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ARTICLE

Rational Design of an Amorphous Poly(2-oxazoline) with a Low Glass-Transition Temperature: Monomer Synthesis, Copolymerization, and Properties

Kristian Kempe,[†] Stefan Jacobs,[‡] Hanneke M. L. Lambermont-Thijs,[‡,§] Martin M. W. M. Fijten,[‡,§] Richard Hoogenboom,*[,‡,§] and Ulrich S. Schubert*[,†,‡,§]

[†]*Laboratory of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Humboldtstr. 10, 07743 Jena, Germany,* [‡]*Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, Den Dolech 2, 5612 AZ Eindhoven, The Netherlands, and* [§]*Dutch Polymer Institute (DPI), John F. Kennedylaan 2, 5612 AB Eindhoven, The Netherlands*

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ABSTRACT: A new poly(2-alkyl-2-oxazoline) having a branched side chain, namely, 2-(3-ethylheptyl)-2-oxazoline (**EHOx**), was synthesized. The microwave-assisted homopolymerization as well as the copolymerization with 2-ethyl-2-oxazoline (**EtOx**) are reported, whereby the determination of the reactivity ratios indicates the occurrence of a random polymerization. Further studies were performed regarding the thermal and the surface properties. p(**EHOx**) showed a glass transition of −6 °C, whereas no melting temperature could be detected, representing the amorphous poly(2-oxazoline) with the lowest reported T_g to date. Furthermore, the systematic random copolymerization with **EtOx** in the range from 0 to 100% **EHOx** revealed a linear dependence of T_g with composition as well as a complex dependence of the surface energy on the composition showing two plateau regimes.

Introduction

In the last years, the interest and activity on the preparation of well-defined (co)polymers with fine-tunable properties resulting in versatile applications has increased significantly. A perfectly suited class of polymers that fulfills these criteria are the poly(2-oxazoline)s, which can be prepared by a living cationic ring-opening polymerization (CROP) of 2-oxazolines. The easy variation of the side chain of the resulting polymer as well as their biocompatibility make them perfectly suitable for a range of potential applications including stabilizers, surfactants, compatibilizers and thermosettings[1−3] and as component in hair dressing formulations or impregnants for paper and textiles.[4−6] The CROP of 2-oxazolines was first reported in 1966 by four independent groups.[7−10] Methyl tosylate was found to be one of the initiators in the CROP of 2-oxazolines, which can attack the monomer under the formation of an oxazolinium species. Possessing a weakened CO bond, the "activated" monomer is prone to undergo a nucleophilic attack of the nitrogen of another monomer.[11−13] The resulting propagating species is growing either as long as monomer is available or up to the addition of a nucleophile to the reaction mixture, which can terminate the polymerization. Because of the living character of this polymerization, the incorporation of a second monomer into the polymer chain after the full consumption of the first monomer yields well-defined block copolymers.[14−16] A schematic representation of the copolymerization mechanism is depicted in Scheme 1. Furthermore, the CROP of 2-oxazolines is characterized by the absence of chain transfer and termination reactions under appropriate conditions, allowing the preparation of polymers with narrow molar mass distributions, as indicated by low polydispersity index (PDI) values.

Nowadays, a large number of various 2-substituted-2-oxazolines are known, ranging from alkyl- and aryl-substituted 2-oxazolines[7,17] to 2-oxazolines with more complex substituents such as, for example, amino,[18] aldehyde,[19] fluorinated,[20] and thioether groups.[21] Among them, the polymerization of 2-(*n*-alkyl)-2-oxazoline was intensively investigated and, in particular, the polymerization behavior and the thermal as well as surface properties of the resulting polymers were studied. Poly(2-oxazoline)s with a linear side chain containing less than five carbon atoms were found to show amorphous behavior, whereas longer side chains resulted in the formation of crystalline polymers. To date, no amorphous poly(2-oxazoline) with a low glass-transition temperature is available, even if poly(2-*n*-butyl-2-oxazoline) shows a T_g of ~13 °C. Although, an appearing melting point after annealing indicates the semi-crystalline character of the polymer.

The preparation of low T_g polymers is desirable in many respects. Adopting the behavior of natural rubber (amorphous behavior and a glass transition below room temperature) polymers with rubberlike properties can be synthesized, having various applications, such as the usage in car tires, engine mountings and inflatable boats.[22] Furthermore, an amorphous low T_g block itself possesses the ability to improve the phase separation between two blocks in a block copolymer which may result in a self-assembly of the block copolymer.[23,24] As such, the availability of a low T_g amorphous poly(2-oxazoline) would expand the application possibilities and might improve the self-assembly behavior of poly(2-oxazoline)s.[25]

Here we report for the first time the synthesis of an amorphous poly(2-oxazoline) with a glass transition temperature below 0 °C. The aim of this contribution is to describe the synthesis as well as the microwave-assisted homopolymerization of a new branched

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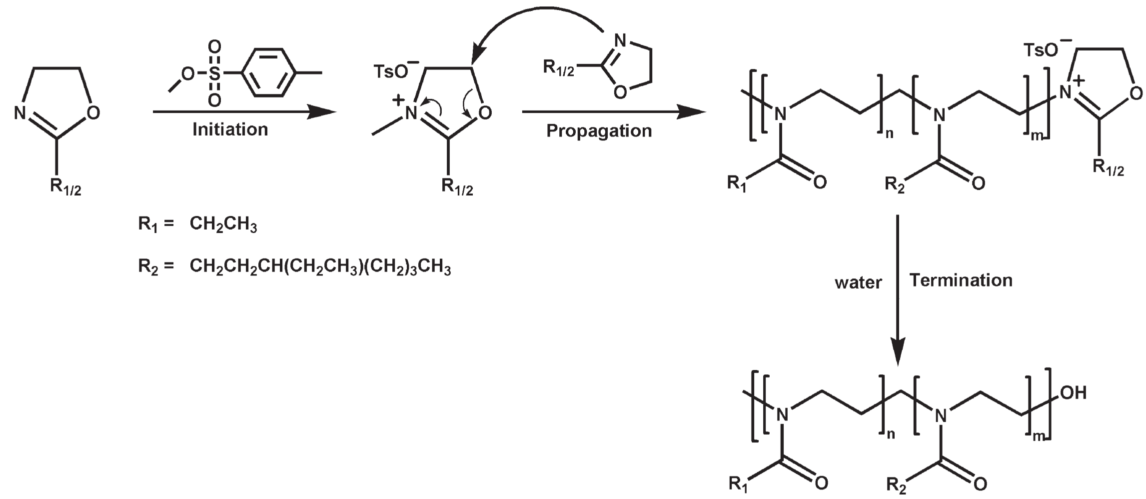
*Corresponding authors. (U.S.S.) E-mail: ulrich.schubert@uni-jena.de. Fax: +49 3641 948 202. (R.H.) E-mail: r.hoogenboom@tue.nl.

Scheme 1. Schematic Representation of the Mechanism of the Cationic Ring-Opening Copolymerization of 2-Oxazolines



2-alkyl-2-oxazoline, namely, the 2-(3-ethylheptyl)-2-oxazoline **EHOx**. Furthermore, the statistical copolymerization with EtOx is presented. In addition, the kinetic parameters and reactivity ratios as well as the dependence of the thermal transitions and the surface energies (SEs) on the composition of the copolymer were investigated.

Experimental Part

Materials. 2-Ethylhexyl bromide, *n*-butyllithium, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) were purchased from Sigma-Aldrich and were used as received. 2-Methyl-2-oxazoline, 2-ethyl-2-oxazoline, and methyl tosylate were obtained from Acros and were distilled to dryness over barium oxide (BaO) and stored under argon.

General Methods and Instrumentation. The polymerizations were performed under microwave irradiation with temperature control in the Emrys Liberator single-mode microwave synthesizer from Biotage equipped with a noninvasive IR sensor (accuracy: ±2%). Microwave vials were heated to 110 °C overnight, allowed to cool to room temperature, and filled with argon before usage. Gas chromatography (GC) was measured on an Interscience Trace gas chromatograph with a Trace Column RTX-5 connected to a PAL autosampler. Size exclusion chromatography (SEC) measurements were performed either 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 or 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). The molar masses were calculated against polystyrene standards. ^1H NMR and ^{13}C NMR spectra of the products were recorded on a Varian AM-400 spectrometer at room temperature in $CDCl_3$ or MeOH-d_4 as solvent. The chemical shifts are given in ppm relative to residual nondeuterated solvent signals. For the measurement of the MALDI spectra, an Ultraflex III TOF/TOF apparatus (Bruker Daltonics, Bremen, Germany) was used. The instrument was equipped with an Nd/YAG laser and a collision cell. All spectra were measured in the positive reflector or linear mode. The instrument was calibrated prior to each measurement with an external PMMA standard from PSS Polymer Standards Services GmbH (Mainz, Germany). Thermal transitions were determined on a DSC 204 F1 Phoenix by Netzsch under a nitrogen atmosphere from −100 to 220 °C with a heating rate of 20 K/min and a cooling rate of 40 K/min. (For the calculations, only the third heating curve of three runs was considered.) Contact angles were measured on thin polymer films that were prepared by spincoating of a chloroform solution with 2 wt % of the poly(2-oxazoline) on precleaned microscopy slides at 1000 rpm during 90 s using a WS400/500 series spin coater from Laurell Technologies Corporation. For the measurements using an OCA30 optical contact angle measuring instrument from Dataphysics, diiodomethane and ethylene glycol were used as apolar and polar test liquids, respectively.

Monomer Synthesis. *2-(3-Ethylheptyl)-2-oxazoline* (***EHOx***). The monomer was prepared by adapting the synthetic procedure for a related compound.[19] A solution of 8 g (0.069 mol) TMEDA in 300 mL of THF was cooled to −78 °C under an argon atmosphere. Within 30 min, 26 mL of *n*-butyllithium (2.5 M in hexane) were added, and the solution was stirred for 60 min. Subsequently, 5.8 g (0.068 mol) 2-methyl-2-oxazoline (**MeOx**) was added dropwise, and stirring was continued for another 2 h at −78 °C. After the addition of 11 g (0.057 mol) 2-ethylhexyl bromide, the solution was allowed to warm to room temperature overnight. The reaction was terminated after 25 h with 150 mL of methanol, and the solvents were evaporated under reduced pressure. The residue was dissolved in 100 mL of chloroform and 100 mL of $NaHCO_3$ solution, and the aqueous phase was extracted twice with 75 mL of chloroform. The combined organic phases were washed with water and brine. After drying over $MgSO_4$, the solvent was removed under reduced pressure, and the crude product was purified by distillation (69 °C, 8.3×10^{-2} Torr) to give 4.5 g (0.023 mol) (**EHOx**) in 34% yield. ^1H NMR (250 MHz, $CDCl_3$, 25 °C, δ): 0.86 (m, 6H, $C\mathit{H}_3$), 1.27 (m, 9H, $C\mathit{H}(C\mathit{H}_2CH_3)(C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3)$), 1.59 (m, 2H, $NCOCH_2C\mathit{H}_2$), 2.24 (t, 2H, $NCOC\mathit{H}_2CH_2$), 3.81 (t, 2H, $CNC\mathit{H}_2$), 4.2 (t, 2H, $COC\mathit{H}_2$). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, δ): 10.69, 14.07 (CH_3), 25.42, 25.52, 28.72, 29.27, 32.42, 38.5 (CH_2), 54.38 ($CN\mathit{C}H_2$), 67.1 ($COC\mathit{H}_2$), 169.01 ($\mathit{C}NCH_2$). MS (*m*/*z*): 196 (M^+), 165 (M^+-C_2H_5), 140 (M^+-C_2H_3NO), 85 (M^+-$C_6H_{10}NO$). Anal. Calcd: C, 59.02; H, 3.85; F, 20.75; N, 7.65. Found: C, 58.78; H, 4.00; N, 7.49.

Microwave-Assisted Homopolymerization of EHOx: Procedure. A stock solution containing initiator (methyl tosylate), monomer **EHOx**, and solvent (acetonitrile) was prepared. The monomer concentration was adjusted to 2 M, and a monomer-to-initiator ratio of 60 was used. The stock solution was divided over six polymerization vials that were capped under argon. For the calculation of the conversion, 3 GC samples were taken before the start of the polymerization, allowing the determination of the initial solvent to monomer ratio. The microwave vials were heated to 140 °C for different times in the microwave synthesizer. After cooling, the reaction was quenched by the addition of 50 μL of water. GC and GPC samples were prepared to determine the monomer conversion and the molar masses of

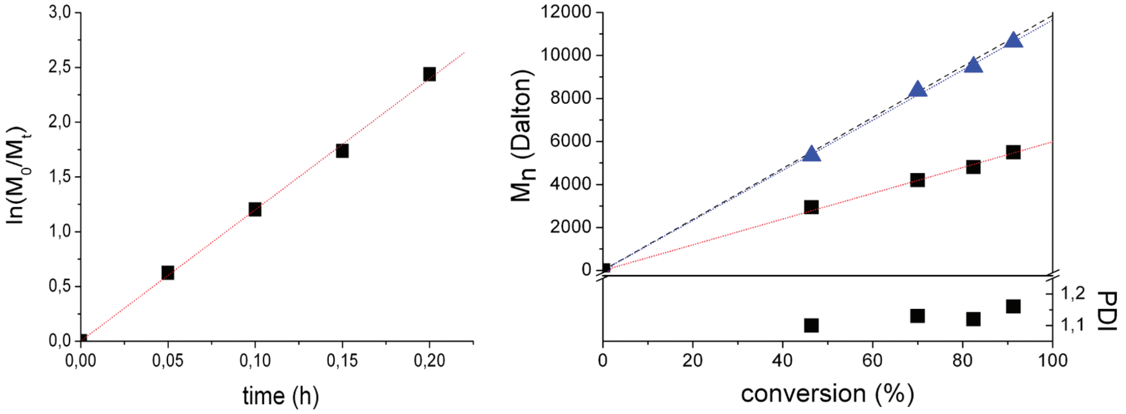
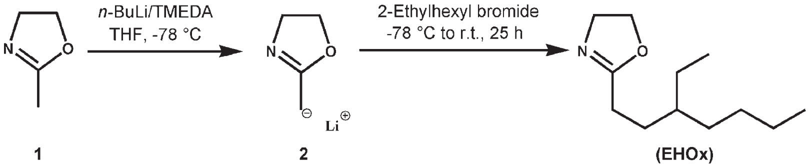


Figure 1. Homopolymerization of **EHOx** under microwave irradiation in acetonitrile at 140 °C using methyl tosylate as initiator. Left: First-order kinetic plot. Right: M_n and PDI value against conversion plot for the kinetic screening, determined by SEC (■) and MALDI-TOF MS (▲).

Scheme 2. Schematic Representation of the Reaction Scheme for the Synthesis of 2-(3-Ethylheptyl)-2-oxazoline (EHOx)



the polymer, respectively. For the calculation of the monomer conversion, the polymerization solvent was used as internal standard.

Microwave-Assisted Copolymerization of EtOx and EHOx: Procedure. For the kinetic studies, a stock solution of initiator (methyl tosylate), monomers (**EtOx** and **EHOx**), and solvent (acetonitrile) was prepared. The total monomer concentration was adjusted to 2 M, and a total monomer-to-initiator ([M]/[I]) ratio of 100 was applied, using different ratios of the monomers (80/20, 60/40, 40/60, 20/80). The stock solution was divided over six polymerization vials that were capped under argon. For the calculation of the conversion, three t_0 samples were taken and subsequently measured with GC. The vials were heated to 140 °C for different times in the microwave synthesizer. After cooling, the reaction was quenched by the addition of 50 μL of water. GC and GPC samples were prepared to determine the monomer conversion and the molar masses of the polymer, respectively. For the calculations of the monomer conversions, the polymerization solvent was used as internal standard.

Preparation of the Random Copolymers of EtOx and EHOx for the Property Studies. To evaluate the thermal and the surface properties, copolymers (**EtOx**/**EHOx**) with ratios from 0/100 to 100/0 were prepared. A polymerization solution containing initiator, appropriate amounts of monomers, and solvent was irradiated in the microwave for a precalculated time to reach full consumption. The full consumption of both monomers was assured by ^{1}H NMR spectroscopy, and the resulting polymer was either precipitated in ice-cold diethyl ether or dried under reduced pressure to remove the residual monomer and solvent.

Results and Discussion

Monomer Synthesis. The synthesis procedure of the 2-(3-ethylheptyl)-2-oxazoline (**EHOx**) was based on a synthesis route for 2-substituted-2-oxazolines that was recently reported in literature;[19] the procedure is depicted in Scheme 2. In a nucleophilic substitution, the anion of an already existing 2-oxazoline, namely, 2-methyl-2-oxazoline (**MeOx**), attacks 2-ethylhexyl bromide under the formation of the chain extended monomer **EHOx**. In a first step, the nucleophile was generated using *n*-butyllithium (*n*-BuLi) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA). To prevent a multiple substitution of the MeOx, *n*-BuLi was added equimolar to the reaction mixture, which was cooled to −78 °C and stirred for 2 h. Subsequently, 2-ethylhexyl bromide was added dropwise, and the reaction solution was allowed to warm to ambient temperature. Meanwhile, the progress of the reaction was monitored using GC-MS measurements, and the reaction was found to be completed after 25 h. After several washing steps, the crude product was purified by distillation. As mentioned above, an excess of *n*-BuLi led to the doubly negatively charged **MeOx**-anion, which is able to attack two 2-ethylhexyl bromides under the formation of a more branched 2-oxazoline, which was also isolated in a minor amount as indicated by ^{1}H NMR spectroscopy and elemental analysis (results not included).

Homopolymerization of EHOx. 2-Oxazolines exhibit the ability to undergo a ring-opening polymerization when reacted with an electrophilic agent. As was shown, this polymerization exhibits a living character under appropriate conditions, as indicated by the absence of chain transfer and termination reactions, which can be demonstrated by linear first-order kinetics, narrow molar mass distributions combined with low PDI values, and a continuous growth of the polymer chains with monomer conversion.[1,3] In view of (block) copolymers, the living manner of the polymerization of each monomer has to be shown, assuring the existence of “living” chain ends, which are necessary for the propagation of the polymer chain during the polymerization as well as for the addition of the second monomer. To obtain the polymerization kinetic for **EHOx**, a polymerization mixture containing a defined amount of initiator, monomer and solvent was prepared and divided over six polymerization vials. Each vial was exposed to microwave irradiation at 140 °C, and subsequent GC and SEC investigations allowed the determination of the monomer conversions and the molar masses of the synthesized polymers before purification. The resulting first-order kinetic plot is shown in Figure 1 left. The linear increase in the ln([M]$_0$/[M]$_t$) with time demonstrates a constant concentration of propagating species indicative of a living polymerization mechanism of the 2-oxazolines. The polymerization rate (k_p) was determined from the slope of

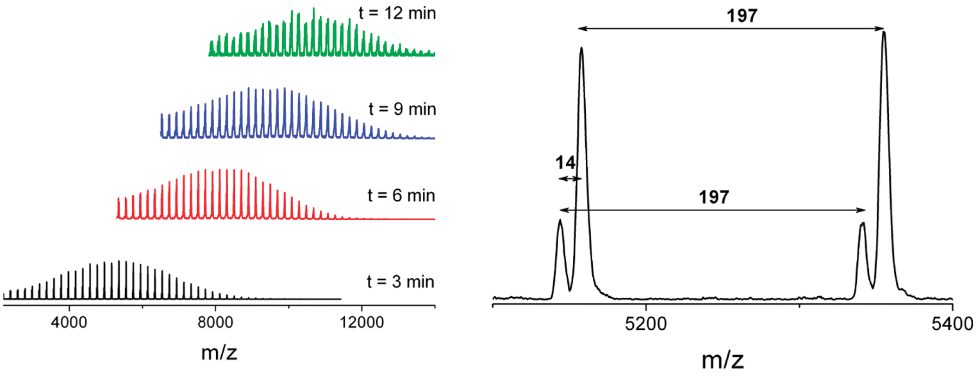


Figure 2. MALDI-TOF MS spectra (matrix: DCTB; ionization salt: NaI; solvent: CHCl$_3$) of p(**EHOx**) with increasing polymerization time (left). In the expanded spectrum the monomer unit is reflected in the distance between two peaks (right).

Table 1. Kinetic Data for the Copolymerizations of EtOx and EHOx with Different Ratios of the Monomers

	EtOx$_{80}$-*r*-EHOx$_{20}$				EtOx$_{60}$-*r*-EHOx$_{40}$			
time [s]	EtOx [%]^a	EHOx [%]^a	M_n [g mol^{-1}]^b	PDI^b	EtOx [%]^a	EHOx [%]^a	M_n [g mol^{-1}]^b	PDI^b
2.5	41.43	41.57	2760	1.17	42.47	40.26	3230	1.21
5	61.63	63.06	4220	1.17	59.60	58.68	4600	1.18
7.5	71.98	73.39	5040	1.17	73.45	74.61	5750	1.16
10	81.55	82.74	5790	1.16	82.43	82.44	6110	1.19
12.5	88.66	89.96	6210	1.18	89.33	89.79	7040	1.17
15	92.48	92.79	6400	1.20	95.40	95.78	7100	1.22

	EtOx$_{40}$-*r*-EHOx$_{60}$				EtOx$_{20}$-*r*-EHOx$_{80}$			
time [s]	EtOx [%]^a	EHOx [%]^a	M_n [g mol^{-1}]^b	PDI^b	EtOx [%]^a	EHOx [%]^a	M_n [g mol^{-1}]^b	PDI^b
2.5	23.31	26.66	3640	1.19	39.24	40.67	4140	1.19
5	49.23	50.98	5120	1.19	62.65	64.43	5410	1.24
7.5	65.55	68.04	5760	1.24	77.47	74.83	5950	1.28
10	82.90	83.49	7060	1.20	84.33	86.13	6360	1.22
12.5	87.08	87.29	7210	1.22	89.03	89.48	6590	1.27
15	91.57	91.31	7700	1.20	93.97	93.89	7064	1.3

^{a}Conversion in percent. ^{b}SEC results (eluent: CHCl$_3$ with 2% isopropanol and 4% triethylamine; PS standards).

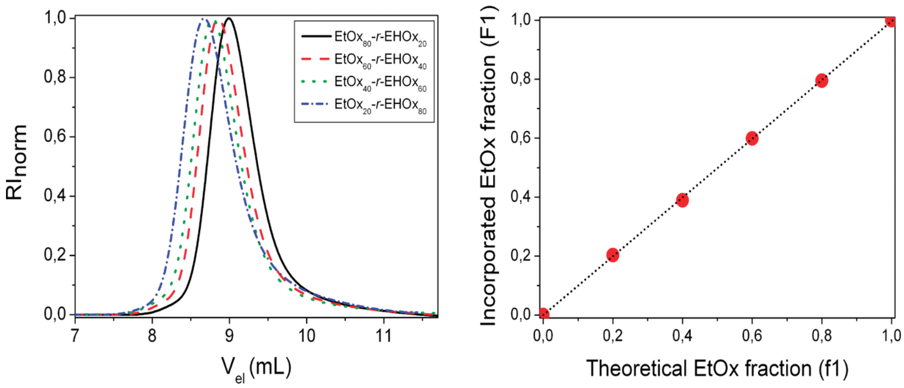


Figure 3. Left: SEC traces of the kinetic samples at 100% conversion of both monomers for different monomer ratios (eluent: CHCl$_3$ with 2% isopropanol and 4% triethylamine). Right: Relation between the fraction of EtOx in the monomer feed (F_1) and the incorporated fraction of EtOx in the random copolymer (F_1) at ~30% conversion.

the graph with the assumption of 100% initiator efficiency. With a value of 106 ± 2 L mol^{-1} s^{-1}, the rate is in the same region as other 2-*n*-alkyl-2-oxazolines in acetonitrile, demonstrating that the branched side chain does not influence the polymerization rate.[17] In particular, compared with its linear analogue 2-nonyl-2-oxazoline (**NonOx**), no significant difference in the polymerization rate was observed.

As shown in Figure 1 right, SEC investigations revealed a linear increase in the molar mass with conversion demonstrating the livingness of the polymerizations, which is supported by the good control over the molar mass and the low PDI values, (PDI ≤ 1.23). The slightly lower molar mass compared with the theoretical molar mass is most likely due to the use of polystyrene standards to calibrate the SEC. Therefore, for an absolute determination of the molar mass of the resulting homopolymers matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry studies were done. The homopolymers were analyzed using 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malo-nonitrile (DCTB) as matrix and sodium iodide to improve the ionization of the polymer. In Figure 2 (left), different MALDI-TOF MS spectra of p(**EHOx**) with increasing polymerization time are visualized, revealing the ongoing growth of the polymer with proceeding time.

Furthermore, from the zoomed section of the mass spectrum in Figure 2 (right), the spacing between the peaks could be assigned to one repeating unit (**EHOx**, 197 Da). The less intensive signal is consistent with the proton initiated polymer resulting from chain transfer reactions that occurred during the polymerization. Furthermore, the M_n values obtained by MALDI-TOF MS are in a perfect agreement with the theoretical values, as can be seen in Figure 2 right.

Copolymerization of EHOx and EtOx. To investigate the influence of the incorporation of **EHOx** in a known polymer system with a defined T_g and well-investigated SE, we chose the copolymerization of **EHOx** and **EtOx**. Kinetic studies of the copolymerization were performed with different ratios of the monomers using 20 mol% increments of **EHOx** to determine the reactivity ratios of both monomers. All of these copolymerizations under microwave irradiation at 140 °C fulfilled the characteristics for a living polymerization: Linear first-order kinetics as well as narrow molar mass distributions. (Kinetic data are listed in Table 1.) SEC revealed relatively narrow molar mass distributions with PDI values below 1.3, as can be seen in Figure 3 (left), for the polymerizations with 100% conversion of both monomers, indicating a good control over the polymerization. The polymerization rates of the monomers for different feed ratios were obtained from the slopes of the linear first-order kinetic plots and are summarized in Table 2.

To calculate the reactivity ratios of the copolymerization, the actual composition of the copolymer was determined at medium conversion because the monomer reactivities in living polymerizations can differ during initiation and propagation,[26,27] as was found for the CROP of 2-substituted-2-oxazolines.[28,29] Therefore, the incorporated **EtOx** fraction (F_1) at 30% conversion was calculated using the polymerization rates of **EtOx** and **EHOx**. The polymerization time required to obtain 30% conversion of **EtOx** was calculated, and the incorporated amount of **EHOx** was also calculated at this time, allowing the determination of the incorporated fraction of **EtOx** (F_1). The graphical illustration (Figure 3 (right)) of F_1 as a function of the theoretical **EtOx** fraction (F_1) reveals all data points on the diagonal, indicating a random incorporation of each monomer into the growing polymer chain. This assumption is supported by the reactivity ratios, which were determined using nonlinear least-squares fitting of the data.[30] With $r_1 = 0.95 \pm 0.08$ and $r_2 = 1.00 \pm 0.07$, the reactivity ratios are equal to unity within the standard deviations, which assured the existence of truly random copolymers.

Table 2. Polymerization Rates Obtained for the Microwave-Assisted Polymerization of 2-Ethyl-2-oxazoline and 2-(3-Ethylheptyl)-2-oxazoline at 140 °C in Acetonitrile (k_p in 10^{-3} L·mol^{-1}·s^{-1}) Using Methyltosylate As Initiator[a]

	EtOx/EHOx ratios			
monomer	80/20	60/40	40/60	20/80
EtOx	88 ± 1	92 ± 1	80 ± 2	94 ± 1
EHOx	91 ± 2	93 ± 1	81 ± 1	95 ± 1

[a] Errors were obtained form linear fits through the data.

Thermal Transitions. The thermal properties of the p(**EHOx**) homopolymer as well as of the p(**EtOx**-*r*-**EHOx**) copolymers were determined by differential scanning calorimetry (DSC). The p(**EHOx**) homopolymer revealed a glass transition at −6 °C. Previous investigations on poly(2-*n*-alkyl-2-oxazoline)s showed glass transitions only for shorter side chains up to five carbon atoms. Linear side chains with a higher amount of carbon atoms resulted in semi-crystalline polymers, whereby the remaining amorphous fraction was too small to be detected by DSC. However, p(**NonOx**), the linear analogous of p(**EHOx**), showed a melting point at ~150 °C, whereas a T_g could not be detected by DSC. Therefore, it can be concluded that the incorporation of a branching point on the side chain suppresses the crystallinity of the polymer. Furthermore, the ethyl side group lowers the T_g, which is consistent with a decrease in the packing density associated with an easier molecular motion of the polymer. In fact, the p(**EHOx**) is the first reported amorphous poly(2-oxazoline) with a T_g below 0 °C.

To study the effect of molecular composition on the thermal properties, p(**EtOx**-*r*-**EHOx**) copolymers with 10 mol% increments of **EHOx** were synthesized. Therefore, polymerization solutions with a total concentration of 2 M and a total monomer-to-initiator ratio of 100 were prepared and exposed to microwave irradiation for a maximum time of 40 min. The resulting polymers were purified either by precipitation in ice-cold diethyl ether or by drying under reduced pressure. The actual compositions of the copolymers were determined by ^{1}H NMR spectroscopy and SEC measurements, revealing polydispersity index values below 1.25, except for the two copolymers with 88 and 94% EHOx, respectively (88%: 1.33; 94%: 1.31) (Table 3). The T_g of p(**EtOx**) (T_g = 59 °C) is significantly higher than the T_g of p(**EHOx**) (T_g = −6 °C), offering a broad window in which the T_g can be tuned by varying the monomer composition. As can be seen from Figure 4 and Table 3, the T_g of the copolymers are linearly decreasing with increasing weight percent of **EHOx**, demonstrating the influence of the more flexible branched side chain of the **EHOx** on the T_g of the copolymer. Therefore, the increasing number of branched side chains causes a lowering of the packing density of the polymer chains by pushing neighbor chains apart. This

Table 3. Molecular Characteristics and Selected Properties of the p(EtOx-*r*-EHOx) Copolymer (SE = Surface Energy)

EHOx[a]			M_n[b]	PDI[b]	T_g[c]	SE[d]	CA	
$\text{mol}_{\text{theor}}$ %	$\text{mol}_{\text{exptl}}$ %	wt_{exptl} %	(g mol^{-1})		(°C)	(mN/m)	(deg; EG)[e]	(deg; DM)[f]
0	0	0	17 700	1.18	58.7	40.9	40	32.6
10	10	18	14 400	1.21	44.9	37.8	55.9	34.5
20	18	30	15 200	1.21	35.2	38.8	52.8	32.4
30	32	48	15 700	1.19	nm[g]	38.6	58.7	30
40	38	55	16 300	1.20	24.1	36.4	74.6	32.4
50	46	63	16 900	1.21	15.6	35.1	83	35.5
60	59	74	17 700	1.18	13.0	35.4	81.5	35
70	70	82	20 000	1.24	nm[g]	35.3	87.9	34.8
80	76	86	19 100	1.33	3.5	35.4	86.3	34.7
90	89	94	19 300	1.31	−2.8	34.6	88.4	37
100	100	100	16 900	1.13	−5.6	33.5	87.1	30

[a] Determined using ^{1}H NMR spectroscopy. [b] SEC results (eluent: *N*,*N*-dimethylacetamide with 2.1 g L^{-1} LiCl; PS standards). [c] From DSC measurements. [d] From contact angle measurements. [e] Contact angle: polar test liquid = ethylene glycol. [f] Contact angle: apolar test liquid = diiodomethane. [g] Not measured because of insufficient amount of polymer.

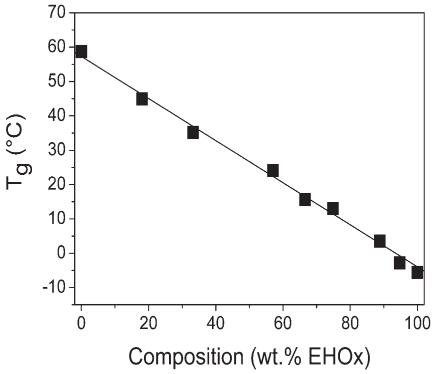


Figure 4. Dependence of the glass transition of the p(**EtOx**-*r*-**EHOx**) random copolymer on the weight percent of 2-(3-ethylheptyl)-2-oxazoline.

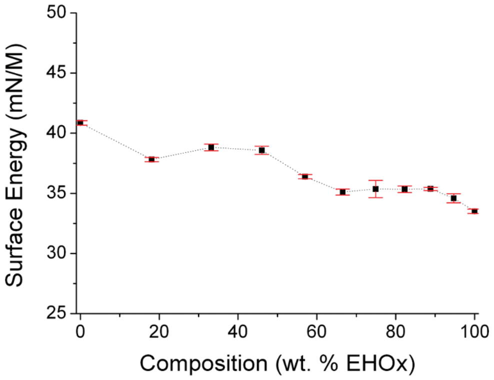


Figure 5. Surface energy values calculated from the contact angles of diiodomethane and ethylene glycol for the p(**EtOx**-*r*-**EHOx**) random copolymer as function of weight percent of EHOx.

perfect linear relationship allows an accurate fine-tuning of the thermal properties for potential specific applications.

Surface Investigations. The surface properties of the polymers were investigated using contact-angle measurements on thin films. The difference between the contact-angle from a polar solvent (e.g., ethylene glycol) and a nonpolar solvent (e.g., diiodomethane) on spin-coated polymer films was used to calculate the SE by the equation of state.[16,31] The SEs of diverse poly(2-*n*-alkyl-2-oxazoline) were extensively studied, demonstrating that short chains result in SEs higher than 40 mN/m and long chains in SEs lower than 25 mN/m.[17,32]

The low SE of poly(2-oxazoline)s with long linear aliphatic side chains was explained by Litt and Herz by a preferred orientation and a close packing of the alkyl chains to the surface.[33] These studies were supported by investigations from Cai et al. on polymer films of poly(2-undecyl-2-oxazoline) using contact angle measurements and electron spectroscopy chemical analysis (ESCA). The authors showed that the surface of this polymer was formed from compact methyl groups, indicating that the undecyl chains are orientated to the surface as well.[34] In the case of the **EHOx** polymer, a complete orientation of the side chains to the surface might be prevented because of the branching ethyl group that prevents close packing of the chains. As a result, the polar polymer backbone of the poly(2-oxazoline) is more easily exposed to the surface leading to a more hydrophilic character of the polymer surface resulting in an SE of 33.5 mN/m. A similar behavior could be observed for poly(2-(*i*-butyl)-2-oxazoline), where the branching methyl group cannot easily orient to the surface.[32] Besides the SEs of the p(**EHOx**) homopolymer, Figure 5 depicts the SEs of all copolymers as a function of the weight percent of **EHOx**. With increasing **EHOx** amount, an increasing part of the surface is covered with long side chains, resulting in a more hydrophobic surface. Therefore, the incorporation of **EHOx** in the copolymer effects a gradual decrease in the SE. A more pronounced decrease in the SE is observed around 55 mol % EHOx. At this molecular composition, the T_g of the polymer approaches room temperature, causing an easier reorganization of the polymer because of a higher chain flexibility.

Conclusions

In this contribution, the successful synthesis of a new 2-substituted-2-oxazoline, namely, 2-(3-ethylheptyl)-2-oxazoline is described. The corresponding homopolymer is the first poly(2-oxazoline) that is amorphous and exhibits a low glass-transition temperature at −6 °C. The significant differences in properties compared with its linear analogue p**NonOx** are caused by the branching of the side chain resulting in a lower packing density, which is consistent with an easier molecular motion of the polymer. Furthermore, we could show that the copolymerization of **EtOx** and **EHOx** yielded truly random copolymers with reactivity ratios of: $r_1 = 0.95 \pm 0.08$ and $r_2 = 1.00 \pm 0.07$. Thermal investigations of the random copolymers revealed a linear dependency of the T_g with weight percent of **EHOx**, allowing simple fine-tuning of the T_g for specific applications. Furthermore, the SEs of the copolymers obtained showed a gradual decrease with increasing amount of **EHOx**.

The syntheses of AB and ABA block copolymers using this new low T_g monomer are ongoing in our laboratories.

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