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Synthesis of Linear High Molar Mass Glycidol-Based Polymers by Monomer-Activated Anionic Polymerization

Matthieu Gervais, Anne-Laure Brocas, Gabriel Cendejas, Alain Deffieux,* and Stephane Carlotti*

Laboratoire de Chimie des Polymères Organiques, Université of Bordeaux, CNRS−ENSCBP, 16 avenue Pey Berland, 33607 Pessac, France

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ABSTRACT: Linear polyglycidols of high molar masses were prepared by the monomer-activated anionic polymerization of the corresponding protected monomers, ethoxyethyl glycidyl ether and *tert*-butyl glycidyl ether, using a system composed of tetraoctylammonium bromide as initiator and triisobutylaluminum as monomer activator. The aluminic compound was used in 1.5−5-fold excess compared to the initiator. Linear poly(ethoxyethyl glycidyl ether) and poly(*tert*-butyl glycidyl ether), with narrow chain dispersity and controlled high molar masses, up to 85 000 g/mol, were prepared at 0 °C in a few hours. Deprotection of hydroxyl functions by acidic treatment of the polymers was shown to proceed quantitatively and cleanly affording the corresponding linear polyglycerol and validating the use of these protecting groups. The copolymerization of protected glycidols with propylene oxide and butene oxide was also investigated with the goal to broaden the scope of this synthetic approach to various polyethers and copolyethers.

Introduction

Polyglycidol, a water-soluble polymer, and its copolymers are of great interest for biomedical applications due to their biocompatibility and high hydroxyl functionality.[1−3] Moreover, glycidol can constitute a significant economical issue for this sector as far as it is readily obtained from glycerol, a byproduct of the synthesis of biodiesel.[4]

Hyperbranched polyglycidols have been recently prepared directly from glycidol by anionic[5−7] or cationic[8−10] polymerizations by combining reactions of epoxide groups and hydroxyl functions. The hyperbranched polymers obtained can reach high molar masses; however, their structure is not well-controlled. The synthesis of linear polyglycidols requires a protection of the monomer hydroxyl function prior the polymerization. The most generally used protection method reported first by Spassky[11] consists in the preparation of ethoxyethyl glycidyl ether (EEGE) by reaction of glycidol with ethyl vinyl ether. The efficiency and ease of the monomer protection step and its deprotection by acidic treatment make EEGE a good candidate as monomer for the synthesis of linear polyglycidols. Many polymerization studies of EEGE have been conducted using both anionic and coordinated type polymerizations.[11−18] Coordinated polymerization using diethylzinc/water or calcium amide alkoxide allows to get high molar mass poly(ethoxyethyl glycidyl ether) (PEEGE), but with either multimodal and/or broad molar mass distributions. Anionic processes involving the use of alkali metal salts and/or phosphazene base initiators permit the synthesis of PEEGE with molar masses limited to 30 000 g/mol due to chain transfer to monomer, as confirmed recently.[18] Despite this drawback, a series of block and random copolymers based on glycidol and ethylene oxide,[15,19−22] propylene oxide,[23] lactide,[22] styrene,[12,24] 2-vinylpyridine,[12] and 4-vinylpyridine[25] have been synthesized to add the hydrophilic behavior and the high functionality of polyglycidol to these polymers. However, the polyglycidol part remained limited to low polymerization degrees. The syntheses of high molar mass polyglycidol and of copolymers with high molar mass polyglycidol block are of great interest to increase the contribution of polyglycidol to the final properties. Recently, other glycidol protecting groups have been reported, including the *tert*-butyl ether group.[13] One interest of *tert*-butyl glycidyl ether (*t*BuGE) deals with its commercial availability, in contrast to EEGE. However, the same limitations are observed in the anionic polymerization of *t*BuGE that allows exclusively the preparation of low molar mass polymers.[13] The preparation of polyglycidol combining high molar mass and a narrow molar mass distribution from an efficient initiating system still remains a challenge to enlarge the scope of applications, especially in the biomedical field.

The present study deals with the use of tetraalkylammonium salts as initiators in the presence of triisobutylaluminum (*i*-Bu_3Al) as activator for the homopolymerization of EEGE and *t*BuGE and for their copolymerization with hydrophobic propylene oxide (POx) or butene oxide (BOx).

Experimental Section

Materials. Triisobutylaluminum (1 mol/L in toluene, Aldrich) was used without further purification. 2,3-Epoxypropan-1-ol (glycidol, 96%, Aldrich) and ethyl vinyl ether (99% Aldrich) were used as received. Propylene oxide (99%, Fluka), butene oxide (99%, Aldrich), and *tert*-butylglycidyl ether (99%, Aldrich) were purified over CaH_2, distilled under vacuum, and stored for 15 min in a glass flask equipped with PTFE stopcocks in the presence of i-Bu_3Al to remove traces of impurities. They were finally distilled under vacuum and stored under vacuum at RT in calibrated glass tubes until use. Toluene (98%, J.T. Baker) was purified with polystyryllithium seeds. It was distilled under vacuum and then stored in calibrated glass tubes under vacuum. Tetraoctylammonium bromide ($NOct_4Br$) (98%, Aldrich) was solubilized into dried toluene and stored in calibrated glass tubes fitted with PTFE stopcocks. Ethoxyethyl glycidyl ether was synthesized from glycidol and ethyl vinyl ether as already

*Corresponding author. E-mail: carlotti@enscpb.fr.

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Scheme 1. Protection and Polymerization of Ethoxyethyl Glycidyl Ether

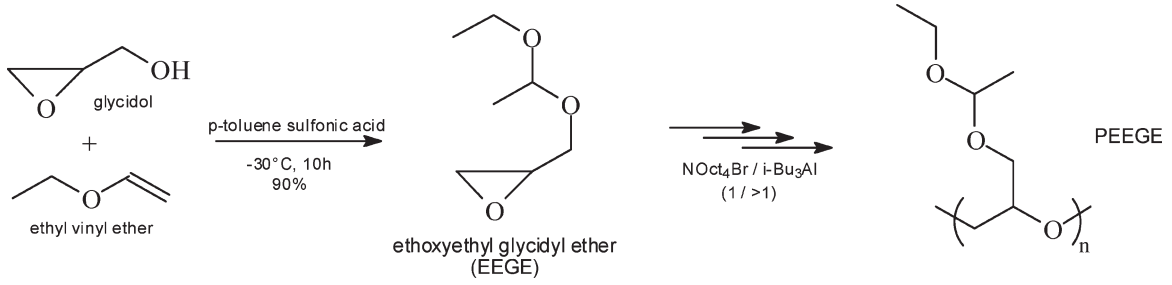


Table 1. Polymerization of Ethoxyethyl Glycidyl Ether (EEGE) Using $NOct_4Br/i\text{-}Bu_3Al$ (Toluene, 0 °C)

run	$[i\text{-}Bu_3Al]/[NOct_4Br]$	[EEGE] (mol/L)	yield[a] (%)	time (h)	$\overline{M}_n$ th[b] (g/mol)	$\overline{M}_n$ exp (g/mol) SEC[c]	$\overline{M}_n$ exp (g/mol) osmo[d]	$\overline{M}_w/\overline{M}_n$[c]
1	2	0.5	63	18	18 900	18 000		1.03
2	2	2	68	28	68 000	50 000		1.18
3	3	1.5	70	24	35 000	35 000		1.30
4	4	0.5	100	9	10 000	10 300	11 000	1.06
5	4	1	100	19	30 000	29 600	31 000	1.06
6	5	2	100	15	100 000	85 000		1.27

[a] Determined gravimetrically. [b] $\overline{M}_n$ th = $[EEGE]_0/[NOct_4Br] \times M_{EEGE} \times$ yield. [c] Determined by size exclusion chromatography in tetrahydrofuran using a calibration with polystyrene standards. [d] Determined by osmometry in toluene.

reported[26] with a yield of 90%, dried with CaH_2, and distilled prior to use.

Procedures. All (co)polymerizations were performed between 0 and 25 °C under argon in a glass reactor equipped with a magnetic stirrer and fitted with PTFE stopcocks. As an example a polymerization reactor was flamed under vacuum and cooled prior introduction of 32 mL of toluene and 6 mL of EEGE (39.4 mmol) through connected glass tubes. Then, 0.87 mL (0.19 mmol) of a toluene solution of $NOct_4Br$ (C = 0.22 M) followed by 0.77 mL (0.77 mmol) of $i\text{-}Bu_3Al$ solution in toluene (C = 1 M) were added via a syringe under argon. The polymerization was allowed to proceed for 19 h at 0 °C and then stopped by addition of ethanol. The yield (100%) was determined gravimetrically after complete drying of the polymer under vacuum at 50 °C. $\overline{M}_n$(SEC) = 29 600 g/mol, I_p = 1.06. ^{1}H NMR of PEEGE: $-O-CH_2(1)-CH(2)[CH_2(3)-O-CH(4)-CH_3(5)-O-CH_2(6)-CH_3(7)]$: 1, 2, 3, 6, 3.35−3.75 ppm; 4, quadruplet at 4.75 ppm; 5, 1.27 ppm; 7, 1.17 ppm.

Polymerization of tBuGE, following the same procedure, was carried out with 1 mL of tBuGE (7 mmol), 6 mL of toluene, 0.14 mL (0.045 mmol) of $NOct_4Br$ solution in toluene (C = 0.32 M), and 0.09 mL (0.09 mmol) of $i\text{-}Bu_3Al$ solution in toluene (C = 1 M) for 3 h at 0 °C. $\overline{M}_n$(SEC) = 20 000 g/mol, I_p = 1.02. ^{1}H NMR of P*t*BuGE: $-O-CH_2(1)-CH(2)[CH_2(3)-O-[CH_3(4)]_3]$: 1, 2, 3, 3.35−3.70 ppm; 4, 1.17 ppm.

A typical copolymerization of EEGE and POx was carried out with 2 mL (28.6 mmol) of POx, 1.8 mL (11.8 mmol) of EEGE, 20 mL of toluene, and 0.78 mL (0.17 mmol) of $NOct_4Br$ solution in toluene (C = 0.22 M) and 0.85 mL (0.85 mmol) of $i\text{-}Bu_3Al$ solution in toluene (C = 1 M) for 3 h at −30 °C. Yield: 100%, $\overline{M}_n$(SEC) = 21 000 g/mol, I_p = 1.30, DP_{EEGE}/DP_{POx} (NMR) = 0.32. ^{1}H NMR of P(EEGE-*co*-POx): $-O-CH_2(1)-CH(2)[-CH_2(3)-O-CH(4)-CH_3(5)-O-CH_2(6)-CH_3(7)]$-*co*-$O-CH_2(8)-CH(9)[CH_3(10)]$: 1, 2, 3, 6, 8, 9, 3.35−3.75 ppm; 4, quadruplet at 4.75 ppm; 5, 1.27 ppm; 7 and 10, 1.17 ppm.

Copolymerization of *t*BuGE and BOx was carried out with 1 mL (11.6 mmol) of BOx, 1 mL (7 mmol) of tBuGE, 16 mL of toluene, 0.38 mL (0.08 mmol) of $NOct_4Br$ solution in toluene (C = 0.22 M), and 0.17 mL (0.17 mmol) of $i\text{-}Bu_3Al$ solution in toluene (C = 1 M) for 8 h at −30 °C. Yield: 100%, $\overline{M}_n$(SEC) = 21 000 g/mol, I_p = 1.16, DP_{tBuGE}/DP_{BOx} (NMR) = 0.57. ^{1}H NMR of P(*t*-BuGE-*co*-BOx): $-O-CH_2(1)-CH(2)[-CH_2(3)-O-C(CH_3)_3(4)]$-*co*-$O-CH_2(5)-CH(6)[-CH_2(7)-CH_3(8)]$: 1, 2, 3, 5, 6, 3.35−3.75 ppm; 4, 1.17 ppm; 7, 1.35−1.65 ppm; 8, triplet at 0.90 ppm.

Deprotection of PEEGE was carried out in ethanol with 3% HCl and stirred for 4 h. The polymer was then evaporated under reduced pressure and finally dried under vacuum. Deprotection of PtBuGE was done in ethanol with 3% HCl under stirring for 24 h at 60 °C. After neutralization by adding sodium carbonate, ethanol was evaporated under reduced pressure and polyglycidol finally dried under vacuum. ^{1}H NMR of polyglycidol: $O-CH_2(1)-CH(2)[CH_2(3)-OH]-O$: 1, 2, 3, 3.60−3.85 ppm.

Analysis. Polymer molar masses were determined by size exclusion chromatography (SEC) at 40 °C using tetrahydrofuran (THF) as eluent. Measurements in THF were performed on a PL GPC50 integrated system with RI and UV detectors and three TSK columns: G4000HXL (particles of 5 μm, pore size of 200 Å, and exclusion limit of 400 000 Da), G3000HXL (particles of 5 μm, pore size of 75 Å and exclusion limit of 60 000 Da), G2000HXL (particles of 5 μm, pore size of 20 Å and exclusion limit of 10 000 Da) at an elution rate of 1 mL/min. Polystyrene were used as standards. Measurements in dimethylformamide (DMF) were performed on a similar apparatus with the same kind of columns, elution rate, and standards.

^{1}H (400 MHz) NMR measurements of the polymers and copolymers were performed on a Brüker Avance 400 spectrometer, in $CDCl_3$ or D_2O at room temperature.

Osmometric measurements were performed on a Gonotec Osmomat 090 device in toluene with a Tac 5 kDa membrane. Osmotic pressures were measured for each sample at five concentrations: 0.2, 0.5, 1, 2, and 5 mg/mL.

Results and Discussion

Polymerization of Ethoxyethyl Glycidyl Ether. A binary initiating system constituted of $NOct_4Br$ as initiator and $i\text{-}Bu_3Al$ as catalyst/activator has been recently reported by us for the controlled anionic polymerization of epoxides[27−30] in hydrocarbon media. This system was investigated for the polymerization of EEGE, as a protected form of glycidol (see Scheme 1).

As indicated in Table 1, polymerization of EEGE proceeds in toluene at low temperature, for $[i\text{-}Bu_3Al]/[NOct_4Br]$ ratios ranging from 2 to 5. However, quantitative polymerization requires the use of ratios higher than 3. Whereas at a ratio of 4 the polymerization of EEGE is achieved up to quantitative

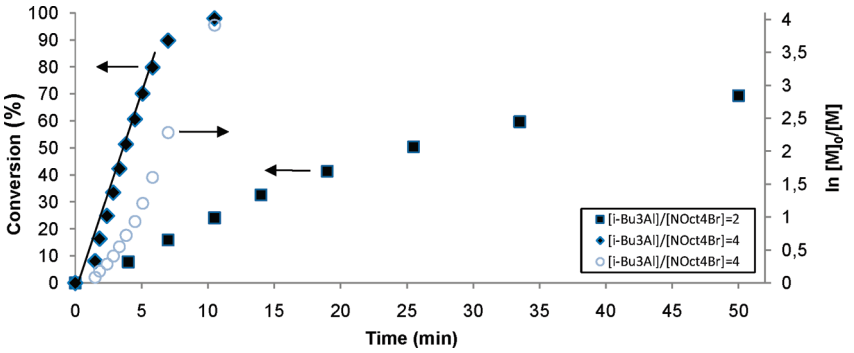


Figure 1. Conversion (filled squares) and $\ln[M]_0/[M]$ (open circles) versus time plots for the polymerization of ethoxyethyl glycidyl ether (EEGE) (toluene, 0 °C, [EEGE] = 0.5 M, $[NOct_4Br] = 7 \times 10^{-3}$ M, [*i*-Bu_3Al]/[$NOct_4Br$] = 2 (■) or 4 (○)).

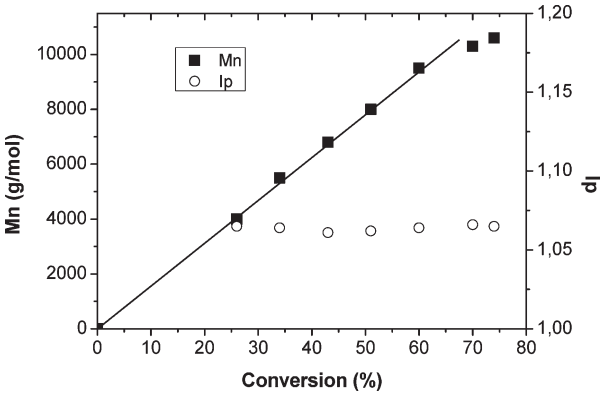


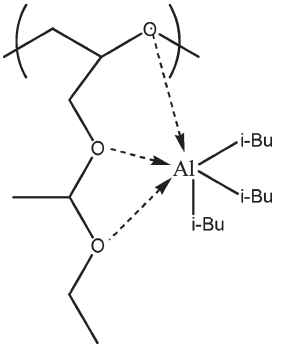
Figure 2. Evolution of molar masses and molar mass distribution (I_p) versus conversion in the polymerization of (EEGE) (toluene, 0 °C, [EEGE] = 0.5 M, $[NOct_4Br] = 7 \times 10^{-3}$ M, [*i*-Bu_3Al]/[$NOct_4Br$] = 2).

conversion when medium molar mass polymers are targeted (runs 4 and 5, Table 1), this ratio should be raised to 5 for high molar mass PEEGE (100 000 g/mol). The increase of the monomer concentration also favors fast reactions. This shows that more *i*-Bu_3Al is required to trigger the EEGE polymerization compared to propylene oxide.[27]

Experimental molar masses, determined by SEC on the basis of a polystyrene calibration, are in the range of the calculated ones, assuming the formation of one PEEGE chain per $NOct_4Br$. A good correlation between SEC PS molar masses and PEEGE ones was shown by osmometry measurements performed on PEEGE samples with molar masses ranging from 10 000 to 30 000 g/mol (see Table 1). The use of higher [*i*-Bu_3Al]/[$NOct_4Br$] ratio and high monomer concentration (>2 mol/L) to speed up the reaction resulted in a broadening of the molar mass distribution, suggesting the contribution of side reactions in these conditions, probably some transfer to *i*-Bu_3Al as already explained for propylene oxide.[27] Concerning the transfer to monomer observed with conventional initiation like potassium alkoxides, precisely described by Keul and Moeller,[18] which limits the molar masses, it was not observed with the initiating system we have used. Indeed, no characteristic peaks of allylic end groups at 4, 5, and 6.6 ppm appeared in the ^{1}H NMR spectra of all protected polyglycidol synthesized (see Figure S1 given as Supporting Information).

EEGE polymerization kinetics were carried out by dilatometry. Typical conversion vs time curves are plotted Figure 1 for [*i*-Bu_3Al]/[$NOct_4Br$] ratios 2 and 4 as well as $\ln([M]_0/[M])$ vs time for a ratio equal to 4. For 2 equiv of [*i*-Bu_3Al], the monomer consumption levels off at about 60% conversion and does not reach completion, although the

Scheme 2. Complexation of Triisobutylaluminum by Oxygens of Poly(EEGE) Chains



final molar masses remains in good agreement with theoretical values at the obtained conversion. Indeed, the PEEGE molar mass increases linearly with the monomer conversion up to the final yield, whereas molar mass distribution remains narrow (see Figure 2). This behavior can be explained by a living-like reaction, without termination and transfer, in which the *i*-Bu_3Al fraction used to trigger the reaction is trapped by complexation with the oxygen of poly(EEGE) chain, as illustrated in Scheme 2.

In contrast, for 4 equiv of *i*-Bu_3Al, a linear consumption, up to 90%, of EEGE is observed in a few minutes, at 0 °C, yielding PEEGE of 10 000 g/mol with a dispersity of 1.11. The $([M]_0 - [M]/[M]_0) = f(t)$ plot follows a linear rate law up to high EEGE conversion, whereas the $\ln([M]_0/[M])$ vs time plot is not linear. This suggests an apparent zero monomer order for the propagation reaction as already proposed for the monomer-activated mechanism of propylene oxide,[27] illustrated for EEGE in Scheme 3.

Kinetics of the EEGE activated anionic polymerization can be expressed by the equation $R_p = k_p[NOct_4Br]_0[M^*]$, where k_p is the propagation rate constant and M* represents the trialkylaluminum activated monomer. At initial polymerization time [M*] can be approximated to $[Al]_0 - [NOct_4Br]_0$ considering that 1 equiv of *i*-Bu_3Al is quantitatively trapped in the 1:1 aluminate complex[27] and that complexation of *i*-Bu_3Al by the poly(EEGE) chain is negligible.

All the results agrees with the formation of a 1:1 initiating and propagating complex of low basicity, which strongly minimizes transfer reactions to monomer, and of high nucleophilicity due to the activation role of the excess of Lewis acid, allowing fast reactions at low temperatures.

The regioregularity and stereospecificity of PEEGE chains were examined by ^{13}C NMR. As can be seen Figure 3 at 65 and 79 ppm corresponding respectively to methylene and

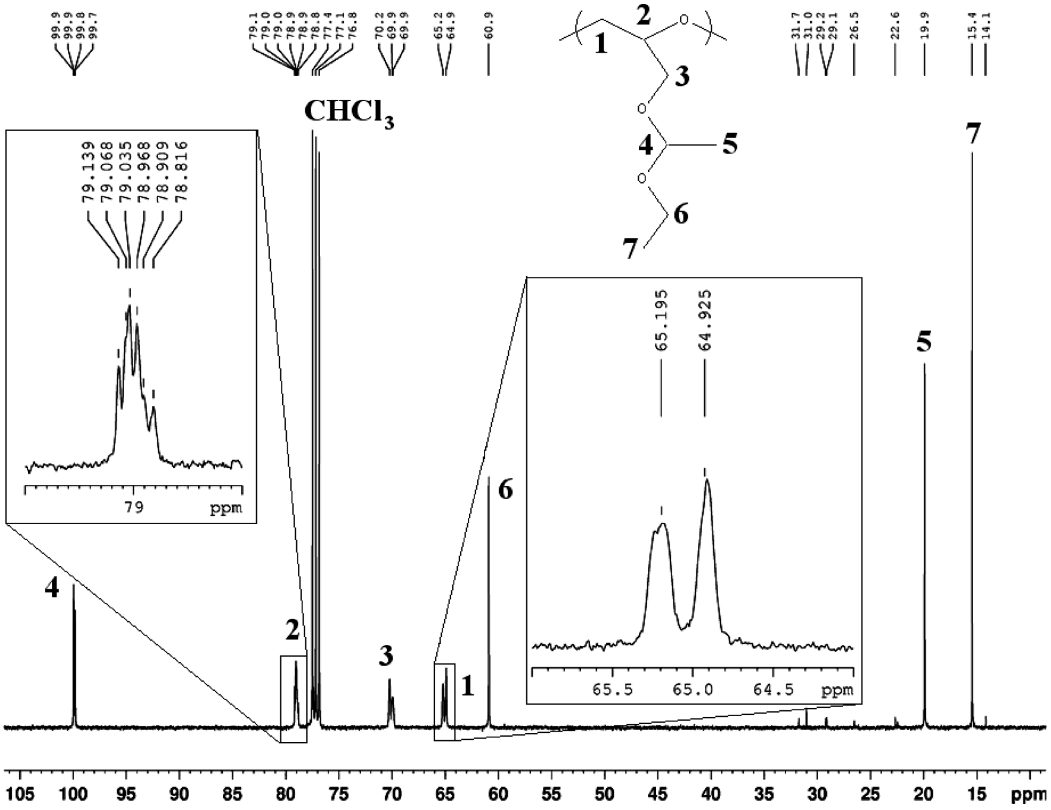
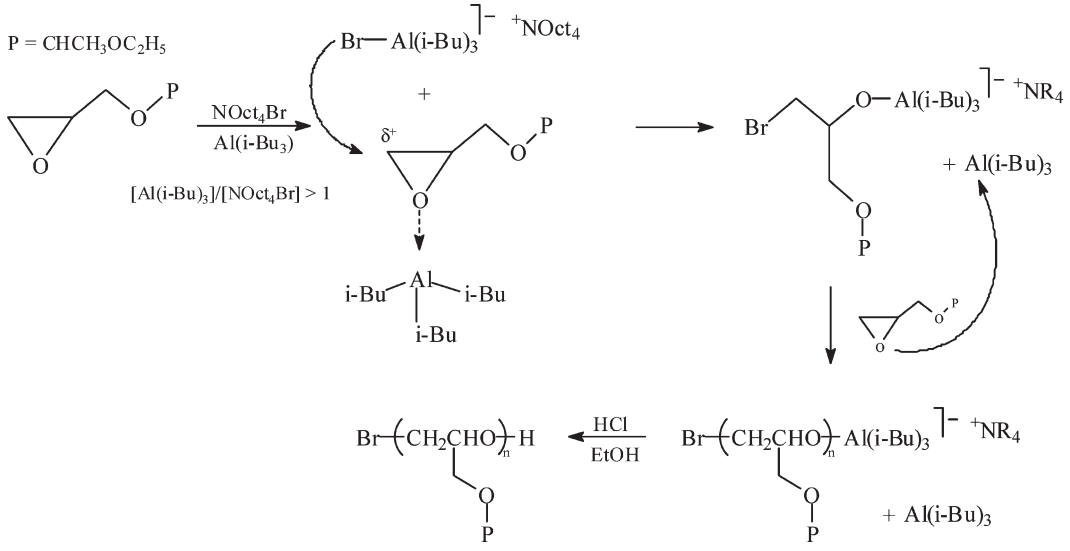


Figure 3. ^{13}C NMR spectra of PEEGE synthesized in the presence of the $NOct_4Br$/i-Bu_3Al initiating system (run 4 Table 1, [*i*-Bu_3Al]/[$NOct_4Br$] = 4, toluene, 0 °C, [EEGE] = 0.5 mol/L).

Scheme 3. Mechanism for the Monomer-Activated Anionic Polymerization of Ethoxyethyl Glycidyl Ether Initiated by the $NOct_4Br$/i-Bu_3Al System



methine groups of the polymer backbone, no small side peaks indicative of head-to-head and tail-to-tail irregularities, as reported for regioirregular poly(propylene oxide),[31] are detected close to the two mentioned chemical shifts. This indicates a highly regioregular insertion of EEGE in agreement with an anionic polymerization mechanism. The splitting of the methylene signal into two main peaks of almost same intensity, at 64.9 and 65.2 ppm, can be attributed to the presence of meso and racemic EEGE diads. The methine peak resolution in a multiplet, between 78.7 and 79.2 ppm, also points out the presence of different stereosequences. This confirms the formation of atactic PEEGE and the absence of stereoregulation during the EEGE polymerization in presence of the $NOct_4Br$/*i*-Bu_3Al initiating system.

Polymerization of *tert*-Butyl Glycidyl Ether. Following the same strategy and conditions, the polymerization of *tert*-butyl glycidyl ether has been carried out in presence of $NOct_4Br$/*i*-Bu_3Al. Typical polymerization results are collected in Table 2.

Compared to EEGE, polymerization of *t*BuGE proceeds more readily and goes to completion in a few hours using only 2 equiv of triisobutylaluminum with respect to the tetraoctylammonium bromide initiator. This can be explained by the presence of a single oxygen atom on the

Table 2. Polymerization of *tert*-Butyl Glycidyl Ether (*t*-BuGE) with $NOct_4Br/i\text{-}Bu_3Al$ (Toluene, 0 °C)

run	[*i*-Bu_3Al]/[$NOct_4Br$]	[*t*-BuGE] (mol/L)	time (h)	yield[a] (%)	$\overline{M_n}$ th[b] (g/mol)	$\overline{M_n}$ exp[c] (g/mol)	$\overline{M_w}/\overline{M_n}$[c]
1	1.5	1	3	54	16 000	20 000	1.13
2	2	1	3	100	10 000	14 000	1.15
3	2	1	3	100	20 200	20 000	1.02
4	3	1	3	100	30 000	26 000	1.15
5	4	3	7[d]	100	65 000	52 000	1.37

[a] Determined gravimetrically. [b] $\overline{M_n}$ th = [*t*-BuGE]/[$NOct_4Br$] × $M_{t\text{-BuGE}}$. [c] Determined by SEC in THF using a calibration with PS standards. [d] The temperature was left to increase up to 25 °C.

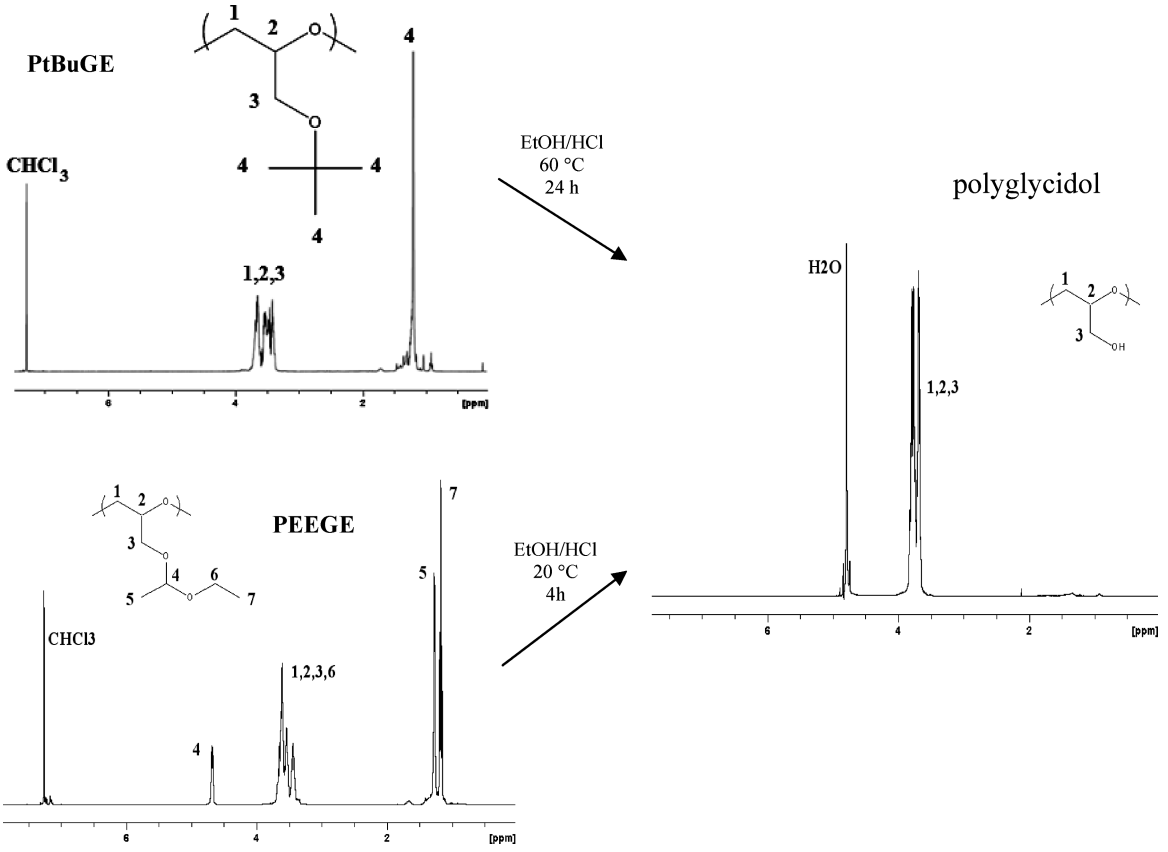


Figure 4. ^1H NMR analysis of poly(EEGE) (run 5 Table 1) and poly(*t*BuGE) (run 4 Table 2) before (in $CDCl_3$) and after (in D_2O) acidic deprotection.

*t*BuGE and on P*t*BuGE units, without counting the oxygen atom of the reactive and reacted epoxide function, which is moreover greatly hindered by its *tert*-butyl substituent. This strongly limits complexation of the aluminum compound by the chain. P*t*BuGE experimental molar masses determined by SEC on the basis of a polystyrene calibration are in the range of calculated ones, and dispersities remain narrow for a molar mass up to 26 000 g/mol or slightly broad for a sample at 52 000 g/mol. This indicates that no significant side reaction occurs during propagation. But the preparation of much higher molar masses starting with this monomer appeared more problematic than EEGE. Polymer solubility difficulties appeared in many solvents and can be one reason. Despite this limitation, the data reported and its commercial availability make *t*BuGE a first ranked raw material for the synthesis of linear polyglycidol by the reported polymerization system, assuming that the deprotection step would proceed cleanly.

Deprotection of Poly(EEGE) and Poly(tBuGE) units. Both acetal[14] and *tert*-butyl[32] protecting groups of glycidol units respectively in PEEGE and P*t*BuGE can be removed by acidic treatment although the deprotection conditions are quite different. Acetal groups of PEEGE can be quantitatively removed by treatment of the polymer in an acidic ethanol solution (3 vol % of HCl) in 4 h at room temperature. Removal of the *tert*-butyl groups of P*t*BuGE using the same

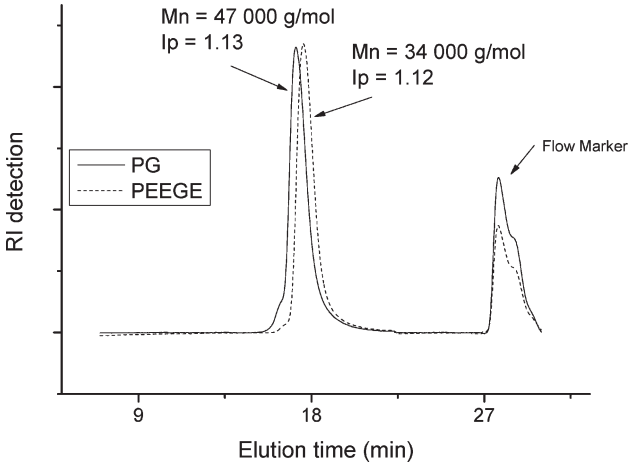


Figure 5. SEC chromatograms and apparent molar mass (polystyrene calibration) of a PEEGE prepared using $NOct_4Br/i\text{-}Bu_3Al$ (1/5) as initiating system before and after deprotection using HCl/ethanol (3/97 in volume).

Table 3. Copolymerization of EEGE with Propylene Oxide (Toluene, [M] = 2 M, −30 °C, [*i*-Bu_3Al]/[$NOct_4Br$] = 5, 3 h) and of *t*BuGE with Butene Oxide (Toluene, [M] = 2 M, −30 °C, [*i*-Bu_3Al]/[$NOct_4Br$] = 2, 8 h)

run	theoretical composition $DP_{EEGE}-DP_{POx}$[a]	DP_{EEGE}/DP_{POx} th[a]	DP_{EEGE}/DP_{POx} exp[b]	$\overline{M_n}$ th[c] (g/mol)	$\overline{M_n}$ exp[f] (g/mol)	conversion[g] (%)	$\overline{M_w}/\overline{M_n}$[f]
1	69−168	0.41	0.32	19 800	21 000	100	1.30
2	69−168	0.41	0.44	19 800	15 000	100	1.43
3	65−262	0.25	0.22	25 000	25 000	100	1.58
4	132−155	0.85	0.84	28 000	31 000	100	1.41
5	137−172	0.80	0.82	30 000	36 000	100	1.34
run	theoretical composition $DP_{tBuGE}-DP_{BOx}$[d]	DP_{tBuGE}/DP_{BOx} th[d]	DP_{tBuGE}/DP_{BOx} exp[b]	$\overline{M_n}$ th[e] (g/mol)	$\overline{M_n}$ exp[f] (g/mol)	conversion[g] (%)	$\overline{M_w}/\overline{M_n}$[f]
6	42−69	0.61	0.52	10 000	12 000	100	1.14
7	87−144	0.55	0.60	21 700	21 000	100	1.16

[a] DP_{EEGE} = [EEGE]/[$NOct_4Br$], DP_{POx} = [POx]/[$NOct_4Br$]. [b] Determined by ^1H NMR. [c] $\overline{M_n}$ th = ([EEGE]/[$NOct_4Br$] × M_{EEGE} + [POx]/[$NOct_4Br$] × M_{POx}) × conversion. [d] DP_{tBuGE} = [*t*BuGE]/[$NOct_4Br$], DP_{BOx} = [BOx]/[$NOct_4Br$]. [e] M_n th = ([*t*BuGE]/[$NOct_4Br$] × M_{tBuGE} + [BOx]/[$NOct_4Br$] × M_{BOx}) × conversion. [f] Determined by SEC in THF using a calibration with PS standards. [g] Determined gravimetrically.

acidic ethanol solution requires 24 h at 60 °C. The ^1H NMR spectra of PEEGE and P*t*BuGE synthesized by the monomer-activated approach and of the corresponding deprotected polyglycidol are shown Figure 4.

SEC analysis carried out in DMF on protected and deprotected polyglycidol shows no peak broadening in agreement with a clean deprotection step (Figure 5). The apparent polyglycidol molar mass are higher than that of the initial PEEGE, although the repetitive unit decreases from 146 to 74 g/mol, leading to a loss of around half of the polymer molar mass. This may be explained by the difference of hydrodynamic volume of PEEGE and polyglycidol.

Copolymerization Studies. The copolymerization of EEGE and *t*BuGE with other epoxides has been investigated to examine the possibility of synthesizing copolyethers of various hydrophilicity or amphiphilicity. Typical results for the copolymerization of EEGE with propylene oxide, mixed at the same time, are collected in Table 3. Copolymerizations go to completion, and the copolymers analyzed by SEC show a monomodal distribution (see Figure S2 given as Supporting Information) and experimental molar masses close to theoretical values. The broadening of dispersities in comparison with hompolymerization results can be attributed to the high $NOct_4Br$/*i*-Bu_3Al ratio used (1/5), necessary to quantitatively polymerize EEGE, which induces a very high reactivity for POx and results in a slight contribution of transfer reaction.[27] The reactivity ratios between EEGE and POx were determined in a series of copolymerization experiments stopped at low conversion, using the Kelen−Tudös method.[33] This yields $r_{POx} = k_{POxPOx}/k_{POxPEEGE} = 3.58$ and $r_{PEEGE} = k_{PEEGEPEEGE}/k_{PEEGEPOx} = 0.18$. These values indicate, in living-like conditions, the formation of copolymers with a gradient composition constituted by a predominant incorporation of POx units at the beginning of the chains and EEGE units at the end. This should yield after release of the hydroxyl groups of the glycidol units copolymers with an amphiphilic character. A quantitative deprotection was achieved following the procedure discussed above as confirmed by ^1H NMR spectroscopy of a poly(propylene oxide-*co*-glycidol) copolymer (Figure S3 given as Supporting Information). A preliminary study of the behavior in solution of this copolymer showed the formation of micelles in water.

In a similar way *t*BuGE was copolymerized with butene oxide a monomer of lower reactivity than propylene oxide and with a more pronounced hydrophobic character with the objective to enlarge the scope of this synthetic approach to other copolymers based on cyclic ethers. Copolymerization results are collected in Table 3. Again, copolymerization proceeds to complete monomers consumption even at low $NOct_4Br$/[*i*-Bu_3Al] ratio, yielding copolymers with similar average composition as the comonomer feed, experimental molar masses in the range of theoretical ones, and low dispersities. A further study will focus on the structures of the copolymers prepared by this approach as well as their properties.

Conclusion

The anionic polymerization of protected glycidols (ethoxyethyl glycidyl ether and *tert*-butyl glycidyl ether) in the presence of a binary initiating system consisting of tetraoctylammonium bromide ($NOct_4Br$) and an excess of triisobutylaluminum (*i*-Bu_3Al) has been investigated. This method allows the controlled syntheses of PEEGE and P*t*BuGE of high molar masses, up to 85 000 g/mol as shown for PEEGE, in short reaction time, at 0 °C. A 1:1 initiating or propagating complex of weak basicity is believed to be formed, which suppresses transfer reactions to monomer. Fast polymerizations at low temperatures support a high nucleophilicity of the system due to the monomer-activation role of the excess of Lewis acid. Its amount required to trigger the reaction and get quantitative yields depends on the glycidyl derivative used as protected form of glycidol, probably in relation to the number of oxygen atoms contained in the epoxide side group. After a clean and quantitative acidic deprotection, polyglycidol as well as a large variety of copolymers of glycidol with controlled molar masses can be obtained, offering new opportunities of applications, in particular in the field of biomaterials.

Supporting Information Available: ^1H NMR spectrum of PEEGE (Figure S1), SEC chromatogram in THF of a P(POx-*ran*-EEGE) (Figure S2), and ^1H NMR spectrum of P(POx-*ran*-EEGE) (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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