Dalton	
1	100	140	30	10 130	8 580	9 070	1.06
2	200	140	60	20 150	19 450	22 090	1.13
3	400	140	120	40 170	28 190	36 070	1.28

traces obtained at different reaction times for the acetyl iodide initiated polymerization of 2-ethyl-2-oxazoline at 140 °C are depicted in Figure 5.

The CROP of EtOx at a polymerization temperature of 160 °C initiated by acetyl iodide was found to be approximately 2 and 190 times faster compared to the acetyl bromide and acetyl chloride initiated polymerizations at 160 °C, respectively. Furthermore, the apparent rate constant values (k_p) of the acetyl bromide and iodide initiated polymerizations at different polymerization temperatures were calculated from the slopes of the regression lines in the semi-logarithmic kinetic plots. However, for the non-linear increase of the first order kinetics of the acetyl chloride initiated polymerizations the initial slope was taken as a measure for the initial polymerization rate (k_i) and the final slope as measure for k_p. The k_p's for the three acetyl halide initiators at different polymerization temperatures are listed in Table 1 demonstrating the influence of the initiator on the polymerization rates. The standard deviation of the polymerization rates is within 10%, except for the k_p's of the acetyl chloride initiated polymerizations for which it is arbitrary how to fit the final slope of the curves. The obtained order in polymerization rate constants for the different initiators is in agreement with the general statement that the polymerization rate increases with lower basicity of the counter ion: $I^- < Br^- < Cl^-$.

The Arrhenius plots for acetyl chloride, acetyl bromide and acetyl iodide initiated polymerizations were drawn by using the data obtained from the corresponding kinetic plots and shown in Figure 6(a), (b), (c) and (d), respectively. From these Arrhenius plots, the activation energies were determined to be 59.5, 47.9, 69.3 and 73.6 kJ · mol^{-1} for the acetyl chloride (k_i and k_p), acetyl bromide and acetyl iodide, respectively. These values are also in the same range to previously reported values for the polymerization of 2-ethyl-2-oxazoline with various initiators (68.7, 71.1, 81.3 and 113 kJ · mol^{-1}).[33–35]

The obtained insights into the polymerization kinetics of 2-ethyl-2-oxazoline in acetonitrile with the different acetyl halide initiators at different temperatures were applied to synthesize poly(2-ethyl-2-oxazoline)s with

higher molecular weights ($\overline{M}_n > 10\,000$ Dalton). Polymerizations were performed at a constant monomer concentration of 4 M and monomer to initiator ratios of 100, 200 and 400 at a polymerization temperature of 140 °C using acetyl bromide as initiator; the vials were reacted for 30, 60, and 120 min, respectively. As a result, poly(2-ethyl-2-oxazoline) homopolymers with relatively high molecular weights were obtained and the data obtained from GPC analysis are listed in Table 2. Furthermore, the obtained GPC traces for the higher molecular weight poly(2-ethyl-2-oxazoline)s are shown in Figure 7. At the high molecular weight region of the GPC traces, a small shoulder was observed for all the obtained polymers. The shoulders become less visible with higher monomer to initiator ratios due to a larger extend of overlap of the 2 peaks. In addition, the peak molecular weight ($\overline{M}_p$) of the shoulders are twice the $\overline{M}_p$ of the main peak, which points to chain coupling. Nonetheless, even with these shoulders, polymers with reasonable low polydispersities (PDI < 1.3) were obtained with molecular weights ($\overline{M}_n$) up to 28 000 g · mol^{-1}.
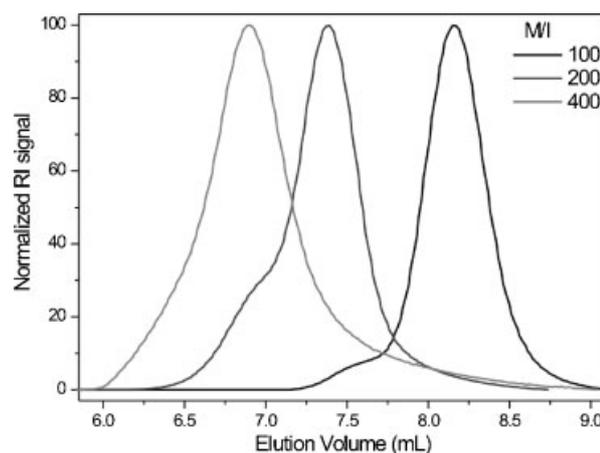

Figure 7. GPC traces of the poly(2-ethyl-2-oxazoline)s that were prepared with different monomer to initiator ([M]/[I]) ratios using acetyl bromide as initiator in acetonitrile at 140 °C (GPC with a chloroform: triethylamine: 2-propanol (94:4:2) mixture as eluent).

Conclusions

The systematic kinetic screening of the polymerization of
2-ethyl-2-oxazoline was investigated with three different
initiators (acetyl chloride, acetyl bromide and acetyl
iodide) at different polymerization temperatures (ranging
from 80 to 220 °C) using a monomer concentration of 4 M
and a monomer to initiator ratio of 60. As expected, the
order in polymerization rate for the different initiators was
found to increase with decreasing basicity of the halide:
acetyl iodide < acetyl bromide < acetyl chloride. In addi-
tion, it was demonstrated that the polymerization rates
increased at higher temperatures, and that the polymer-
izations were living (PDI ≈ 1.10) at all polymerization
temperatures. MALDI-TOF MS confirmed that the acetyl
group was present at the chain end of the resulting
polymers. From the first order kinetic plots, the polymer-
ization rates and activation energies were calculated for
the polymerizations with the three acetyl halide initiators.

The kinetic insights in the 2-ethyl-2-oxazoline poly-
merizations with these acetyl halide initiators were used
to synthesize polymers with relatively high monomer to
initiator ratios of 100, 200 and 400 using acetyl bromide as
initiator at 140 °C. Even though GPC analysis indicated the
occurrence of some chain transfer and/or chain coupling
reactions, reasonably well-defined polymers were
obtained with polydispersity indices below 1.3.

As a result, acetyl halide initiators are presented as
suitable new initiators to obtain well defined poly(2-
oxazoline)s by using the CROP technique. The advantages
of using these initiators over the tosylate and triflate
derivatives are their commercial availability and the
simple access to acid halides from a wide variety of acid
functionalized compounds, which opens up the way to a
large variety of possible new initiators for the CROP of
2-oxazolines.

[1] D. A. Tomalia, D. P. Sheetz, *J. Polym. Sci., Part A: Polym. Chem.*
1966, *4*, 2253.

[2] W. Seeliger, E. Aufderhaar, W. Diepers, R. Feinauer, R. Nehring,
W. Thier, H. Hellmann, *Angew. Chem.* **1966**, *20*, 913.

[3] W. Seeliger, E. Aufderhaar, W. Diepers, R. Feinauer, R. Nehring,
W. Thier, H. Hellmann, *Angew. Chem., Int. Ed. Engl.* **1966**, *5*,
875.

[4] T. G. Bassiri, A. Levy, M. Litt, *Polym. Lett.* **1967**, *5*, 871.

[5] K. Aoi, M. Okada, *Prog. Polym. Sci.* **1996**, *21*, 151.

[6] S. Kobayashi, H. Uyama, *J. Polym. Sci., Part A: Polym. Chem.*
2002, *40*, 192.

[7] O. W. Webster, *Science* **1991**, *496*, 887.

[8] S. Kobayashi, T. Igarashi, Y. Moriuchi, T. Saegusa, *Macromol-
ecules* **1986**, *19*, 535.

[9] R.-H. Jin, *Adv. Mater.* **2002**, *14*, 889.

[10] R. Hoogenboom, F. Wiesbrock, H. Huang, M. A. M. Leenen,
S. F. G. M. van Nispen, M. van der Loop, C.-A. Fustin,
A. M. Jonas, J.-F. Gohy, U. S. Schubert, *Macromolecules*
2006, *39*, 4719.

[11] R. Hoogenboom, F. Wiesbrock, M. A. M. Leenen, H. M. L. Thijs,
H. Huang, C. A. Fustin, P. Guillet, J.-F. Gohy, U. S. Schubert,
Macromolecules **2007**, *40*, 2837.

[12] H. Huang, R. Hoogenboom, M. A. M. Leenen, P. Guillet,
A. M. Jonas, U. S. Schubert, J.-F. Gohy, *J. Am. Chem. Soc.*
2006, *128*, 3784.

[13] R. Hoogenboom, M. W. M. Fijten, U. S. Schubert, *J. Polym. Sci.,
Part A: Polym. Chem.* **2004**, *42*, 1830.

[14] T. Saegusa, H. Ikeda, *Macromolecules* **1973**, *6*, 808.

[15] T. Saegusa, H. Ikeda, H. Fujii, *Macromolecules* **1972**, *5*, 359.

[16] T. Saegusa, H. Ikeda, H. Fujii, *Macromolecules* **1973**, *6*, 315.

[17] Q. Lui, M. Konnas, J. S. Riffle, *Macromolecules* **1993**, *26*,
5572.

[18] A. Dworak, *Macromol. Chem. Phys.* **1998**, *199*, 1843.

[19] M. Einzmann, W. H. Binder, *J. Polym. Sci., Part A: Polym. Chem.*
2001, *39*, 2821.

[20] R. D. Puts, D. Y. Sogah, *Macromolecules* **1997**, *30*, 7050.

[21] Y. Wang, W. J. Brittain, *Macromol. Rapid Commun.* **2007**, *28*,
811.

[22] A. Dworak, *Polym. Bull.* **1997**, *38*, 7.

[23] J.-S. Park, Y. Akiyama, F. M. Winnik, K. Kataoka, *Polymer* **2004**,
37, 6786.

[24] F. Wiesbrock, R. Hoogenboom, C. H. Abeln, U. S. Schubert,
Macromol. Rapid Commun. **2004**, *25*, 1895.

[25] F. Wiesbrock, R. Hoogenboom, M. A. M. Leenen, M. A. R. Meier,
U. S. Schubert, *Macromolecules* **2005**, *38*, 5025.

[26] R. Hoogenboom, R. M. Paulus, A. Pilotti, U. S. Schubert, *Macro-
mol. Rapid Commun.* **2006**, *27*, 1556.

[27] R. M. Paulus, T. Erdmenger, C. R. Becer, R. Hoogenboom,
U. S. Schubert, *Macromol. Rapid Commun.* **2007**, *28*, 484.

[28] M. A. R. Meier, U. S. Schubert, *Rapid Commun. Mass Spectrom.*
2003, *17*, 713.

[29] R. Hoogenboom, R. M. Paulus, M. W. M. Fijten, U. S. Schubert,
J. Polym. Sci., Part A: Polym. Chem. **2005**, *43*, 1487.

[30] M. Litt, A. Levy, J. Herz, *J. Macromol. Sci. Chem.* **1975**, *5*,
703.

[31] B. L. Rivas, E. Sanhueza, *Polym. Bull.* **1999**, *42*, 281.

[32] J. Kadokawa, K. Ikuma, H. Tagaya, *Eur. Polym. J.* **2002**, *38*,
7.

[33] R. Hoogenboom, M. W. M. Fijten, C. Brandli, J. Schroer,
U. S. Schubert, *Macromol. Rapid Commun.* **2003**, *24*, 98.

[34] T. Kagiya, T. Matsuda, R. Hirata, *J. Macromol. Chem. Sci.* **1972**,
6, 451.

[35] T. Kagiya, T. Matsuda, *J. Macromol. Chem. Sci.* **1971**, *5*, 1265.