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Accelerated pressure synthesis and characterization of 2-oxazoline block copolymers

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Abstract

The cationic ring-opening polymerization of 2-oxazolines in acetonitrile was investigated under pressure conditions utilizing methyl tosylate as initiator of which the single crystal X-ray structure is described as well. The polymerization kinetics were studied and compared with previously reported microwave-assisted pressure polymerizations. Moreover, a series of block copolymers was synthesized in an automated parallel synthesis robot utilizing this pressure polymerization method. The resulting block copolymers were characterized with both differential scanning calorimetry and contact angle measurements to determine the effect of copolymer composition on glass transition temperature, melting point and surface energy. Atomic force microscopy was applied to further investigate the possible phase separation.

Keywords: Cationic polymerization; Living polymerization; Ring-opening polymerization

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1. Introduction

The living cationic ring-opening polymerization (CROP) of 2-oxazolines was first reported in 1966–67 [1–4]. The polymerization can be initiated by electrophiles such as benzyl bromide, methyl iodide, methyl tosylate or methyl triflate [5,6]. The formed oxazolinium species is prone to nucleophilic attack of the next monomer resulting in ring-opening at the C–O bond and formation of the poly(2-oxazoline) as depicted in Scheme 1. When all monomer is consumed, a second monomer can be added to synthesize block copolymers or a nucleophile can be added to introduce a functional end-group (Scheme 1 depicts the addition of water as terminating agent). The properties of the resulting poly(2-oxazoline)s can be varied by changing the substituents [4,7]. Methyl and ethyl side-groups result in water soluble polymers, whereas longer alkyl chains or aromatic side chains result in hydrophobic polymers. As a result, amphiphilic block copolymers are easily accessible [8–10]. These (amphiphilic) poly(2-oxazoline)s are an interesting class of polymers [11,12] for applications as compatibilizers [13], emulsifiers [14,15] or dispersants [16]. Moreover, poly(2-oxazoline)s have been used for micellar catalysis [17], the preparation of hollow nanotubes [18] and for the modification of enzymes [19,20].

A serious disadvantage of the cationic ring-opening polymerization of 2-oxazolines are the long reaction times from several hours [21] up to several weeks [22] to reach full conversion. However, recently this disadvantage has been overcome by applying microwave irradiation to heat the polymerization mixture, which reduced the polymerization time to several minutes under superheated conditions (heating beyond the boiling point of acetonitrile under pressure conditions) [23–26]. Since microwave-assisted synthesis is not a common method in polymer research laboratories (yet), we were interested to develop a fast polymerization process for the cationic ring-opening polymerization of 2-oxazolines that excludes the usage of microwave irradiation. Therefore, we investigated the cationic polymerization of 2-oxazolines under superheated conditions utilizing conventional heating. These investigations were performed in an automated synthesis robot equipped with pressure reactors. Moreover, a series of amphiphilic block copoly(2-oxazoline)s was prepared under

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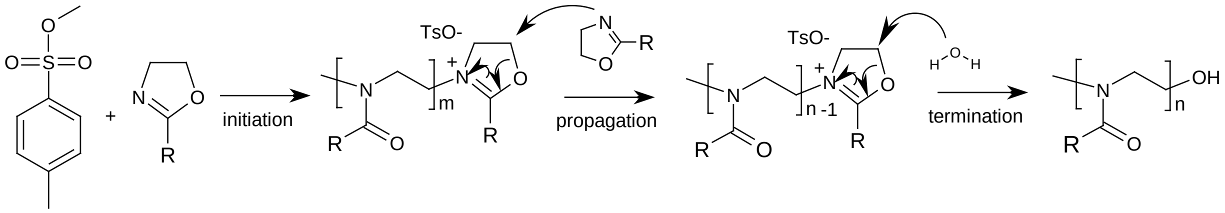

Scheme 1. Reaction mechanism for the cationic ring-opening polymerization of 2-oxazolines utilizing methyl tosylate as initiator.

pressure with conventional heating utilizing the synthesis robot.

2. Experimental part

2.1. Materials and instrumentation

Acetonitrile (Biosolve Ltd) and butyronitrile (Aldrich) were dried over molecular sieves (size 3 Å). 2-Methyl-2-oxazoline (Aldrich), 2-ethyl-2-oxazoline (Aldrich), 2-phenyl-2-oxazoline (Henkel), 2-nonyl-2-oxazoline (Henkel) and methyl tosylate (Aldrich) were distilled and stored under argon. The 2-oxazolines were distilled over barium oxide (Aldrich).

Pressure reactions were carried out on a computer controlled Chemspeed Accelerator SLT100 automated synthesizer equipped with an array of pressure reactors (16 parallel reaction vessels of 13 mL) and the reflux polymerizations were performed on a Chemspeed ASW2000 synthesis robot equipped with an array of glass reactors (16 parallel reaction vessels of 13 mL)[27]. The reaction vessels have a heating jacket, which was connected to a Huber Unistat Tango (−40 to 145 °C). Agitation was performed by a vortex movement of the reactors. An inert atmosphere was maintained by applying a 1.1 bar argon flow over the reactors and a 1.5 bar argon flow through the hood of the automated synthesizer. External pressure was applied to the reactors from a nitrogen gas cylinder (Hoekloos, 99.9% purity).

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-10A 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 a chloroform: triethylamine: 2-propanol (94:4:2) mixture as eluent at a flow rate of 1 mL/min. The molecular weights were calculated against polystyrene standards. GPC analysis of the largest poly(2-methyl-2-oxazoline) containing block copolymers were measured on a Waters system consisting of an isocratic pump, solvent degasser, column oven, 2414 refractive index detector, 717plus autosampler and a Styragel HT 4 GPC (DMF/5 mM NH_4PF_6, 50 °C, flow rate of 0.5 mL/min, PEG calibration). ^{1}H NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 on a Varian Mercury 400 or a Varian Gemini 300 spectrometer, whereby the chemical shifts are given in ppm relative to TMS or residual solvent signals.

Thermal transitions were determined on a DSC 204 F1 Phoenix by Netzsch under a nitrogen atmosphere from −100 °C to 200 °C with a heating and cooling rate of 40 K/min for the glass transition temperature and a heating rate of 10 K/min for the melting temperature (the initial first heating run was not considered for the subsequent calculations). Contact angle measurements were performed on polymer films that were prepared by spincoating of chloroform solutions (20 mg/mL) of the polymers on pre-cleaned microscopy slides at 1000 rpm during 90 seconds using a WS-400/500 series spin coater from Laurell Technologies Corporation. An OCA30 optical contact angle measuring instrument from Dataphysics was used to determine the contact angles of both diiodomethane and ethylene glycol as apolar and polar testliquids, respectively. AFM images were recorded on a Nanoscope IIIa Multimode scanning force microscope (SFM) of Digital Instruments. Images of spincoated polymer films were obtained in tapping mode with standard silicon SFM tips using a typical force constant of 0.6–1.75 N/m (NSG36, obtained from Mikro Masch).

2.2. X-ray crystal structure refinement.

X-ray crystal structures were measured by mounting a selected crystals on a Bruker-AXS APEX diffractometer with a CCD area detector. Graphite-monochromated Mo-K_α radiation (71.073 pm) was used for the measurements. The nominal crystal-to-detector distance was 5.00 cm. A hemisphere of data was collected by a combination of three sets of exposures at 173 K. Each set had a different ϕ angle for the crystal, and each exposure took 20 s and covered 0.3° in ω. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied [28]. The cell dimensions were refined with all unique reflections. The structures were solved by direct methods (SHELXS97). Refinement was carried out with the full-matrix least-squares method based on F^2 (SHELXL97 [29]) with anisotropic thermal parameters for all non-hydrogen atoms. Details of the X-ray diffraction analysis can be found in the supporting material [30].

2.3. Parallel 2-ethyl-2-oxazoline pressure polymerizations

After one hour waiting time to flush the hood of the synthesizer with argon, the reaction vessels were heated to 120 °C, evacuated for 15 min and subsequently filled with argon. This procedure was repeated three times to create an inert atmosphere inside the reactors.

Four reactors were filled with EtOx (1.27 g, 12.8 mmol) and 1.9 mL of a MeOTs stock solution (0.11 M; 0.70 g MeOTs in 25.9 g acetonitrile), resulting in 3.2 mL reaction mixtures with 4 M EtOx (40 w%) and a monomer to initiator ratio of 60. From these reaction mixtures, zero time GC samples (75 μL aliquots) were taken and stored into 2 mL vials that were prefilled with chloroform saturated with water (1 mL). After applying a pressure of 15 bar to the reactors, the polymerization mixtures were heated to 120 °C or 140 °C (external temperature control: internal temperatures were 116 °C and 134 °C, respectively) for a predefined time. Subsequently, the reactors were cooled to 60 °C, the pressure was released and GC samples were withdrawn from the reaction mixtures (75 μL aliquots). The final polymerization mixtures were transferred into 8 mL vials that were prefilled with chloroform saturated with water (1 mL). Four different reaction times were investigated for 120 °C (10, 20, 30 and 40 min) and 140 °C (4, 8,12 and 16 min) utilizing this procedure. All final mixtures were analyzed by GC and GPC. The experiments at 120 °C were performed with two different heating rates (10 °C/min and 30 °C/min), whereas the experiments at 140 °C were performed with 30 °C/min.

2.4. Parallel 2-phenyl-2-oxazoline pressure polymerizations

The polymerizations of 2-phenyl-2-oxazoline were performed in a similar manner as the polymerizations of 2-ethyl-2-oxazoline.

Two reactors were filled with PhOx (1.1 g, 7.5 mmol) and 1.4 mL of a MeOTs stock solution (0.091 M; 0.41 g MeOTs in 19 g acetonitrile), resulting in 2.5 mL reaction mixtures with 3 M PhOx (45 w%) and a monomer to initiator ratio of 60. After applying a pressure of 15 bar to the reactors, the polymerization mixtures were heated to 120 or 140 °C for a predefined time (for these polymerizations the temperature was controlled via a PT-100 temperature probe in a reference cell filled with PhOx). Subsequently, the reactors were cooled to 60 °C, the pressure was released and the polymerizations were quenched with water (100 μL). This procedure was repeated for four different reaction times (120 °C: 15, 25, 95 and 155 min; 140 °C: 15, 25, 35 and 50 min) after which all mixtures were characterized by ^{1}H NMR and GPC. As a consequence, the first quenched polymerization mixtures were heated three additional times to 120 °C before analysis.

2.5. Polymerizations in refluxing butyronitrile under ambient pressure

The reflux polymerizations were performed in a similar manner as the pressure polymerizations with the exception that samples were taken in time from one reflux polymerization, whereas separate pressure polymerization had to be performed for different reaction times.

The monomers, a solution of MeOTs in BCN and BCN, were transferred into the 13 mL reaction vessels resulting in 4 mL reaction mixtures with a [M]/[I] ratio of 60 and the same monomer concentrations as described above for the different monomers. The reactors were heated to 130 °C and vortexed at 600 rpm with the reflux condensers set to −5 °C. During these reflux polymerizations, samples were withdrawn from the polymerization mixtures automatically at predefined times. These samples were used for GC analysis to determine the polymerization kinetics.

2.6. Parallel chain extension and block copolymerizations

The chain extension experiments and block copolymerizations were performed in a similar manner as the previously described homopolymerizations. The block copolymerizations are described in detail in this section. The chain extension experiments were performed in the same way with 2-ethyl-2-oxazoline as both first and second monomer.

Each block copolymerization was performed four times in parallel at a 2.5 g scale. After polymerization of the first block with 4 M monomer concentration at 120 °C (**1**, **3**, **6** and **8**: 40 min; **2**, **4**, **5**, **7**, **9** and **10**: 15 min), the reactors were cooled to 60 °C, samples (75 μL aliquots) were taken into 2 mL vials (prefilled with 1 mL chloroform saturated with water) and the second monomer was added. For the longer block copolymers **1**, **3**, **6** and **8**, a stock solution of the second monomer in acetonitrile was added (NonOx: 2 M; PhOx: 3 M), whereas the second monomer was added without dilution for the other block copolymers. The second block was polymerized at 120 °C as well (**1**, **3**, **6** and **8**: 30 min; **2**, **4**, **7** and **9**: 15 min), except for block copolymers **5** and **10** (140 °C; 15 min). For work-up, all four identical parallel polymerizations were added together, after it was verified by GPC that the final products were similar, and diluted with chloroform (50 mL). This chloroform solution was poured into *n*-hexane (250 mL) and the product was obtained as white solid upon evaporation to dryness.

3. Results and discussion

The cationic ring-opening polymerization of 2-oxazolines in acetonitrile was investigated under pressure conditions with conventional heating. The investigated polymerizations were performed at 120 and 140 °C in acetonitrile under 15 bar external nitrogen pressure. Methyl tosylate was utilized as initiator as depicted in Scheme 1. To eliminate side-reactions and termination reactions, which is a prerequisite to obtain a living polymerization, the monomers were purified by distillation over barium oxide, the solvent was dried on molecular sieves and the methyl tosylate was distilled without drying agent. Even though the methyl tosylate (MeOTs) is supplied as viscous oil, it crystallized after distillation indicating the enhanced purity of the initiator. From this bulk crystallization, single crystals suitable for X-ray analysis were obtained [30]. The observed molecular structure (ORTEP-plot) and the packing diagram are displayed in Fig. 1. The packing diagram shows that the molecules are packed in an optimal space filling order, without any π-stacking between the phenyl

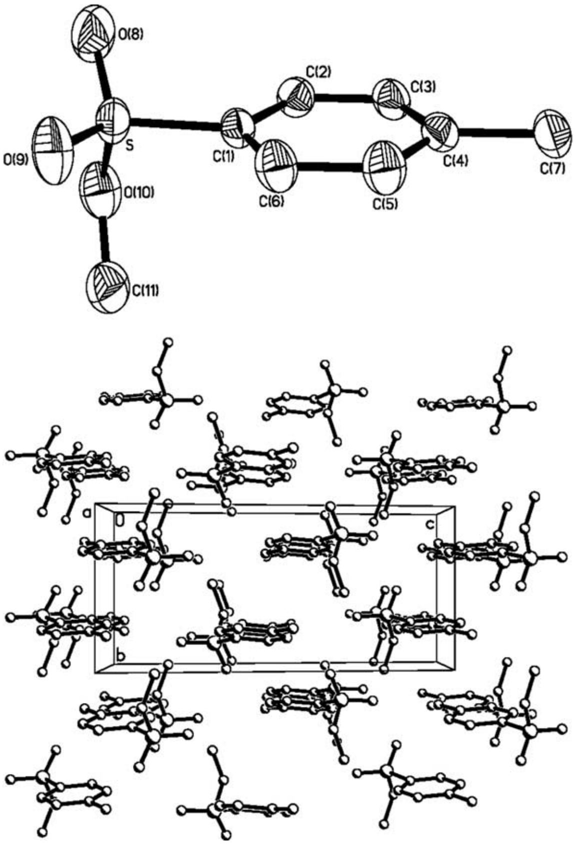

Fig. 1. ORTEP plot (50% probability, top) and packing diagram (bottom) of the structure of methyl tosylate. Hydrogen atoms are omitted for clarity.

rings. Bond lengths and angles of the structure can be found in the supporting material.

3.1. Pressure polymerization of 2-ethyl-2-oxazoline

The pressure polymerizations with conventional heating were performed in an automated Chemspeed Accelerator synthesis robot with external nitrogen pressure. First the cationic ring-opening polymerization of 2-ethyl-2-oxazoline (EtOx) was investigated. In one experimental run, four parallel polymerizations were performed with four different reaction times resulting in 16 different polymerizations. For each polymerization time, the monomer and initiator stock solutions in acetonitrile were transferred into the reactors resulting in 3.2 mL solutions with 4 M EtOx concentration in acetonitrile and a monomer to initiator ratio of 60. Subsequently, 15 bar nitrogen pressure was applied to the reactors and the reactors were heated to the set temperature, whereby the temperature was externally controlled resulting in internal reaction temperatures of 116 and 134 °C with set temperatures of 120 and 140 °C, respectively. After the predefined reaction time, the reactors were cooled to 60 °C, pressure was released and the reaction mixtures were transferred into sample vials that were prefilled with chloroform saturated with water to quench the polymerization. This procedure was repeated for four different reaction times to investigate the polymerization kinetics. The conversion of the polymerizations was determined with gas chromatography (GC) [31] and the molecular weight of the resulting polymers was analyzed by gel permeation chromatography (GPC). The obtained polymerization kinetics are plotted in Fig. 2. The first order kinetic plot (Fig. 2 left) shows very similar linear first order kinetics for the microwave polymerizations (solid lines [23]) and the conventional pressure polymerizations at 120 °C. Furthermore, conventional polymerizations at 140 °C showed a similar polymerization rate as the microwave-assisted polymerization (solid line) as well. However, the lower conversion at shorter polymerization times is due to slower heating (from 90 to 140 °C where the polymerization is already started) of the polymerization mixture with conventional heating. As a result, the effective polymerization time at 140 °C is overestimated resulting in too low conversions. In addition, the effect of the heating rate on the polymerization was investigated. This effect is especially interesting for up-scaling since at a larger scale the heating rate will be limited when using conventional heating. Therefore, the polymerization kinetics at 120 °C were investigated with both 10 °C/min (closed symbols) and 30 °C/

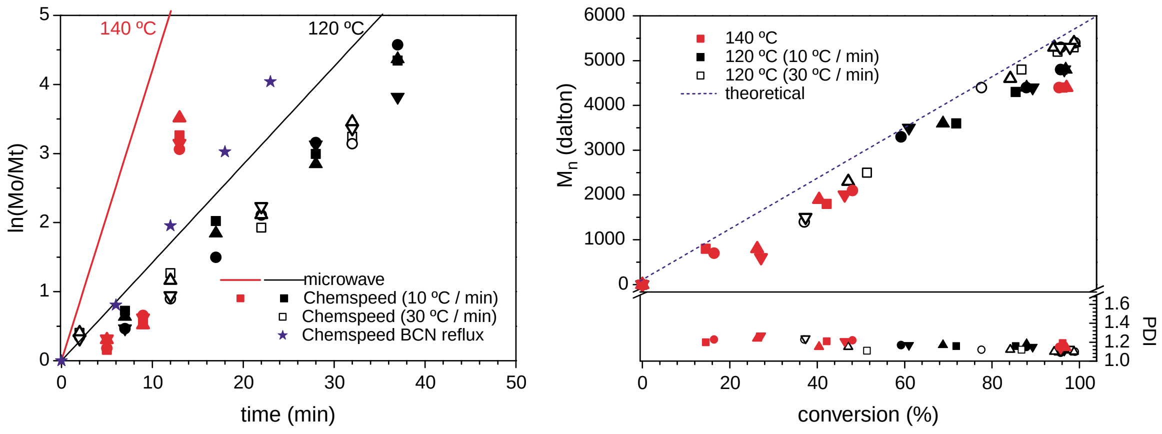

Fig. 2. Left: First order kinetic plot for the polymerization of 2-ethyl-2-oxazoline in acetonitrile under pressure [●, ■, ▲, ▼: 140 °C (heating rate = 30 °C/min); ●, ■, ▲, ▼: 120 °C (10 °C/min) and □ or □, ○, △, ▽: 120 °C (30 °C/min); external temperature control]. The solid lines represent microwave-assisted polymerization kinetics (internal temperature control) and the star symbols (★) show the comparison to reflux polymerizations at ambient pressure in butyronitrile (BCN). Right: Corresponding molecular weight (M_n) against conversion plots.

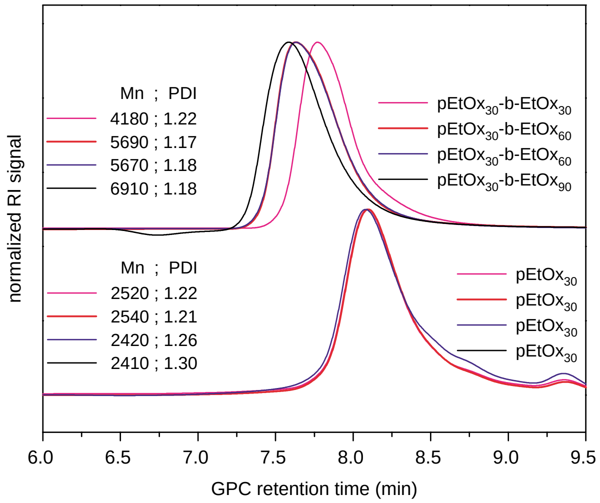

Fig. 3. GPC traces obtained for chain-extension experiments with EtOx in acetonitrile at 120 °C (GPC eluent: chloroform: triethylamine: 2-propanol = 94: 4:2).

min (open symbols) heating rates. The polymerization kinetics plotted in Fig. 2 left show the same trend for both heating rates, whereby it should be noted that t_0 was set to the point where the polymerization reached 90 °C. This result clearly demonstrates the possibility of up-scaling the pressure polymerization of 2-ethyl-2-oxazoline with conventional heating. The effect of pressure on the cationic ring-opening polymerization of 2-ethyl-2-oxazoline was investigated by comparison of the obtained results with a polymerization in refluxing butyronitrile (boiling point = 117 °C) at ambient pressure. The resulting kinetic data (Fig. 2 left; star symbols) demonstrate that the reflux polymerization has a similar polymerization rate as the microwave-assisted polymerization and a slightly higher rate than the conventional pressure polymerization due to its slightly lower temperature resulting from the external temperature control.

The cationic ring-opening polymerization of 2-ethyl-2-oxazoline in superheated acetonitrile at different polymerization temperatures and at different heating rates revealed a linear increase of number average molecular weight (M_n) with conversion demonstrating the living nature of the polymerization (Fig. 2 right). Moreover, narrow molecular weight distributions were obtained (polydispersity indices (PDI’s) < 1.20). The livingness of the polymerizations under pressure was further investigated by chain extension experiments. After polymerization of a first portion of EtOx, the reactors were cooled to 60 °C and a second portion of EtOx was added. Fig. 3 shows the GPC traces before and after chain extension. These traces and the corresponding M_n and polydispersity indices (PDI) prove the livingness of the polymerization by successful chain extension. Moreover, the good reproducibility of the polymerizations is verified by the perfect overlap of the two traces of p(EtOx$_{30}$-*b*-EtOx$_{60}$).

3.2. Pressure polymerization of 2-phenyl-2-oxazoline

In addition to the polymerization of EtOx, the polymerization of 2-phenyl-2-oxazoline (PhOx) was investigated under pressure with conventional heating. PhOx was chosen as second monomer to investigate since it normally shows different (slower) polymerization kinetics due to stabilization of the oxazolinium species by the phenyl ring and due to the lower nucleophilicity of this monomer [11,32,33]. The polymerization kinetics of PhOx were investigated at 120 °C [34] and 140 °C in a similar manner as the polymerization of EtOx with 3 M PhOx concentration in acetonitrile and a monomer to initiator ratio of 60. However, the polymerizations were performed with internal temperature control and the finished polymerization mixtures were quenched with water instead of transferred to sample vials due to their high viscosity. As a result, the first quenched polymerization mixtures remained in the reactors and have been heated several times to 120 or 140 °C (see also Section 2). Moreover, the polymerization temperature was controlled by a PT-100 probe in a reference cell, whereby the t_0 was set to the moment that the set temperature was reached. Even though the first order kinetic plot (Fig. 4 left) does not show an ideal linear behavior

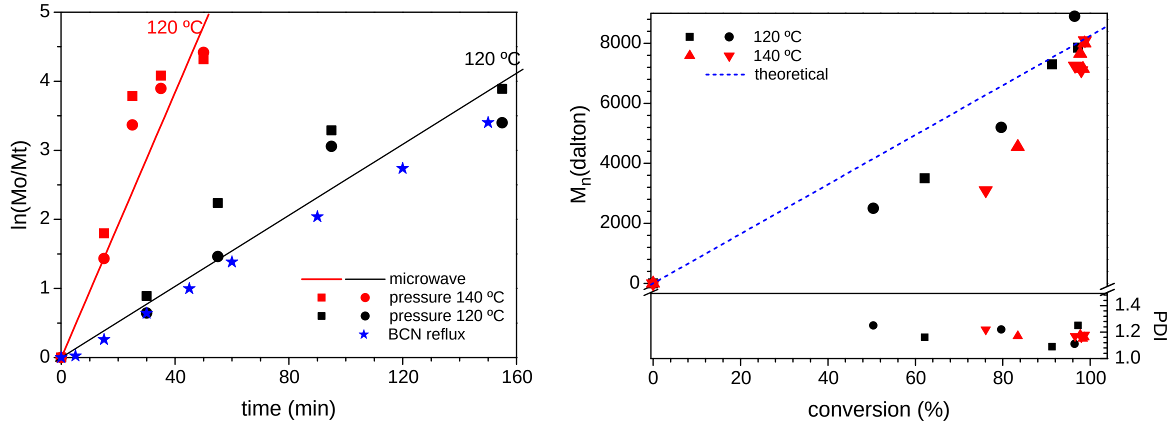

Fig. 4. Left: First order kinetic plot for the polymerization of 2-phenyl-2-oxazoline in acetonitrile under pressure [●, ■: 140 °C (heating rate = 30 °C/min) and ●, ■: 120 °C (30 °C/min); internal temperature control]. The solid lines represent microwave-assisted polymerization kinetics (internal temperature control) and the star symbols (★) show the comparison to reflux polymerizations at ambient pressure in butyronitrile (BCN). Right: Corresponding molecular weight (M_n) against conversion plots.

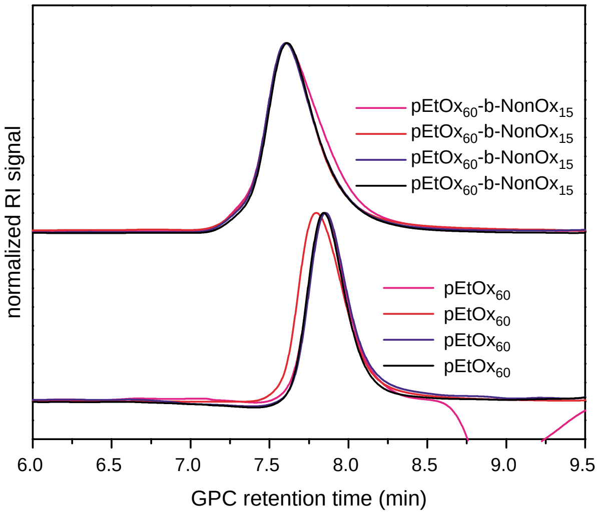

Fig. 5. GPC traces obtained for a representative set of block copolymerizations in acetonitrile at 120 °C, namely p($EtOx_{60}$-*b*-$NonOx_{15}$) **6** (GPC eluent: chloroform: triethylamine: 2-propanol = 94:4:2).

for both temperatures, the trend in the polymerization speed is very comparable with the microwave-assisted polymerizations (solid lines [24]). The $\ln([M]_0/[M]_t)$ values level slightly off above three (corresponding to 95% conversion), which might be due to insufficient stirring of the viscous mixture by the vortex shaking. Also for the polymerization of PhOx, an increase of M_n with conversion was observed with narrow molecular weight distributions (PDI <1.20) demonstrating the living nature of the polymerization. The observed polymerization kinetics under pressure conditions (both conventional and microwave) are comparable to the polymerization rate of the 2-phenyl-2-oxazoline polymerization in refluxing butyronitrile (Fig. 4 left; star symbols [34]), which demonstrates that the observed acceleration of the polymerization is a temperature effect and not a pressure effect.

3.3. Block copolymerizations of 2-oxazolines under pressure

In the previous two sections, it was demonstrated that both EtOx and PhOx can be successfully polymerized under pressure with conventional heating resulting in very fast living cationic ring-opening polymerizations: full conversion was reached within 15 min polymerization time for EtOx and within 50 min for PhOx. In a next step, the synthesis of a series of amphiphilic block copolymers with a large content (~ 70 w%) of a water-soluble 2-methyl-2-oxazoline (MeOx) or EtOx first block and a small content (~30 w%) of a hydrophobic 2-nonyl-2-oxazoline (NonOx) or PhOx second block. For all these combinations both a long (~70 monomer units) and a short copolymer (~30 monomer units) were synthesized to investigate the effect of polymer length on the polymer properties.

The block copolymers were synthesized comparable to the chain extension experiments of EtOx. After polymerization of the first block, the reaction mixtures were cooled to 60 °C and the second monomer was added after which the temperature was increased again to 120 °C. For the longer copolymers (~70 monomer units) the second block was added as stock solution in acetonitrile to prevent too viscous solutions, whereas for the short block copolymers the second monomer was added as pure liquid. Each block copolymerization was performed four times in parallel to check the reproducibility resulting in total in 10 g of final product. Fig. 5 depicts the GPC traces obtained for the first block and the block copolymers of p($EtOx_{60}$-*b*-$NonOx_{15}$) **6** demonstrating the successful synthesis and the good reproducibility of the block copolymerizations. The M_n and PDI data obtained by GPC for all different block copolymerizations are depicted in Fig. 6. All GPC analysis were performed with chloroform as eluent, except for block copolymers **1** and **3** (DMF), because the longer pMeOx segments show strong interactions with the column material (these column interactions were already observed previously

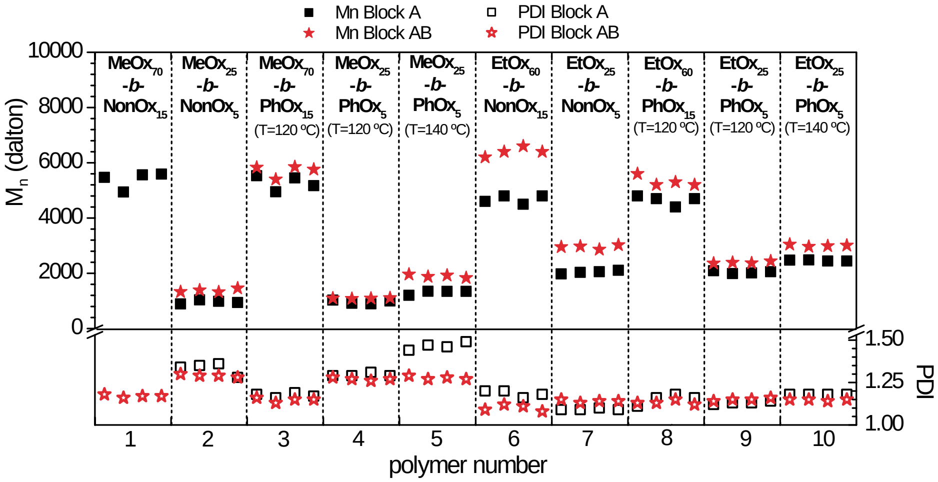

Fig. 6. GPC data for all sets of block copolymers that were synthesized under pressure in acetonitrile at 120 °C or 140 °C (only some PhOx blocks). All measured were performed with chloroform: triethylamine: 2-propanol = 94:4:2 as eluent except for polymer series **1** and **3** which were measured with DMF (containing 5 mM NH_4PF_6) as eluent. The AB block copolymers of series **1** could not be measured with chloroform (column interactions) neither with DMF (insoluble).

Table 1
Structural characterization of the synthesized block copolymers

Polymer	Monomer A	Monomer B	$DP_{A,th}$	$DP_{B,th}$	$DP_{A,NMR}$	$DP_{B,NMR}$	$M_{n,AB,,th}$	$M_{n,AB,GPC}$	PDI
1	MeOx	NonOx	70	15	64	15	8950	4600[a]	1.20[a]
2	MeOx	NonOx	25	5	23	4	3150	1370±60	1.29
3	MeOx	PhOx	70	15	64	2	8200	5710±210[a]	1.15[a]
4	MeOx	PhOx	25	5	22	2	2900	1100±10	1.27
5	MeOx	PhOx	25	5	21	5	2900	1900±60	1.30
6	EtOx	NonOx	60	15	52	13	9000	6400±160	1.10
7	EtOx	NonOx	25	5	27	4	3500	2950±70	1.14
8	EtOx	PhOx	60	15	52	3	8250	5330±190	1.13
9	EtOx	PhOx	25	5	21	1	3250	2400±40	1.15
10	EtOx	PhOx	25	5	21	4	3250	3000±40	1.15

All polymers (except **1** and **3**) were measured with $CHCl_3$:NEt_3:2-PrOH (94:4:2) as eluent.

[a] Measured with DMF containing 5 mM NH_4PF_6 as eluent (PEG calibration).

[24]). These interactions are also present for the shorter pMeOx first blocks of **2**, **4** and **5** resulting in higher PDI values. However, for these short MeOx containing block copolymers the non-interacting second block is sufficient to overrule these interactions resulting in reliable GPC data with chloroform as eluent. For p($MeOx_{70}$-*b*-$NonOx_{15}$) **1** the final molecular weight data are missing in Fig. 6 due to these column interactions when measuring in chloroform and due to bad solubility in DMF. Based on the good reproducibility of the GPC data obtained for the block copolymers, the four batches of each block copolymer were combined and final products were solidified from hexane. The theoretical composition, the composition calculated from ^{1}H NMR spectroscopy, the theoretical molecular weight and the obtained GPC data (M_n and PDI) of the ten different block copolymers **1–10** are summarized in Table 1. GPC analysis of a low concentrated sample of the combined batches of block copolymer **1** succeeded in DMF and the results are included in Table 1. The block copolymers **3**, **4**, **8** and **9** with PhOx as second block showed a low incorporation of PhOx at 120 °C, which is due to the low reactivity of PhOx in combination with insufficient polymerization time (15 min). Therefore, the block copolymerizations of the short PhOx containing polymers were repeated with a polymerization temperature of 140 °C for the second blocks resulting in full incorporation of the PhOx monomer (polymers **5** and **10**). The measured GPC data show a similar trend as the theoretical molecular weights, but they are systematically lower due to the lower monomer incorporation (from ^{1}H NMR spectroscopy). Moreover, the molecular weight of the MeOx containing polymers **2**, **4** and **5** is underestimated due to the column interactions.

3.4. Properties of the synthesized block copolymers

The thermal properties (glass transition temperature T_g and melting temperature T_m) and the surface properties of the synthesized copolymers were determined to investigate the effect of the different monomers and the length of the polymer on the final properties. The thermal properties were measured by differential scanning calorimetry (DSC) and the surface energy was calculated from contact angle measurements (see experimental part). The obtained bulk T_g's and T_m's and the surface energies (SE's) of spincast films (non-annealed) are summarized in Table 2 and, for comparison, the literature data for T_g, T_m [35] and SE [36] of the four homopolymers pMeOx, pEtOx, pNonOx and pPhOx are also included. In addition, the polymer

Table 2
Thermal properties and surface energy of the synthesized block copolymers

Polymer	Monomer A	Monomer B	$DP_{A,NMR}$	$DP_{B,NMR}$	w% B	$T_{g,DSC}$	$T_{m,DSC}$	Surface energy
1	MeOx	NonOx	64	15	35.2	75 °C	142 °C	34.9±0.3
2	MeOx	NonOx	23	4	28.7	71 °C	–	29.9±0.4
3	MeOx	PhOx	64	2	5.1	76 °C	–	43.7±0.5
4	MeOx	PhOx	22	2	13.6	70 °C	–	42.2±0.5
5	MeOx	PhOx	21	5	29.2	69 °C	–	42.3±0.5
6	EtOx	NonOx	52	13	36.7	44 °C	122 °C	43.3±0.2
7	EtOx	NonOx	27	4	25.6	41 °C	–	38.7±0.5
8	EtOx	PhOx	52	3	9.1	58 °C	–	47.1±0.2
9	EtOx	PhOx	21	1	7.6	58 °C	–	45.0±0.4
10	EtOx	PhOx	21	4	24.8	57 °C	–	47.2±0.4
pMeOx[a]	MeOx	–	100	–	–	79 °C	–	44.1
pEtOx[a]	EtOx	–	100	–	–	59 °C	–	46.4
pNonOx[a]	NonOx	–	100	–	–	–	147 °C	22.2
pPhOx[a]	PhOx	–	100	–	–	107 °C	–	45.9

[a] Values reported in literature: thermal properties [35] and surface energy [36].

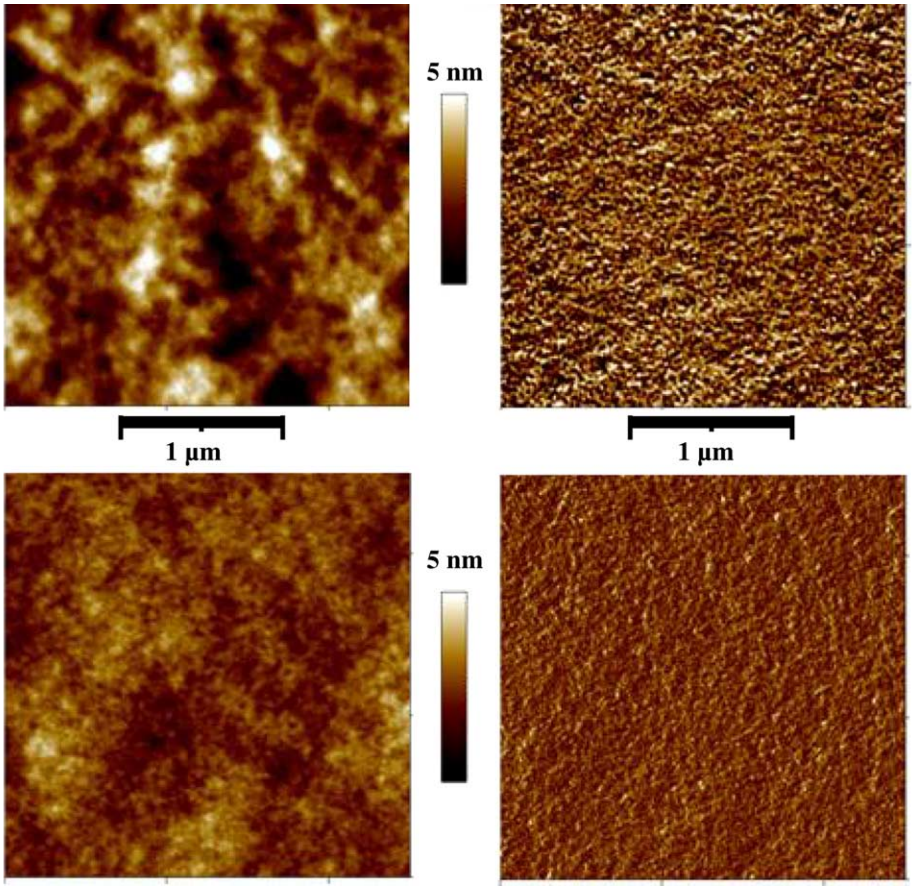

Fig. 7. AFM topography (left) and phase (right) images of the p($MeOx_{70}$-*b*-$NonOx_{15}$) **1** (top) and p($EtOx_{60}$-*b*-$NonOx_{15}$) **6** (bottom) block copolymers.

composition determined by ^1H NMR spectroscopy [37] and the weight percent of hydrophobic monomer are also summarized (Table 2). The pNonOx shows rather different properties than the other three homopolymers: The pNonOx does not show a glass transition and it is the polymer that exhibits a melting point [35]. In addition, a significantly lower SE is observed for pNonOx when compared to the other three homopolymers due to preferential orientation of the nonyl chains towards the surface [36]. Therefore, a large influence on thermal and surface properties is expected upon incorporation of NonOx as second block. Indeed, the two block copolymers **1** and **6** that contain a large NonOx segment are the only block copolymers that showed a melting point. The melting point of the p(MeOx-*b*-NonOx) **1** (142 °C) is much closer to the pNonOx melting point (147 °C) than the p(EtOx-*b*-NonOx) **6** melting point (122 °C). This difference can be explained by more effective phase separation in the case of the p(MeOx-*b*-NonOx) resulting in larger crystalline pNonOx domains and partial mixing of the two blocks in the case of p(EtOx-*b*-NonOx). This hypothesis is further confirmed by the glass transition temperatures: The T_g of **1** is close to the T_g of pMeOx, whereas the T_g of **6** is lower than the T_g of pEtOx. This different phase separation behavior of polymers **1** and **6** was further investigated by atomic force microscopy (AFM). Topography (left) and phase (right) images were recorded from spincoated polymer films in tapping mode as depicted in Fig. 7. The p(MeOx-*b*-NonOx) **1** showed large features in the topography image and a more pronounced contrast in the phase image (Fig. 7, top images) indicating a phase separation. In contrast, the p(EtOx-*b*-pNonOx) **6** showed a smooth film with only little phase contrast demonstrating the absence of significant phase separation. These results also emphasize the difference between these MeOx (**1**) and EtOx (**2**) containing block copolymers. Apparently, the more flexible ethyl side-chains of the EtOx are better compatible with the long flexible nonyl side-chains than the short methyl side-groups of the MeOx.

When a shorter NonOx segment is built-in while retaining the 30 w% fraction of NonOx (polymers **2** and **7**), amorphous polymers are obtained: The small number of NonOx units per chain cannot orient into a crystalline phase. However, the NonOx has a similar effect on the T_g of the shorter polymers **2** (T_g close to the T_g of pMeOx) and **7** (T_g lower than the T_g of pEtOx) as it has on the T_g of the longer block copolymers **1** and **6**. Furthermore, the more effective phase separation for p(MeOx-*b*-NonOx) **1** and **2** when compared to p(EtOx-*b*-NonOx) **6** and **7** is also expressed in the surface energy of thin films: The MeOx containing block copolymers show lower SE's than the EtOx containing block copolymers. Moreover, the shorter block copolymers **2** and **7** show lower SE's than the longer copolymers **1** and **6** even though they have a lower

NonOx content. This difference is most likely due to the higher mobility of the shorter polymers that facilitate the orientation of the NonOx side chains to the surface.

The block copolymers with PhOx as second block **3–5** and **8–10** do not show such clear trends as the NonOx containing block copolymers. For all p(EtOx-*b*-PhOx) block copolymers **8-10** both T_g and SE are comparable with pEtOx. However, due to the small differences between pEtOx and pPhOx and due to the low number of PhOx units these results cannot conclusively be interpret as phase separation but they are a first indication in this direction. The p(MeOx-*b*-PhOx) block copolymers **3–5** show all similar SE's, but the T_g's are lower for the shorter copolymers **4** and **5** as is was also observed for the short p(MeOx-*b*-NonOx) **2**. These lower T_g's are most likely due to the short pMeOx segment, which might be in the range where the T_g depends on the molecular weight as it has been shown for polystyrene by Gibbs [38]. However, this effect was not observed for the short EtOx containing block copolymers. As a result, no clear conclusions can be drawn about possible phase separation for the p(MeOx-*b*-PhOx) and the p(EtOx-*b*-PhOx) block copolymers on the basis of the obtained results.

4. Conclusions

The living cationic ring-opening polymerization of 2-ethyl-2-oxazoline and 2-phenyl-2-oxazoline in acetonitrile could be accelerated using conventional heating under pressure conditions with methyl tosylate as initiator. The single crystal X-ray structure of methyl tosylate was successfully resolved. Kinetic investigations of the conventionally heated pressure polymerizations demonstrated a similar acceleration as previously reported for microwave-assisted pressure polymerizations. Moreover, the pressure polymerizations proceeded in a living manner resulting in polymers with narrow molecular weight distributions. The livingness of the 2-ethyl-2-oxazoline polymerization was further demonstrated by the possibility of chain extension.

The pressure polymerization procedure was applied for the synthesis of a series of block copolymers with a pMeOx or pEtOx as first block (∼70 w%) and a pNonOx or pPhOx as second block (∼30 w%). Ten different block copolymers were successfully synthesized in a reproducible manner (polymerizations were performed in quadruplicate in an automated synthesizer). The thermal (T_g and T_m) and surface (surface energy) properties of these block copolymers were determined by DSC and contact angle measurements, respectively. From these analyses, it could be concluded that p(MeOx-*b*-NonOx) phase separates to a large extend, whereas p(EtOx-*b*-NonOx) does not exhibit such clear phase separation. This difference in phase separation was further confirmed by topography and phase images determined by AFM. For the PhOx containing block copolymers, no definite conclusions could be drawn about a possible phase separation.

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