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Chain transfer reactions limit the molecular weight of polyglycidol prepared via alkali metal based initiating systems

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ABSTRACT

Anionic polymerization of EEGE with alkali metal based initiators has been shown to yield polyglycidol with low polydispersity indices for molecular weights up to $M_n \approx 30{,}000$. Higher molecular weights have not been obtained due to the occurrence of a chain transfer reaction to the monomer. Chain transfer to the monomer leads to P(EEGE) with an alcohol end group and an allylic alcoholate, which reinitiates the polymerization of EEGE. In the present study, the influence of temperature (in a range from 20 °C to 120 °C) and of different initiating systems, such as 3-phenylpropanol/potassium 3-phenylpropanolate, potassium *tert*-butoxide and *sec*-butyllithium/phosphazene base, on the chain transfer reaction is investigated. In all cases, the basicity of the alkoxide at the propagating chain end induces chain transfer. The formation of allylic end groups was evidenced by ^{1}H NMR spectroscopy.

1. Introduction

During the past years, polyglycidol and its derivatives have attracted the attention of a number of research groups. Its biocompatibility and its high functionality make polyglycidol interesting for applications in biomedical and many other fields [1–4]. Anionic and cationic polymerization of glycidol was found to lead to highly branched oligomeric products [5–8]. In general, the microstructure of the hyperbranched polyglycidols is not well controlled, especially at higher molecular weights the distribution of branching is irregular and molecular weight of branches varies.

To obtain architecturally well-controlled polyglycidol, the hydroxy group of glycidol must be protected by a suitable group and the polymerization must be initiated by multifunctional initiators. Tertiary butyl glycidyl ether, allyl glycidyl ether and ethoxy ethyl glycidyl ether (EEGE) have been found to be stable under the conditions of anionic polymerization [9,10]. Mostly EEGE is used as it is easily deprotected under acidic conditions. Thus, anionic polymerization of the protected monomer followed by removal of the protection group yields polyglycidol with well-defined architectures such as linear, star-shaped or arborescent-branched [9,11–14].

Recently, the interest in polyether and poly(ether–ester) conjugates with well-defined microstructures has increased. Various amphiphilic block copolymers with polyglycidol as building blocks have been synthesized, e.g., polyglycidol-*b*-poly(ethylene oxide) [15], polyglycidol-*b*-poly(propylene oxide)-*b*-polyglycidol [16,17], poly(lactic acid)-*b*-poly(ethylene oxide)-*b*-polyglycidol [18,19], polystyrene-*b*-poly(ethylene oxide)-*b*-polyglycidol [20]. Studies of their behavior in aqueous solution have revealed interesting properties, like the formation of micelles. The preparation of star-shaped ABC copolymers of polystyrene–poly(ethylene oxide)–polyglycidol was described [21]. Comb-shaped and well-defined highly branched copolymers have been obtained by the "grafting from" reaction using polyglycidol or poly(glycidol-*co*-ethylene oxide) as macroinitiator [14,22–24]. By the use of an enzymatic catalyst for the grafting reaction, hetero-grafted molecular bottle brushes and copolymers with exceptional degradation profiles have been obtained [25,26]. Furthermore, the hydroxy groups of polyglycidol are an ideal precursor for the insertion of different functionalities, leading, for example, to thermosensitive polymers [27,28]. In conclusion, the polyglycidol chemistry gives rise to numerous novel polymeric materials with distinct properties, which make them promising candidates for future applications in biomedical, surfactant and other fields.

In all the previously cited articles, the molecular weight of P(EEGE) or P(EEGE) blocks synthesized by anionic polymerization was well controlled, but did not exceed $M_n = 30{,}000$ ([M]/[I] ≈ 200). Polyglycidol with $M_n > 30{,}000$ and narrow molecular weight distribution is desirable. This has been achieved by the use of partially hydrolyzed diethylzinc as catalyst [27,29,30]. A

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drawback of this method is the lack of control concerning molecular weight and high polydispersity indices.

It is assumed, that chain transfer to the monomer inhibits the synthesis of high molecular weight polyglycidol by anionic polymerization. Such a chain transfer reaction has already been observed for the polymerization of propylene oxide and phenyl glycidyl ether [31–33]. In our group, the synthesis of polyglycidol with M_n higher than 30,000 using different alkali metal based initiators was explored. Due to the transfer reaction this remained unsuccessful. In this work the influence of temperature and initiator on the transfer reaction is presented.

2. Experimental part

2.1. Materials

Potassium *tert*-butoxide (*t*-BuOK, 1 M solution in THF, Aldrich), *sec*-butyllithium (*sec*-BuLi, 1.3 M solution in hexane, Aldrich) and 1-*tert*-butyl-4,4,4-*tris*-(dimethylamino)-2,2-*bis*-[*tris*-(dimethylamino)-phosphoranylidenamino]-2^5,4^5-catenadi-(phosphazen) (phosphazene base *t*-BuP_4, 1 M solution in hexane, Fluka) were used as received. 3-Phenylpropanol (PPOH, ≥98%, Fluka) was reacted with small amounts of sodium and subsequently distilled. Diglyme was distilled over sodium. Tetrahydrofuran was distilled over potassium. Benzene was distilled over lithium aluminium hydride. Ethoxy ethyl glycidyl ether (EEGE) was synthesized from 2,3-epoxypropan-1-ol (glycidol) and ethyl vinyl ether according to Fitton et al. and purified by distillation [34]. A fraction with a purity exceeding 99.8 GC% was used. For the use in the glove box, EEGE was additionally dried over dibutyl magnesium and benzene over *sec*-butyllithium, both were degassed by three freeze–thaw cycles and collected by condensation in vacuum.

Reactions were carried out in the glove box or in nitrogen atmosphere in Schlenk flasks dried by heating gun. Nitrogen (Linde, 5.0) was passed over molecular sieves (4 Å) and finely distributed potassium on aluminium oxide.

2.2. Syntheses

2.2.1. P(EEGE) (**1**–**4**) prepared via ring-opening polymerization with PPOH/PPOK as initiator

Synthesis of P(EEGE) **1**. 3-Phenylpropanol (194 mg, 1.43 mmol) was dissolved in diglyme (5 mL) and *t*-BuOK (0.15 mL of a 1 M solution in THF, 0.15 mmol) was added. The *tert*-butanol formed was removed by distillation. EEGE (5.0 g, 34 mmol) was added and the mixture was stirred for 16 h at 120 °C. The solvent was removed in vacuum at 60 °C and a viscous liquid was obtained. $M_{n,SEC} = 3600$, $M_w/M_n = 1.09$. ^{1}H NMR (DMSO-d_6): δ 1.09 (tr, $J = 7.0$ Hz, CH_2CH_3), 1.18 (d, $J = 5.2$ Hz, $CHCH_3$), 1.78 (qui, $J = 7.0$ Hz, $ArCH_2CH_2$), 2.61 (tr, $J = 7.6$ Hz, $ArCH_2CH_2$), 3.30–3.70 (m, $CH_2OCH_2CH(CH_2O)O$, OCH_2CH_3), 4.64 (d, $J = 5.0$ Hz, $OCHO$), 7.12–7.33 (m, Ar). The ^{1}H NMR spectrum of **1** is presented in Fig. 1. ^{13}C NMR (DMSO-d_6): δ 15.1 (CH_2CH_3), 19.6 ($CHCH_3$), 30.9, 31.6 ($ArCH_2CH_2$), 60.1 (CH_2CH_3), 64.6 ($OCH_2CH(CH_2O)O$), 66.7 ($OCH_2CH(CH_2O)OH$), 68.8 ($ArCH_2CH_2CH_2$), 69.4 ($OCH_2CH(CH_2O)O$), 78.3 ($CH_2OCH_2CH(CH_2O)O$), 99.1 ($CHCH_3$), 125.6, 128.1, 141.6 (Ar).

2.2.2. P(EEGE) (**5**–**7**) prepared via ring-opening polymerization with t-BuOK as initiator

Synthesis of P(EEGE) **5**. *tert*-Butoxide (0.23 mL of a 1 M solution in THF, 0.23 mmol), EEGE (8.0 g, 55 mmol) and tetrahydrofuran (8 mL) were introduced into a Schlenk flask. The mixture was stirred for 48 h at 60 °C. The solvent was removed at 50 °C in vacuum and a viscous liquid was obtained. $M_{n,SEC} = 25{,}200$, $M_w/M_n = 1.13$. The signals of the NMR spectra are the same as for **1**, except the signals of the 3-phenylpropyl group are replaced by the signals of the *tert*-butyl group.

2.2.3. P(EEGE) (**8**–**13**) prepared via ring-opening polymerization with Li^+/t-BuP_4 as initiator

Synthesis of P(EEGE) **10**. In the glove box, EEGE (5.0 g, 34 mmol) and benzene (5 mL) were introduced into a flask. *sec*-BuLi (0.13 mL of a 1.3 M solution in hexane, 0.17 mmol) was added and after stirring 1 h at room temperature *t*-BuP_4 (0.17 mL of a 1 M solution in hexane, 0.17 mmol) was added. After 5 days of stirring at room temperature, the solvent was removed in vacuum and a viscous liquid was obtained. $M_{n,SEC} = 12{,}100$, $M_w/M_n = 1.12$. The signals of the NMR spectra are the same as for **5**.

2.3. Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300 spectrometer at 300 MHz and 75 MHz, respectively. Deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (DMSO-d_6) was used as a solvent, and tetramethylsilane served as internal standard.

SEC analyses were carried out at 35 °C using a high-performance liquid chromatography pump (ERC HPLC 64200) and a refractive index detector (ERC-7215a). The eluting solvent was tetrahydrofuran (HPLC grade) with 250 mg L^{-1} 2,6-di-*tert*-butyl-4-methylphenol and a flow rate of 1 mL min^{-1}. Five columns with MZ gel were applied. The length of the first column was 50 mm and of the four other columns it was 300 mm. The diameter of each column was 8 mm, the diameter of the gel particles was 5 μm, and the nominal pore widths were 50, 50, 100, 1000 and 10,000 Å, respectively. Calibration was achieved using narrow distributed poly(methyl methacrylate) standards.

3. Results and discussion

In general, the initiators used for the anionic ring-opening polymerization of protected glycidol are based on alkali metal derivatives; especially potassium or cesium alcoholates are used [11,22]. Attempts to synthesize polyglycidols at 120 °C with high molecular weights by using 3-phenylpropanol/potassium 3-phenylpropanolate as initiator were not successful. As in all polymerizations quantitative monomer conversion was observed, the limitation of the molecular weight was attributed to the afore mentioned chain transfer reaction. In order to study the influence of different reaction parameters on the transfer reaction, such as ROH/ROK ratio, temperature, solvent, and monomer concentration a series of reactions (not shown) was performed. It was found, that temperature is the most important factor influencing the transfer reaction. Therefore, the polymerization of EEGE was performed at 60 °C with PPOH/PPOK and *t*-BuOK as initiators. The maximum molecular weight obtained was $M_n = 29{,}000$; higher values could not be achieved. A further increase of the molecular weight was expected by polymerization at lower temperatures. Recently, the successful use of the Li^+/t-BuP_4 complex as counterion has been reported for the polymerization of EEGE at room temperature [20]. A series of reactions was performed at 20 °C using this initiating system, but the M_n values remained even lower than in the case of the polymerization with *t*-BuOK at 60 °C. In the following, the influence of temperature and of the different initiating systems PPOH/PPOK, *t*-BuOK and Li^+/t-BuP_4 on the chain transfer reaction occurring in the anionic polymerization of EEGE is presented and discussed.

3.1. Synthesis of polyglycidol at 120 °C with PPOH/PPOK as initiating system

A first series of P(EEGE) was synthesized at 120 °C in diglyme with 3-phenylpropanol as initiator. 10% of the alcohol groups of

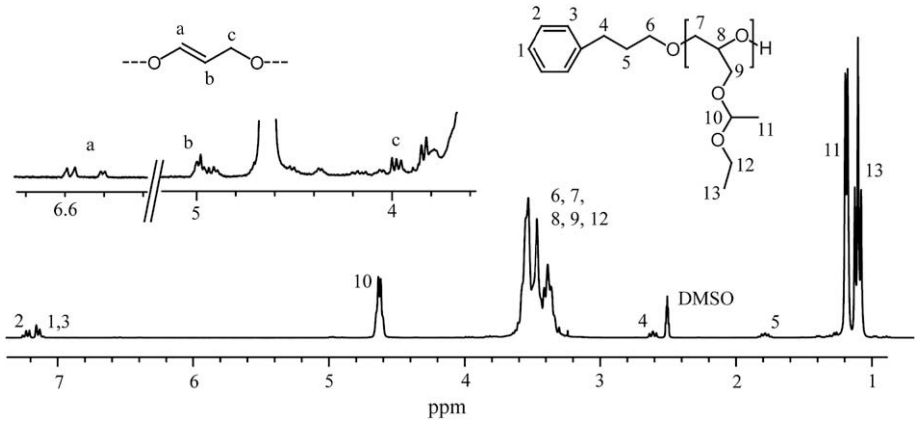


Fig. 1. ^{1}H NMR spectrum of P(EEGE) **1** synthesized at 120 °C with PPOH/PPOK as initiator in DMSO-d_6.

3-phenylpropanol were activated with potassium *tert*-butoxide. The emerging *tert*-butanol was removed in vacuum, before EEGE was added. After polymerization, P(EEGE) was obtained by removal of the solvent in vacuum. Three different initiators to monomer ratios were applied.

NMR analyses of preceeding reactions revealed signals of sp2 hybridized carbon atoms resulting from end groups in the synthesized polymers. It is assumed, that due to the basicity of the alkoxide at the propagating chain end, chain transfer to the monomer is occurring. An allyl alkoxide is formed upon proton abstraction from the methylene group adjacent to the oxirane ring beside hydroxy terminated P(EEGE) (Scheme 1). Such a chain transfer reaction has already been described in literature for the polymerization of propylene oxide and phenyl glycidyl ether [31–33].

In Table 1 the reagent ratios, the monomer conversions, the molecular weights, the polydispersity indices and the percentage of chains with an allylic end group of the polymers **1**–**3** synthesized at 120 °C are listed.

Monomer conversions were determined from the ^{1}H NMR spectrum of a sample before workup. As the monomer conversion was 100% for the polymers **1**–**3** the calculated molecular weights result from the monomer to initiator ratios in the feed. The ^{1}H NMR spectrum of (PEEGE) **1** is shown in Fig. 1. At first view, only the expected peaks are observed, but upon enlargement of the spectrum additional peaks resulting from the allylic end group become visible.

Thus, in order to determine the molecular weights by end group analysis the additional initiating groups have to be taken into account. The obtained molecular weights do not correspond anymore to the theoretical ones, because from one molecule of initiator more chains are initiated by transfer reactions to the monomer. By comparison of the signal of the allylic double bond (a) and the aromatic signals of 3-phenylpropanol (1,2,3) in the ^{1}H NMR spectrum the percentage of the number of chains initiated by chain transfer is determined using equation (1).

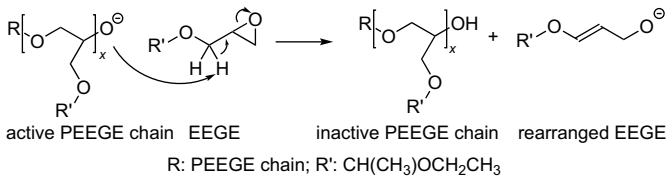
$$\mathrm{AEG} = \frac{\mathrm{Int}(a)}{(0.2\cdot\mathrm{Int}(1,2,3)) + \mathrm{Int}(a)}\cdot 100 \qquad (1)$$

From Table 1 it can be observed, that the amount of allylic initiator (AI) is increasing strongly with higher monomer to initiator ratios in the feed. In order to determine the molecular weights by end group analysis, equation (2) is used; with $M_{\mathrm{EEGE}} = 146$ g/mol.

$$M_{\mathrm{n,NMR}} = \frac{\mathrm{Int}(10)}{(0.2\cdot\mathrm{Int}(1,2,3)) + \mathrm{Int}(a)}\cdot M_{\mathrm{EEGE}} \qquad (2)$$

The molecular weight of the initiating groups is neglected. At higher degrees of polymerization, the discrepancy between the calculated and the determined molecular weight is increasing drastically. Thus the occurrence of chain transfer reaction is increasing with increasing monomer to initiator ratios.

The trend of the number average molecular weights determined by SEC analysis confirms the previous results. With increasing the monomer to initiator ratio, the discrepancy of the determined number average molecular weight and the calculated value is increasing. The observed tailing in the SEC traces of polymers **2** and **3** is probably due to short polymer chains initiated in the course of the polymerization by the allylic alcoholate formed upon chain transfer to the monomer (Fig. 2). The polydispersity indices are also increasing with higher [M]/[I] ratios.



Scheme 1. Possible mechanism of the chain transfer to the monomer in the anionic polymerization of ethoxy ethyl glycidyl ether (EEGE) involving alkali metal alkoxides as active species.

Table 1
Reagent ratios, monomer conversions, molecular weights, polydispersity indices and percentage of chains with an allylic end group of P(EEGE) (**1**–**3**) synthesized at 120 °C with PPOH/PPOK as initiator.

P(EEGE)	[M]/[I][a]	Conv.[b] [%]	$M_{n,calc.}$[c]	NMR[d]		SEC[e]		AEG[f] [%]
				M_n	DP_n	M_n	M_w/M_n	
1	24	100	3600	3200	22	3600	1.09	10
2	50	100	7400	5600	38	6400	1.16	23
3	100	100	14,700	8100	55	8300	1.19	44

[a] Monomer to initiator ratio in the feed.
[b] Ethoxy ethyl glycidyl ether conversion.
[c] Calculated molecular weight (M_n).
[d] Molecular weight (M_n) and degree of polymerization (DP_n) determined from NMR by equation (2).
[e] Molecular weight (M_n) and polydispersity index (M_w/M_n) determined by size exclusion chromatography (SEC) using narrow distributed poly(methyl methacrylate) standards and tetrahydrofuran as eluent.
[f] Percentage of chains with an allylic end group (AEG) calculated according to equation (1).

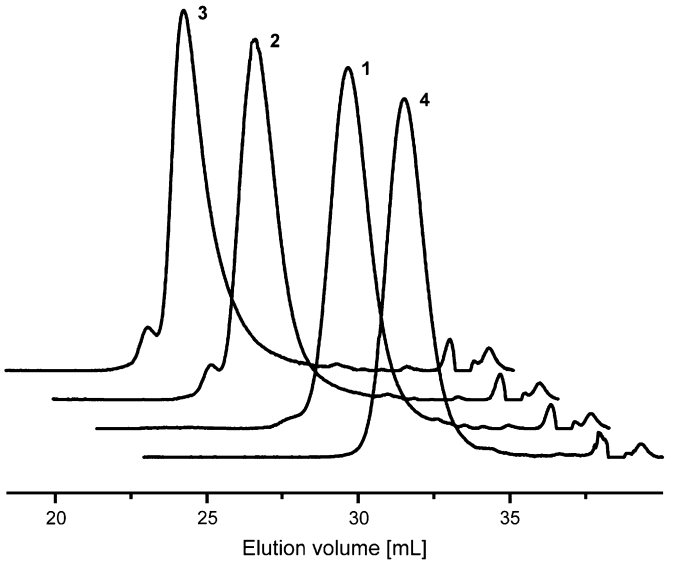


Fig. 2. SEC traces of P(EEGE) synthesized at 120 °C (**1**–**3**) and at 60 °C (**4**) containing different amounts of allylic end groups.

3.2. Synthesis of polyglycidol at 60 °C with PPOH/PPOK or t-BuOK as initiating system

From a series of preceeding polymerizations (not shown), which were performed to study the influence of different reaction parameters on the chain transfer reaction, the following observations were made: a) by lowering the temperature the occurrence of the chain transfer reaction is considerably reduced; b) with potassium as a counterion, 60 °C has been found to be the lower temperature limit to perform the polymerization in tetrahydrofuran; c) performing the reaction in diglyme, benzene or tetrahydrofuran as a solvent did not have a considerable influence on the amount of chain transfer; d) higher dilution than monomer:solvent = 1:1 led to an increase of chain transfer reactions.

Taking into account the previous conclusions, a second series of P(EEGE) was synthesized at 60 °C in tetrahydrofuran or diglyme. At higher [M]/[I] ratios (P(EEGE) **5**–**7**), potassium *tert*-butoxide had to be used directly as initiator, because upon 10% deprotonation of 3-phenylpropanol hardly any monomer conversion was observed. In Table 2 the monomer conversions, the molecular weights, the polydispersity indices and the percentage of chains with an allylic end group of the polymers **4**–**7** are listed.

The reactions with *t*-BuOK (**5**–**7**) as initiator were stopped after 48 h, however at higher [M]/[I] ratios monomer conversion was not completed at this point (82% for P(EEGE) **6** and 89% for P(EEGE) **7**). In the case of copolymers **5**–**7**, the signal of *tert*-butyl initiating group is overlayed by the methyl signals of EEGE and the amount of allylic end groups cannot be determined directly by end group analysis. Therefore, the signal of the methine group at 4.65 ppm (10), was normed to the number of repeating units in the polymer, which was calculated from the monomer to initiator ratio in the feed and the conversion (example: for polymer **5** the integral of the methine peak (10) is set to 240 · 0.82 = 197). Assuming that all *tert*-butoxide groups initiated the polymerization the amount of allylic end groups can be calculated by equation (3),

$$\mathrm{AEG} = \frac{\mathrm{Int}(a)}{1+\mathrm{Int}(a)} \cdot 100 \tag{3}$$

and the molecular weights by equation (4); with $M_{\mathrm{EEGE}} = 146$ g/mol.

$$M_{\mathrm{n,NMR}} = \frac{\text{normed Int}(10)}{1+\mathrm{Int}(a)} \cdot M_{\mathrm{EEGE}} \tag{4}$$

At 60 °C the chain transfer to the monomer was considerably reduced compared to the polymerization at 120 °C. At a [M]/[I] ratio of 24 (**4**) no allylic end group was detected and it can be concluded that no chain transfer occurred. Also for P(EEGE) **5** ([M]/[I] = 100), hardly any chain transfer was observed at 60 °C, compared to P(EEGE) **3** synthesized at 120 °C. Up to a [M]/[I] ratio of 240 (P(EEGE) **6**), the molecular weights determined by NMR are in good agreement with the calculated values. Upon further increase of the monomer to initiator ratio in the feed, a significant higher amount of allylic end groups was observed. Thus, also at 60 °C, the basicity of the alkoxide chain end induces chain transfer and limits the molecular weight of P(EEGE).

The number average molecular weights determined by SEC analysis are in good agreement with the values determined by end group analysis. Monomer to initiator ratios higher than [M]/[I] ≈ 200 do not lead to an increase of the molecular weight. The elution curves of P(EEGE) **5**–**7** are similar and have the same shape as already observed for **2** and **3**. The origin of the peak in the high

Table 2
Reagent ratios, monomer conversion, molecular weights, polydispersity indices and percentage of chains with an allylic end group of P(EEGE) synthesized at 60 °C in diglyme with PPOH/PPOK as initiator (**4**) or in tetrahydrofuran with *t*-BuOK as initiator (**5**–**7**).

P(EEGE)	[M]/[I][a]	Conv.[b] [%]	$M_{n,calc.}$[c]	NMR[d]		SEC[e]		AEG[f] [%]
				M_n	DP_n	M_n	M_w/M_n	
4	24	100	3600	3500	24	3400	1.07	0
5	100	100	14,700	13,600	93	14,500	1.08	7
6	240	82	28,800	25,500	175	25,200	1.13	12
7	400	89	52,100	27,400	188	28,900	1.22	47

[a] Monomer to initiator ratio in the feed.
[b] Ethoxy ethyl glycidyl ether conversion.
[c] Calculated molecular weight (M_n).
[d] Molecular weight (M_n) and degree of polymerization (DP_n) determined from NMR by equation (4).
[e] Molecular weight (M_n) and polydispersity index (M_w/M_n) determined by size exclusion chromatography (SEC) using narrow distributed poly(methyl methacrylate) standards and tetrahydrofuran as eluent.
[f] Percentage of chains with an allylic end group (AEG) calculated according to equation (3).

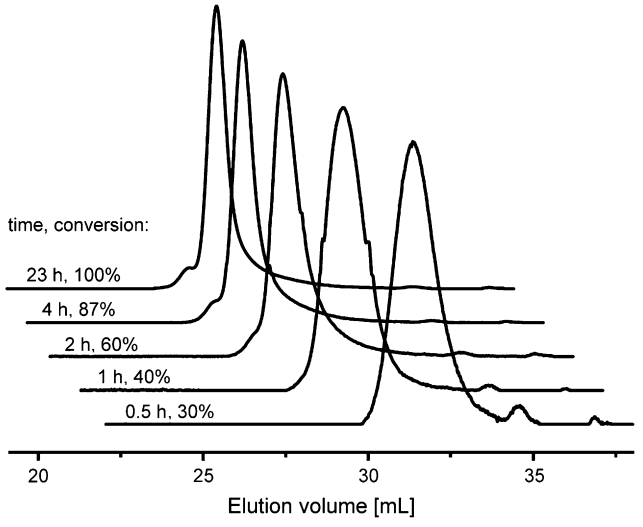
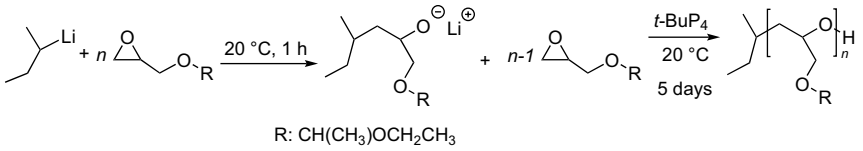


Fig. 3. SEC traces of a kinetic study of the anionic polymerization of EEGE at 100 °C with a [M]/[I] ratio = 100.



Scheme 2. Anionic polymerization of EEGE at 20 °C using *sec*-BuLi and *t*-BuP_4 as initiating system.

molecular weight region seems to result from a side reaction related to the presence of the allylic end group. In fact, it is not observed for polymer **4**, where no allylic end group is formed (Fig. 2). Additionally, a kinetic investigation at 100 °C ([M]/[I] ratio = 100) showed that the high molecular weight peak is only occurring at higher monomer conversions, corresponding to higher degrees of polymerizations, when there are already allylic end groups present in the reaction mixture (Fig. 3). A deconvolution of the SEC traces of **2** and **3** (Fig. 2) showed, that the molecular weight of the high-molecular-weight shoulder is twice the molecular weight of the main peak. It is assumed that a coupling reaction is taking place. In literature, proton abstraction from the epoxide ring by the initiator or the living chain has been described [33]. This transfer reaction results in an enolate able to initiate the EEGE polymerization and produces a polymer with a ketone group at the chain end. A coupling reaction of the ketone group and the alkoxide of a propagating chain end could yield a polymer with exactly the double molecular weight. Coupling reactions have also been observed in the anionic polymerization of styrene, however, the origin of such coupling reactions has not been fully elucidated [35]. In addition, the polydispersity indices increase with higher [M]/[I] ratios.

Under these reaction conditions, the molecular weight of P(EEGE) is limited to $M_n \approx 28{,}000$ ($DP_n \approx 190$). This is in accordance with literature as, to the best of our knowledge, there has never been reported a P(EEGE) synthesized by alkali metal derivatives with $M_n > 30{,}000$. The occurrence of the chain transfer to the monomer might also explain problems encountered by other groups upon quantitative end capping after EEGE polymerization or attempts to synthesize P(EEGE) with higher degrees of polymerization [17,36]. In summary, at 60 °C anionic polymerization with potassium as a counterion is suitable for the synthesis of P(EEGE) up to a molecular weight of $M_n \approx 25{,}000$.

3.3. Synthesis of polyglycidol at 20 °C with Li^+/t-BuP_4 as initiating system

It has been shown, that ethylene oxide can be polymerized in the presence of Li^+ counterions using the phosphazene base *t*-BuP_4 [37,38]. The role of the phosphazene base is to withdraw the Li^+ counterion from the alkoxide by complexation, thus increasing the nucleophilicity of the alkoxide and allowing the polymerization of oxiranes with lithium alkoxides. This approach has already been successfully applied for the synthesis of diblock and triblock copolymers containing P(EEGE) with a maximum degree of polymerization for the EEGE block of $DP_n = 83$ [20]. Due to the bulky nature of the Li^+/*t*-BuP_4 complex, acting as counterion, the reactivity of the alkoxide at the chain end is higher than in the case of K^+ as a counterion. Therefore polymerization at lower temperatures is possible and a further decrease of the extent of the chain transfer reaction is expected. A series of P(EEGE) was synthesized in the glove box at 20 °C in benzene to minimize the influence of impurities and of oxygene. The solvent, EEGE and *sec*-BuLi were introduced into a flask and stirred for 1 h before the phosphazene base *t*-BuP_4 was added. The polymerization is assumed to proceed according to Scheme 2.

After polymerization, the solvent is removed in vacuum and the polymer subjected to analysis. Different [M]/[I] and *sec*-BuLi/*t*-BuP_4 ratios have been used. In Table 3 the monomer conversions, the molecular weights, the polydispersity indices and the percentage of chains with an allylic end group of the polymers **8**–**13** are listed.

For all reactions, 100% monomer conversion was obtained after 5 days. An induction period of 2 days was observed, which is attributed to the formation of aggregates upon formation of the secondary alcoholates. As conversion was quantitative, the theoretical degree of polymerization results from the EEGE to *sec*-BuLi ratio in the feed and the calculated molecular weight is determined thereof. In the ^1H NMR spectra, the presence of allylic end groups is observed and as it is increasing with the [M]/[I] ratio the occurrence of the chain transfer reaction is confirmed. The amount of AEG was determined following the same procedure as for polymers **5**–**7**. As *sec*-BuLi is a stronger base than potassium alkoxides, a side reaction in the first step of the reaction might be proton abstraction from EEGE resulting in additional allylic end groups not originating from transfer reactions of the living alkoxide chain during the polymerization, thus leading to an overestimation of transfer reactions. In this case, the molecular weights determined by NMR would be underestimated, especially for the reactions with low [M]/[I] values. However, the reasonable accordance between the molecular weights determined by NMR and by SEC indicates that proton abstraction from EEGE by *sec*-BuLi can be neglected and is not the reason for the relatively high AEG values. The influence of the Li^+/*t*-BuP_4 ratio was studied and it seems, that the phosphazene base itself is also able to abstract a proton from the monomer and thus to contribute to the formation of allylic alcoholate groups. In fact, for the same [M]/[I] ratios in the feed, the amount of allylic end groups is increasing with the concentration of phosphazene base (P(EEGE) **10**, **12** and **13** in Table 3).

Again, the number average molecular weights determined by SEC confirm the values obtained by NMR. The SEC elution curves are monomodal with a tailing in the low molecular weight region (Fig. 4). The peak in the high molecular weight region, which has been observed for the polymerizations with K^+ as a counterion, is not detected. Accordingly polydispersity indices remain low.

Table 3
Reagent ratios, monomer conversions, molecular weights, polydispersity indices and percentage of chains with an allylic end group of P(EEGE) (**8**–**13**) synthesized at 20 °C with Li^+/*t*-BuP_4 as initiating system.

P(EEGE)	[M]/[I][a]	Li^+/*t*-BuP_4 ratio	$M_{n,calc.}$[b]	NMR[c]		SEC[d]		AEG[e] [%]
				M_n	DP_n	M_n	M_w/M_n	
8	24	1	3500	2500	17	2800	1.16	29
9	100	1	14,600	8100	55	10,700	1.15	45
10	200	1	29,200	14,200	97	12,100	1.12	51
11	400	1	58,400	22,400	153	18,000	1.13	62
12	200	2	29,200	15,700	108	15,000	1.11	46
13	200	0.5	29,200	12,500	85	11,900	1.14	57

[a] Monomer to initiator ratio in the feed.
[b] Calculated molecular weight (M_n).
[c] Molecular weight (M_n) and degree of polymerization (DP_n) determined from NMR.
[d] Molecular weight (M_n) and polydispersity index (M_w/M_n) determined by size exclusion chromatography (SEC) using narrow distributed poly(methyl methacrylate) standards and tetrahydrofuran as eluent.
[e] Percentage of chains with an allylic end group (AEG) calculated according to equation (3).

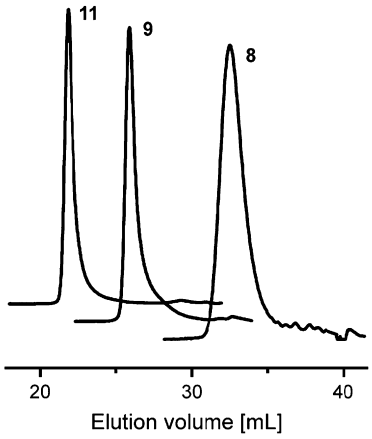


Fig. 4. Exemplary SEC traces for the anionic ring-opening polymerization of EEGE at 20 °C with Li^+/*t*-BuP_4 as initiating system.

Chain transfer to the monomer seems even more probable with the Li^+/*t*-BuP_4 complex than with K^+ as a counterion. The obtained molecular weights are lower and the percentage of detected allylic end groups is higher than for the polymerization at 60 °C with potassium as a counterion. By using the Li^+/*t*-BuP_4 the nucleophilicity of the alkoxide chain end is increased, making the polymerization at 20 °C possible. On the other hand, it seems that the relative increase of the basicity is higher and the proton abstraction from the monomer is enhanced.

It is concluded, that due to the basicity of the alkoxide chain end it will not be possible to obtain polyglycidol with high degrees of polymerization by conventional alkali metal catalyzed polymerization. Thus, the key in obtaining high molecular weight polyglycidol with low polydispersity indices is not to change the reactivity of the propagating chain end by different counterions or complexation of the counterion, but to decrease the basicity of the propagating chain end without decreasing its nucleophilicity.

It has been shown, that if the propagating chain end is not a "free" alkoxide, high molecular weight polyglycidol can be obtained. By the use of partially hydrolyzed diethylzinc as catalyst, the basicity of the propagating alkoxide is suppressed by coordination to the zinc [27,29,30]. Proton abstraction is efficiently avoided. A new approach is the use of onium salts in the presence of trialkylaluminium species, especially triisobutylaluminium, as initiating system [39–41]. It has already been successfully applied for the synthesis of poly(propylene oxide) with molecular weights up to 150,000 and low polydispersity indices. The triisobutylaluminium plays a double role: it activates the monomer making it more prone to nucleophilic attack and it reduces the basicity of the growing chain end by complexation. These findings support the assumption, that the key to obtain high molecular weight polyglycidol is the decrease of the basicity of the alkoxide at the propagating chain end.

4. Conclusions

The polymerization of EEGE was studied with regard to the occurrence of chain transfer to the monomer. Different alkali metal based initiating systems, such as 3-phenylpropanol/potassium 3-phenylpropanolate, potassium *tert*-butoxide and Li^+/*t*-BuP_4 were used and different temperatures were applied. In all cases, the formation of allylic end groups by chain transfer to the monomer was evidenced by ^{1}H NMR spectroscopy and confirmed by SEC analysis. With potassium as a counterion, temperature has been shown to be the most important factor influencing the extent of chain transfer. By lowering the temperature to 60 °C, P(EEGE) up to a molecular weight of $M_n \approx 26{,}000$ was obtained with hardly any chain transfer. A further decrease of the temperature to 20 °C by the use of Li^+/*t*-BuP_4 as initiator did not lead to higher molecular weights. In contrast, this system seemed even more prone to enhance the chain transfer reaction. Thus, the basicity/nucleophilicity ratio of the alkoxide chain ends using Li^+/*t*-BuP_4 as counterion is changed in favor of basicity. Additionally, the base itself may lead to proton abstraction and prevent higher molecular weights. This study shows the limitations in obtaining polyglycidol with high molecular weights by conventional initiators based on alkali metals since the basicity of the propagating alkoxide at the chain end induces proton abstraction from the monomer.

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References

[1] Kainthan RK, Janzen J, Levin E, Devine DV, Brooks DE. Biomacromolecules 2006;7:703.
[2] Sunder A, Muelhaupt R, Haag R, Frey H. Adv Mater 2000;12:235.
[3] Stiriba SE, Kautz H, Frey H. J Am Chem Soc 2002;124:9698.
[4] Chen Y, Shen Z, Barriau E, Kautz H, Frey H. Biomacromolecules 2006;7:919.
[5] Sandler SR, Berg F. J Polym Sci Part A Polym Chem 1966;4:1253.
[6] Vandenberg EJ. J Polym Sci Part A Polym Chem 1985;23:915.
[7] Tokar R, Kubisa P, Penczek S, Dworak A. Macromolecules 1994;27:320.
[8] Sunder A, Hanselmann R, Frey H, Muelhaupt R. Macromolecules 1999;32:4240.
[9] Taton D, Leborgne A, Sepulchre M, Spassky N. Macromol Chem Phys 1994;195:139.
[10] Erberich M, Keul H, Moeller M. Macromolecules 2007;40:3070.
[11] Dworak A, Panchev I, Trzebicka B, Walach W. Macromol Symp 2000;153:233.
[12] Walach W, Kowalczuk A, Trzebicka B, Dworak A. Macromol Rapid Commun 2001;22:1272.
[13] Lapienis G, Penczek S. Biomacromolecules 2005;6:752.
[14] Hans M, Gasteier P, Keul H, Moeller M. Macromolecules 2006;39:3184.
[15] Dworak A, Baran G, Trzebicka B, Walach W. React Funct Polym 1999;42:31.
[16] Dimitrov P, Rangelov S, Dworak A, Tsvetanov CB. Macromolecules 2004;37:1000.
[17] Halacheva S, Rangelov S, Tsvetanov C. Macromolecules 2006;39:6845.
[18] Porjazoska A, Dimitrov P, Dimitrov I, Cvetkovska M, Tsvetanov CB. Macromol Symp 2004;210:427.
[19] Slomkowski S, Gadzinowski M, Sosnowski S, Radomska-Galant I, Pucci A, De Vita C, et al. J Nanosci Nanotechnol 2006;6:3242.
[20] Toy AA, Reinicke S, Mueller AHE, Schmalz H. Macromolecules 2007;40:5241.
[21] Huang J, Wang G. Macromol Rapid Commun 2007;28:298.
[22] Walach W, Trzebicka B, Justynska J, Dworak A. Polymer 2004;45:1755.
[23] Li P, Li Z, Huang J. Macromolecules 2007;40:491.
[24] Li Z, Li P, Huang J. J Polym Sci Part A Polym Chem 2006;44:4361.
[25] Hans M, Keul H, Heise A, Moeller M. Macromolecules 2007;40:8872.
[26] Hans M, Keul H, Moeller M. Biomacromolecules 2008;9:2954.
[27] Dworak A, Trzebicka B, Walach W, Utrata A, Tsvetanov C. Macromol Symp 2004;210:419.
[28] Utrata-Wesolek A, Trzebicka B, Dworak A, Ivanova S, Christova D. e-Polymers 2007.
[29] Haouet A, Sepulchre M, Spassky N. Eur Polym J 1983;19:1089.
[30] Rangelov S, Trzebicka B, Jamroz-Piegza M, Dworak A. J Phys Chem B 2007;111:11127.
[31] Price CC, Atarashi Y, Yamamoto R. J Polym Sci Part A Polym Chem 1969;7:569.
[32] Stpierre LE, Price CC. J Am Chem Soc 1956;78:3432.
[33] Stolarzewicz A. Makromol Chem 1986;187:745.
[34] Fitton AO, Hill J, Jane DE, Millar R. Synthesis 1987:1140.
[35] Fetters LJ, Firer EM. Polymer 1977;18:306.
[36] Mendrek S, Mendrek A, Adler HJ, Walach W, Dworak A, Kuckling D. J Polym Sci Part A Polym Chem 2008;46:2488.
[37] Esswein B, Molenberg A, Moeller M. Macromol Symp 1996;107:331.
[38] Esswein B, Moeller M. Angew Chem Int Ed 1996;35:623.
[39] Labbe A, Carlotti S, Billouard C, Desbois P, Deffieux A. Macromolecules 2007;40:7842.
[40] Rejsek V, Sauvanier D, Billouard C, Desbois P, Deffieux A, Carlotti S. Macromolecules 2007;40:6510.
[41] Billouard C, Carlotti S, Desbois P, Deffieux A. Macromolecules 2004;37:4038.