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In this communication we demonstrate that dispersities of poly(allyl glycidyl ether) and poly(ethoxy ethyl glycidyl ether) can be reduced using a slow monomer addition technique with potassium tert-butoxide as initiator and THF as solvent at 45 °C. Different feed rates were examined in triplicate and analysed by SEC.

Poly(allyl glycidyl ether) (poly(AGE)) homo- and copolymers are promising alternatives to low-functional poly(ethylene oxide) (PEO).\textsuperscript{1} Ethylene oxide (EO), ethoxy ethyl glycidyl ether (EEGE) and other oxirane-monomers have already been statistically or block copolymerized with allyl glycidyl ether (AGE) to improve functionalization options.\textsuperscript{2,4} Using this approach, modification of the unsaturated side-chains (e.g. via thiol-ene click chemistry) allowed the synthesis of multifunctional PEO-derivatives over the past decades.\textsuperscript{5-7}

Side-reactions and their control in glycidyl ether polymerizations were investigated as it determines the applicability, i.e. reproducibility, control over molar masses and dispersity. Challenges in syntheses were believed to be due to isomerization reactions and transfer reactions. Depending on media, temperature, and polymerization parameters the transfer reactions limit the degree of polymerization and increase dispersity.\textsuperscript{5,6} Hans et al.\textsuperscript{8} assumed that chain transfer occurs in EEGE polymerization by methylene-group deprotonation in \( \alpha \)-position to the oxirane as it is known for propylene oxide (PO) and other oxiranes for decades.\textsuperscript{12} Here the newly formed allyl-alkoxide initiates a new polymerization that leads to an additional low molar-mass fraction and tailing in SEC-traces. Furthermore, at higher temperatures dimerization can occur that leads to polymer fractions with twice the molar mass of the main polymer fraction. Mechanistically, deprotonation at the oxirane-ring leads to a ketone group and a carbanionic species. This initiates a new polymerization and gives a ketone-terminal polymer that can couple with other oxyanionic species.\textsuperscript{9} The two mentioned side-reactions lead to low and high molar-mass impurities. Erberich et al.\textsuperscript{10} assumed that controlled polymerization of AGE proceeds only up to 80 % conversion. Afterwards deprotonation reactions occur that terminate the active chain. The authors used potassium alkoxide as initiator (with only 10 % of active alkoxides) at 120 °C in diglyme. The obtained poly(allyl glycidyl ether) had a DP of 21 and a dispersity of 1.27. In contrast, Lee et al.\textsuperscript{11} used potassium benzoxide and polymerized AGE in diglyme or neat at 30-80 °C and a controlled polymerization with DP up to 800 was possible. At higher temperatures the authors observed isomerization reactions that lead to cis-prop-1-enyl side-chains. Please note that this isomerization at the side-reaction does not terminate the polymerization.\textsuperscript{12}

Caesium-alkoxides are one promising alternative to potassium-alkoxides for the polymerization of glycidyl ethers as the Cs\textsuperscript{+}-alkoxides exhibits a pronounced ionic character and increases the activity of the chain ends.\textsuperscript{13} Furthermore, isomerization reactions are reduced using Cs\textsuperscript{+} as counterion enhancing the control over unwanted side-reactions.\textsuperscript{14} Unfortunately, the use of caesium-alkoxides is limited due to solubility issues of caesium-initiators in various solvents. For example, caesium 2-methoxyethoxide was used as initiator although it shows a low solubility in THF. To increase the solubility DMSO was added.\textsuperscript{6} For benzene as solvent a PEG initiator with M\textsubscript{n} > 1000 g mol\textsuperscript{-1} is required to dissolve the initiator properly if both hydroxyl groups were activated with CsOH.\textsuperscript{15} In contrast to caesium-alkoxides, low molar-mass potassium alkoxides such as potassium ethoxide\textsuperscript{16} and potassium tert-butoxide readily dissolve in THF or benzene. Furthermore, upon preparation of the caesium-alkoxides protic compounds are often required and H\textsubscript{2}O is released that has to be completely removed before polymerization.\textsuperscript{1,17,18}

During the synthesis of statistical poly(EEGE-co-AGE) with [M]:[I] of 50:1 and various fractions of AGE, bimodal SEC elugrams were obtained in our labs. The bimodality was more pronounced than described for poly(EEGE) homopolymers by Hans et al.\textsuperscript{8} It is known that a long-term standing of poly(AGE) induces an uncontrolled radical process and cross-linking of...
AGE. Bimodal SEC elugrams having one polymer fraction with the intended molar mass and one fraction having twice the molar-masses were obtained. This indicated the aforementioned ketone-coupling theory rather than an uncontrolled radical cross-linking of the unsaturated side-chains of the polymers. Dispersities and elugrams were compared with literature, but Hans et al. reported that the fraction with twice the molar mass occurs at higher temperatures for EEGE. A further look into the polymerization fraction with twice the molar mass occurs at higher compared with literature, but Hans et al. reported that the chains of the polymers. Dispersities and elugrams were obtained. This indicated the aforementioned ketone-coupling theory rather than an irreversible dimerization of low molar-mass polymers would lead to low molar-mass fractions visible by a tailing in SEC elugrams. Monomer deprotonation reactions that occur preferably at the end of polymerization do also not result in polymer fractions with twice the molar mass. Here, the residual monomer content is not sufficient high to increase the molar mass of the polymers to such an extent. The polymer fraction with twice the molar mass is therefore most probable by an initial deprotonation reaction. Concurrently with the polymerization, a reversible ketone-alkoxide coupling occurs. The equilibrium between the active (non-coupled) and dormant (coupled) species is furthermore assumed to be rapid compared to the polymerization itself. If this is not the case a trimer would be observable in SEC elugrams. The formed alkoxide-functional dimer would initiate a new polymerization (Scheme 1).

For a detailed investigation, commercially available KOtBu (1 M in THF) was used as initiator. The polymerization was conducted at 45 °C as isomerization reactions are suppressed at this temperature. After adding the total monomer volume in a step-wise manner, the reactions were additionally stirred for 20-24 h at 45 °C to fully polymerize all monomer. Experiments were conducted with AGE and EEGE as monomers with feed rates between $V' = 50-5000 \, \mu L \, h^{-1}$. A syringe pump was used to control the feed rate. Briefly, a glovebox 100 µL of the initiator was placed into a flask which was sealed with a rubber septum. A syringe equipped with the monomer was punctured through the septum. The syringe/flask-assembly was wrapped with parafilm\textsuperscript{8} from the neck of the flask to the connection-side of the needle with the syringe to maintain air-tightness. The syringe–flask construct was placed into the syringe-pump and the flask heated in an oil bath. For AGE-experiments 570 µL ([M]:[I]=50:1) and for EEGE-experiments 731 µL ([M]:[I]=50:1) of the monomer were added via the programmed syringe pump. After complete addition of the monomer, the flasks were stirred at 45 °C either in an oil bath or an incubator. The samples were analysed by \textsuperscript{1}H-NMR spectroscopy and SEC measurements. All experiments were performed in triplicate to determine standard deviations of the final number-average molar mass ($\bar{M}_n$) and dispersity ($\tilde{D}$). \textsuperscript{1}H-NMR experiments were checked for conversion but in no cases residual monomer was detectable. Poly(AGE) was analysed using SEC with DMF (+1 g L\textsuperscript{-1} LiBr) as eluent and PEG as calibration standard. All elugrams were evaluated in the same run time region (16-22 min, total run time 30 min) to gain comparability. For poly(AGE) $\bar{M}_n$ and $\tilde{D}$ are shown in Figure 1. $\bar{M}_n$ was between 3800-4400 g mol\textsuperscript{-1} ($V' = 50-2000 \, \mu L \, h^{-1}$) corresponding to DPs of 33-38, whereas \textsuperscript{1}H-NMR analyses gave DPs of 47-56 using the terminal tert-butyl group as internal reference. The results were in accordance with the theoretical DP of 50. The differences between the DPs obtained by \textsuperscript{1}H-NMR spectroscopy and SEC measurements were assigned to a different coiling behaviour of poly(AGE) compared to PEG in DMF.

With an increasing feed rate a slight but steady increase in $\bar{M}_n$ was observed. This can be explained by the also observed steady increase of $\tilde{D}$ from 1.16±0.01 to 1.30±0.01. Increasing side-reactions lead to a higher fraction of coupled polymers. The resulting polymers with twice the molar mass of the main polymer fraction led to a shift of $\bar{M}_n$ towards higher values. Dispersity $\tilde{D}$ evolved from 1.16±0.01 to 1.20±0.01 if the feed rate was increased from 50 µL h\textsuperscript{-1} to 500 µL h\textsuperscript{-1}, respectively. Between 500 µL h\textsuperscript{-1} and 2000 µL h\textsuperscript{-1} no significant dispersity alteration was observed. An increase of the feed rate from 2000 µL h\textsuperscript{-1} to 5000 µL h\textsuperscript{-1} yielded polymers with dispersities of 1.21±0.02 and 1.30±0.01, respectively. Qualitatively, SEC elugrams further indicate the hypothesized coupling. The signal of the polymer fraction with twice the molar mass rose with increased feed rates and bimodal molar-mass distributions were obtained (Figure 2).

Poly(EEGE) was also synthesized with the same [M]:[I] ratio of 50 via the slow monomer addition route. With this, the influence of the monomer on the polymerization was investigated. In general, it was observed that dispersities of poly(EEGE) are lower than dispersities of poly(AGE). The polymer fraction with twice the molar mass is also present, but less pronounced than for poly(AGE) (see Supporting Information). For EEGE, feed-rate reduction also lowers the dispersity (Figure 3). Dispersities were between 1.11±0.01 and 1.16±0.01 for feed rates of 100 µL h\textsuperscript{-1} and 5000 µL h\textsuperscript{-1}, respectively. Especially below a threshold of 500 µL h\textsuperscript{-1} dispersity reductions were observed for both monomers (Figure 1 and Figure 3). We assume that the balance between...
chain propagation and monomer feed is responsible for this drop in dispersity.

If the monomer supply (feed rate) is too high, monomer concentration will rise with time. With a higher monomer content the number of above mentioned side-reaction is more likely to occur. Below the threshold, it is assumed that monomer consumption is higher than the monomer supply and [M] is kept low. With this the deprotonation reaction can be reduced.

First-order kinetics plots were investigated for the polymerizations of AGE and EEGE with an “infinite feed rate” and an initial [M]:[I] ratio of 50:1. The term “infinite feed rate” is referred to experiments without a syringe-pump. Here all monomer is present in the reaction mixture from the beginning. The data plots show a small induction period for the polymerizations of both monomers (Figure S4). These induction periods were ascribed to K-alkoxide clusters that can form in THF and are present at the beginning of the polymerization.20, 21 These clusters disintegrate with ongoing polymerization due to the increasing steric demand of the polymer chains. After the induction period, linear regions in the plots indicate a living polymerization. For AGE, the linear region was between 43 % and 89 % conversion, whereas it was between 36 % and 92 % conversion for EEGE. The slopes obtained from the linear region of the plots were used to determine the propagation rates. AGE polymerizes slightly faster than EEGE with propagation rates of $k_{\text{AGE}} = 2.4 \times 10^{-3}$ L mol$^{-1}$ s$^{-1}$ and $k_{\text{EEGE}} = 2.2 \times 10^{-3}$ L mol$^{-1}$ s$^{-1}$, respectively. Earlier investigations by Erberich et al. show a slower polymerization of AGE compared to EEGE.3 This was assigned to the modified polymerization conditions used. The kinetic data indicate that the dispersity drop in AGE polymerization should be achievable at higher feed rates as the propagation rate is slightly higher and the monomer faster consumed. First-order kinetics plots for the slow monomer-addition experiment were not performed. The condition of a constant concentration of the active species cannot be fulfilled. The number of active species is assumed to be constant but the reaction volume and the monomer content continuously change with time. With this, the first order plot cannot directly be applied and a linear relation in the $-\ln(M_t/M_0)$–time plot is not expected.

Regarding the feed rate and intended DPs of 50, the total monomer volume has to be considered as well. For above mentioned experiments the total monomer volumes were 570 µL and 731 µL for AGE and EEGE, respectively. With a feed rate of 500 µL h$^{-1}$, all AGE was injected after 66 min, whereas the addition of all EEGE requires 88 min. This means that polymerization of AGE is faster and additionally monomer injection requires less time.

In conclusion, it was shown that dispersity reduction of poly(glycidyl ether)s can be obtained using a slow monomer addition technique. Feed rate adjustment keeps the monomer concentration constantly low and monomer deprotonation reactions are significantly reduced. This side-reaction commonly leads to bimodal SEC elugrams with a polymer fraction having twice the molar mass of the main polymer. In general, lower dispersities were obtained for poly(EEGE) compared to poly(AGE) and the effect of slow monomer...
addition was more pronounced for poly(AGE). For a DP of 50, dispersities of poly(AGE) could be reduced from 1.30 ±0.01 to 1.16 ±0.01, whereas for poly(EEGE) dispersities were reduced from 1.16 ±0.01 to 1.11 ±0.01. By lowering the feed rate SEC elugrams showed qualitatively the change from bimodal to monomodal elugrams. In the future, poly(AGE) and poly(EEGE) are attempted having molar masses higher than 20,000 g mol⁻¹. This shall further evaluate the scope of this technical dispersity control. Additionally, further polymerization parameters will be investigated and the hypothesis evaluated for other glycidyl-ether monomers.

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Notes and references