Polyglycidols with Two Orthogonal Protective Groups: Preparation, Selective Deprotection, and Functionalization

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ABSTRACT: Anionic ring-opening polymerization and copolymerization of allyl glycidyl ether (AGE), *tert*-butyl glycidyl ether (*t*BuGE), and ethoxyethyl glycidyl ether (EEGE) was performed using potassium 3-phenyl-1-propanol as initiator. The polymers poly(AGE), poly(*t*BuGE), poly(EEGE) as well as poly(AGE-*co*-*t*BuGE), poly(AGE-*co*-EEGE), and poly(EEGE-*co*-*t*BuGE) were obtained with controlled degree of polymerization, narrow molecular weight distribution and a predetermined ratio of repeating units. First-order kinetics with respect to the glycidyl monomers were found for homo- and copolymerization. The removal of protection groups from the homopolymers was achieved using trifluoroacetic acid for poly(*t*BuGE), aqueous hydrochloric acid for poly(EEGE), and a palladium catalyst for poly(AGE); in all cases a linear poly(glycidyl ether) (poly(GE), **1**) was obtained. The following conversions were achieved by selective removal of only one protection group: using aqueous hydrochloric acid, poly(AGE-*co*-EEGE) was converted to poly(AGE-*co*-GE) **4**; using trifluoroacetic acid, poly(AGE-*co*-*t*BuGE) was converted to poly(AGE-*co*-glycidyl trifluoroacetate), **5**; and by using Pd/C and *p*-toluenesulfonic acid poly(AGE-*co*-*t*BuGE) was converted to poly(GE-*co*-*t*BuGE), **3**. A selective removal of only one protection group from poly(EEGE-*co*-*t*BuGE) was not possible. Treatment with aqueous hydrochloric acid or with trifluoroacetic acid lead to poly(GE), **1**, and poly(glycidyl trifluoroacetate), **2**, respectively. Finally free hydroxymethyl groups of the polymers poly(GE-*co*-*t*BuGE), **3**, and poly(AGE-*co*-GE), **4**, were partially converted in a polymer analogous reaction using propargyl bromide to the corresponding polymers with glycidyl propargyl ether (GPE) repeating units. In a model reaction one of these polymers with GPE repeating units was successfully converted with an azido sugar moiety in a (2 + 3) cycloaddition reaction.

1. Introduction

First reports on the anionic polymerization of glycidols go back to Vandenberg and Spassky.[1,2] In recent years the preparation of polyglycidols starting with unprotected and protected glycidol (2,3-epoxypropan-1-ol) monomers has been studied intensely.[3−10] Hyperbranched polymers prepared by anionic ring-opening polymerization of glycidol formed the basis of *core*−*shell* type polyethers.[8−10] These polymers have been studied for medical applications, i.e., nanocapsule preparation for controlled drug release.[9] In general, the microstructure/architecture of the hyperbranched polyglycidols is not well controlled, especially at higher molecular weights the distribution of branching variations and molecular weight increases. Alternative to this approach, well-defined linear and star shaped polyglycidols were obtained when a protected glycidol monomer was polymerized with mono and multifunctional initiators.[11] Ethoxyethyl glycidyl ether (EEGE)[3,12] with an acetal protection group was first synthesized by Fitton et al.[12] The acetal is stable under polymerization conditions and complete deprotection is achieved under acidic conditions. Tertiary butyl glycidyl ether (*t*BuGE) is another protected glycidol monomer, that has been polymerized before to study the dielectrical properties of this polymer, chain dynamics, segmental motion, and rotation of side groups.[13] To our knowledge, there are no systematic attempts for a controlled polymerization of this monomer, and deprotection of the poly(*tert*-butyl glycidyl ether) (P*t*BuGE) to polyglycidol has not been attempted yet. However, tertiary butyl ether groups can be cleaved with trifluoroacetic acid.[14] The ring-opening polymerization of allyl glycidyl ether (AGE) has been studied in order to determine its reactivity compared to other oxiranes.[15] Diblock copolymers with poly(ethylene oxide) were prepared for micellar drug delivery systems.[16] No attempt was made to convert the allyl ether groups to free hydroxymethyl groups, although allyl ethers can be cleaved by $Pd(PPh_3)_4$/*p*-toluenesulfinate[17] or Pd(0)/charcoal/*p*-toluenesulfonic acid.[18]

Block copolymers of EEGE, *t*BuGE, and AGE with other oxirane monomers have been prepared, i.e., glycidol/EEGE, EEGE/propylene oxide or even glycidol/ethylenoxide[19] as well as AGE and propylene oxide.[15] These reactions were performed in order to study the polymer behavior in solution[19] and the relative reactivity of the monomers.[15]

Here we report on binary copolymers of EEGE, *t*BuGE, and AGE followed by selective removal of one protection group and subsequent functionalization of the free hydroxyl groups and removal of the second protection group. The concept of this research is directed toward orthogonal conversion of the different blocks in order to obtain well-defined functional block copolymers. We studied the kinetics of the homo- and copolymerization, of EEGE, *t*BuGE, and AGE and the reaction conditions for selective removal of protection groups. Propargyl ether modified polymers were subjected to a Huisgen (2 + 3) dipolar cycloaddition,[20] which is also known as "click"-reaction,[21,22] using an azide functionalized glucose derivative.

2. Experimental Part

Materials. Allyl glycidyl ether (99%, Fluka), *tert*-butyl glycidyl ether (99%, Fluka) and 3-phenyl-1-propanol (3-PP, 99%, Aldrich) were distilled from molecular sieves (4 Å) at reduced pressure and stored under nitrogen before use. Diglyme was dried by distillation at reduced pressure over sodium and stored under nitrogen before use. Potassium *tert*-butoxide (1 M solution in tetrahydrofuran (THF), Aldrich), trifluoroacetic acid (TFA, 99%, Aldrich), propargyl

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Table 1. Ring-Opening Polymerizations of Protected Glycidols:[a] Starting Materials and Yields[b]

polymer no.[c]	M_1/M_2	M_1 [g (mmol)]	M_2 [g (mmol)]	3-PP [mg (mmol)]	KO*t*Bu (mmol)	*t* (h)	yield[d] [g (%)]
P(*t*BuGE)	*t*BuGE	17.831 (136.96)	/	581 (4.28)	0.43	20	16.879 (91.7)
P(AGE)	AGE	15.633 (136.96)	/	595 (4.37)	0.43	20	10.963 (67.6)
P(EEGE)	EEGE	19.920 (136.26)	/	584 (4.29)	0.43	20	19.877 (97)
P(*t*BuGE)-*co*-P(EEGE)-1	*t*BuGE/EEGE	4.244 (32.60)	4.766 (32.60)	308 (2.26)	0.23	40	9.028 (97)
P(*t*BuGE)-*co*-P(EEGE)-2		6.651 (51.10)	7.468 (51.10)	462 (3.40)	0.35	19	12.209 (84)
P(AGE)-*co*-P(EEGE)-1	AGE/EEGE	4.405 (38.60)	5.643 (38.60)	340 (2.50)	0.25	21	10.388 (100)
P(AGE)-*co*-P(EEGE)-2		6.388 (56.00)	8.181 (56.00)	510 (3.70)	0.38	19	13.591 (90)
P(*t*BuGE)-*co*-P(AGE)-1	*t*BuGE/AGE	4.830 (37.10)	4.360 (38.20)	216 (2.56)	0.26	23	6.270 (66)
P(*t*BuGE)-*co*-P(AGE)-2		5.185 (39.80)	4.545 (39.80)	216 (2.56)	0.26	21	7.134 (72)

[a] The polymerization was performed in diglyme at 120 °C for 20 h. [b] The composition of the copolymers (r.u. monomer 1)/(r.u. monomer 2), and SEC data are summarized in Table 6 (Results and Discussion). [c] *t*BuGE: *tert*-butyl glycidyl ether. AGE: allyl glycidyl ether. EEGE: ethoxyethyl glycidyl ether. [d] Determined gravimetrically after workup.

bromide (80% g/g solution in toluene, Aldrich) and 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosylazide (GlcNAc; referred to as "azido sugar", 99%, GlyconBioChem) were used as received.

Ethoxyethyl glycidyl ether was synthesized from glycidol (99%, Fluka) and ethyl vinyl ether (99%, Fluka)[12] and purified by distillation from molecular sieves.

Polymerizations were carried out under nitrogen atmosphere. Nitrogen (Linde 5.0) was passed over molecular sieves (4 Å) and finely distributed potassium on alumina.

Measurements. NMR measurements were carried out on a Bruker DPX 300 at 300 MHz (^{1}H) and 75 MHz (^{13}C), respectively. As solvents, deuterated chloroform ($CDCl_3$) and deuterated dimethyl sulfoxid (DMSO-d_6) were used. Size exclusion chromatography (SEC) was carried out at 80 °C using a high-pressure liquid chromatography pump (Bischoff HPLC 2200) and a refractive index detector (Waters 410). The eluting solvent was *N*,*N*′-dimethylacetamide (DMAc) with 2.44 g L^{-1} LiCl and a flow rate of 0.8 mL·min^{-1}. Four columns with MZ-DVB gel were applied. The length of each column was 300 mm, the diameter was 8 mm, the diameter of the gel particles was 5 μm, and the nominal pore widths were 100, 1000, and 10000 Å. Conventional calibration was achieved using poly(methyl methacrylate) (PMMA) standards. The number-average molecular weight M_n, the weight-average molecular weight M_w and the polydispersity $Q = M_w/M_n$ were calculated by the program NTeqGPC.

Synthesis of Protected Polymers. P(*t*BuGE). 3-Phenylpropanol (581 mg, 4.28 mmol) was dissolved in dry diglyme (15 mL) under nitrogen atmosphere, and potassium *tert*-butoxide (0.43 mmol, 0.43 mL of solution in THF) was added. After 10 min of stirring, *tert*-butanol was removed by distillation in vacuo and at 40 °C and the protected glycidol monomer, *t*BuGE (17.831 g, 136.96 mmol), was added. The reaction mixture was stirred for 20 h at 120 °C. The solvent was removed by distillation in vacuum at 80 °C. The residual viscous oil was purified by dissolving in CH_2Cl_2, washing with water, drying of the organic phase over anhydrous sodium carbonate and removing of the solvent in vacuum to give a yellow oil. Yield: 16.879 g (91.7%). M_n (SEC, DMAc) = 2800, M_w/M_n (SEC, DMAc) = 1.12. P_n(NMR) = 32. For starting materials and yields, see Table 1; for the NMR assignment, see Scheme 1.

The polymers poly(*tert*-butyl glycidyl ether) (P(*t*BuGE)), poly(allyl glycidyl ether) ((P(AGE)), poly(ethoxy ethyl glycidyl ether) (P(EEGE)), P(*t*BuGE)-*co*-P(AGE), P(*t*BuGE)-*co*-P(EEGE), and P(AGE)-*co*-P(EEGE) were prepared according to this procedure. For further analytical data, see Table 6.

Poly(*tert*-butyl glycidyl ether). ^{1}H NMR ($CDCl_3$): $\delta = 1.17$ (s br, 9 H, CH_3-12), 1.88 (m, 2 H, CH_2-6), 2.68 (m, 2 H, CH_2-5), 3.37−3.64 (m, 7 H, CH_2-7, 8, 10; CH-9), 7.17−7.19 (m, 3 H, CH-1,3), 7.25−7.30 (m, 1 H, CH-2) ppm. ^{13}C NMR ($CDCl_3$): δ = 27.57 (C-12), 31.36 (C-6), 32.33 (C-5), 62.09, 62.25 (C-10), 70.48, 70.53 (C-8), 72.67 (C-7), 72.66 (C-11), 79.13, 79.33 (C-9), 125.71 (C-1), 128.28, 128.46 (C-2,3), 142.05 (C-4) ppm.

Poly(allyl glycidyl ether). ^{1}H NMR ($CDCl_3$): $\delta = 1.81-1.93$ (m, 2 H, CH_2-6), 2.63−2.71 (m, 2 H, CH_2-5), 3.71−3.41 (m, 7 H, CH_2-7, 8, 10, CH-9), 3.98 (d, $^3J = 5.2$ Hz, 2 H, CH_2-11), 5.20 (dd, $^2J = 31.3$ Hz, $^3J = 13.8$ Hz, 2 H, CH_2-13), 5.88 (m, 1 H, CH-12), 7.12−7.20 (m, 3 H, CH-1, 3), 7.26 (m, 2 H, CH-2) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 31.27$ (C-6), 32.27 (C-5), 70.10, 70.20 (C-8), 71.88 (C-7), 72.18 (C-10), 78.76, 78.84 (C-9), 116.62 (C-11), 125.72 (C-1), 128.26, 128.41 (C-2,3), 134.50, 134.89 (C-12), 141.86 (C-4) ppm.

Poly(ethoxyethy glycidyl ether). ^{1}H NMR ($CDCl_3$): $\delta = 1.19$ (t, $^3J = 7.0$ Hz, 3 H, CH_3-14), 1.29 (d, $^3J = 4.9$ Hz, 3 H, CH_3-12), 1.88 (m, 2 H, CH_2-6), 2.68 (m, 2 H, CH_2-5), 3.44−3.70 (m, 9 H, CH_2-7, 8, 10, 13; CH-9), 4.70 (q, $^3J = 5.1$ Hz, 1 H, CH-11), 7.17−7.19 (m, 3 H, CH-1,3), 7.25−7.30 (m, 1 H, CH-2) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.33 (C-14), 19.79 (C-12), 31.30 (C-6), 32.29 (C-5), 60.78 (C-13), 64.75, 65.02 (C-10), 69.82, 70.10 (C-8), 71.93 (C-7), 78.86, 78.93 (C-9), 99.68, 99.81 (C-11), 125.771 (C-1), 128.31, 128.44 (C-2,3), 141.89 (C-4) ppm.

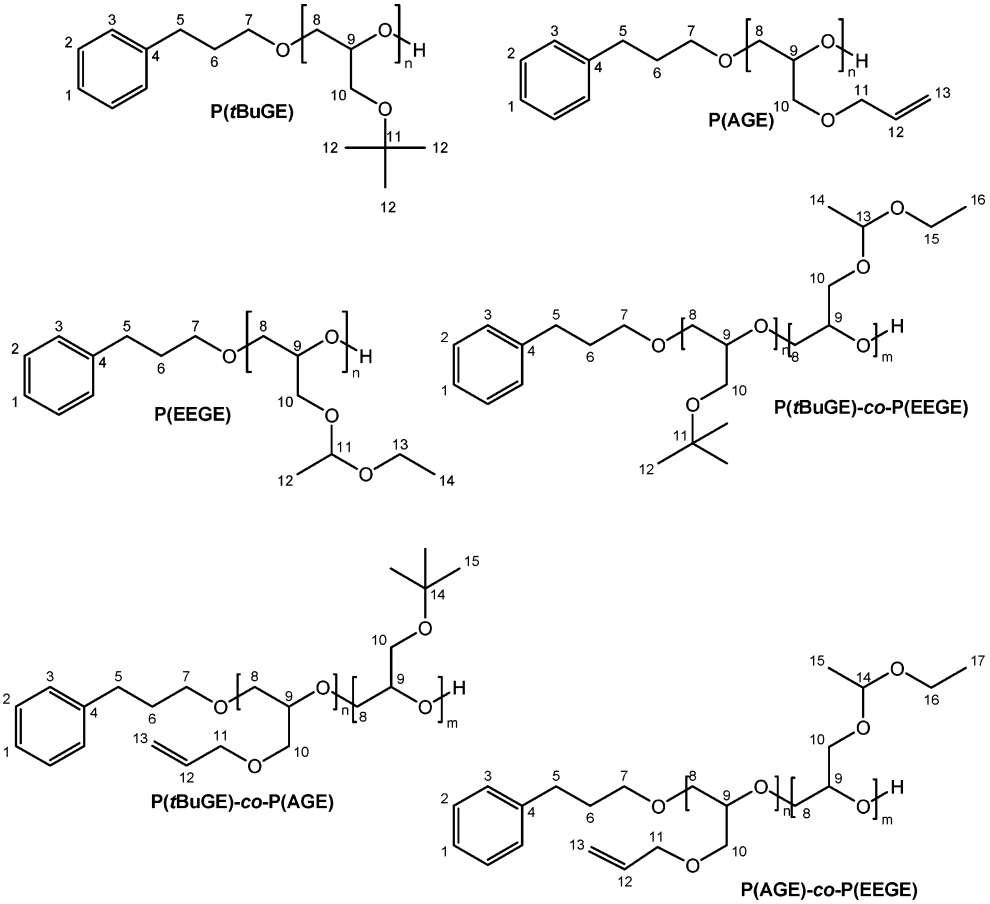
Poly(*tert*-butyl glycidyl ether-*co*-ethoxyethyl glycidyl ether). ^{1}H NMR ($CDCl_3$): $\delta = 1.17-1.21$ (m, 12 H, CH_3-12, 16), 1.29 (d, $^3J = 4.9$ Hz, 3 H, CH_2-14), 1.83−1.93 (m, 2 H, CH_2-6), 2.65−2.70 (m, 2 H, CH_2-5), 3.41−3.67 (m, 9 H, CH-9, CH_2-7, 8, 10, 15), 4.70 (d, $^3J = 5.0$ Hz, CH-13), 7.17−7.19 (m, 3 H, CH-1, 3), 7.25−7.30 (m, 2 H, CH-2) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.34 (C-16), 19.81 (C-14), 27.54 (C-12), 31.33 (C-6), 32.30 (C-5), 60.75 (C-15), 65.08 (C-10), 71.93 (C-7), 72.72 (C-11), 79.31, 79.35 (C-9), 99.68, 99.82 (C-13), 125.77 (C-1), 128.31, 128.45 (C-2, 3), 141.93 (C-4) ppm.

Poly(allyl glycidyl ether-*co*-ethoxyethyl glycidyl ether). ^{1}H NMR ($CDCl_3$): $\delta = 1.19$ (t, $^3J = 7.1$ Hz, 3 H, CH_3-17), 1.29 (d, $^3J = 5.1$ Hz, 3 H, CH_3-15), 1.82−1.94 (m, 2 H, CH_2-5), 2.63−2.71 (m, 2 H, CH_2-6), 3.41−3.72 (m, 9 H, CH-9, CH_2-7, 8, 10, 16), 3.98 (d, $^3J = 5.3$ Hz, 2 H, CH_2-11), 4.70 (quart, $^3J = 5.2$ Hz, 1 H, CH-14), 5.21 (dd, $^2J = 31.6$ Hz, $^3J = 13.8$ Hz, $^3J = 10.3$ Hz, 2 H, CH_2-13), 5.88 (m, 1 H, CH-12), 7.15−7.19 (m, 3 H, CH-1, 3), 7.27−7.30 (m, 2 H, CH-2) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 15.33$ (C-17), 19.80 (C-15), 31.29 (C-6), 32.28 (C-5), 60.79 (C-16), 70.19 (C-8), 71.92 (C-10), 72.25 (C-11), 78.79, 78.90 (C-9), 99.69, 99.82 (C-14), 116.72 (C-13), 125.77 (C-1), 128.31, 128.45 (C-2, 3), 134.89 (C-12), 141.92 (C-4) ppm.

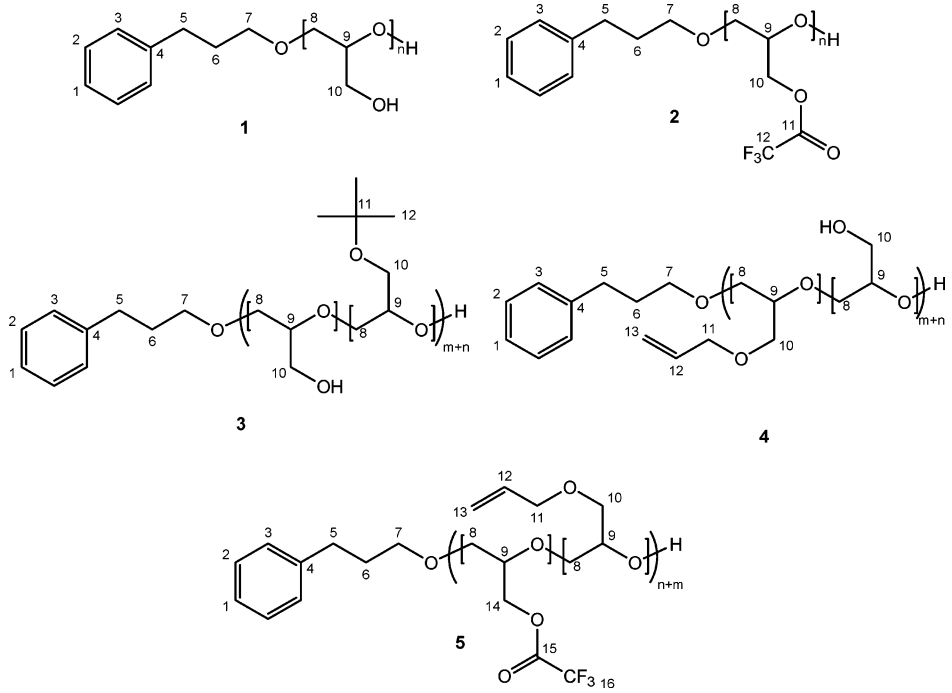
Poly(*tert*-butyl glycidyl ether-*co*-allyl glycidyl ether). ^{1}H NMR ($CDCl_3$): $\delta = 1.17$ (s, 9 H, CH_3-15), 1.82−1.93 (m, 2 H, CH_2-6), 2.64−2.72 (m, 2 H, CH_2-5), 3.27−3.78 (m, 9 H, CH-9, CH_2-7, 8, 10), 3.99 (d, $^3J = 5.1$ Hz, CH_2-11), 5.20 (dd, $^2J = 32.8$ Hz, $^3J = 13.8$ Hz, 2 H, CH_2-13), 5.82−5.95 (m, 1 H, CH-12), 7.15−7.19 (m, 3 H, CH-1, 3), 7.24−7.33 (m, 2 H, CH-2) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 27.54$ (C-15), 31.33 (C-6), 32.28 (C-5), 61.88−62.04 (C-10), 70.10−70.52 (C-8), 72.23 (C-11), 72.73 (C-14), 78.53 (C-7), 79.17, 79.31 (C-9), 116.66 (C-13), 125.74 (C-1), 128.30, 128.46 (C-2, 3), 134.93, 134.96 (C-12) ppm.

Synthesis of Polyglycidol (1). (a) P(EEGE) (3.01 g, 0.63 mmol) was dissolved in THF (360 mL) and treated with 16 mL of aqueous HCl (32%). The reaction was complete within a few minutes, and the polymer precipitated as yellow oil. The solvent was decanted, and the residue was washed twice with THF. After being dried in a vacuum at 40 °C overnight, the polymer was isolated in a yield of 1.27 g (0.5 mmol, 81%). M_n (SEC, DMAc) = 6300, $Q = 1.09$). For NMR assignment, see Scheme 2.

Scheme 1. Structure of the Homopolymers and Copolymers Prepared via Anionic Ring-Opening Polymerization with Numbers for NMR Assignment



Scheme 2. Structure of the Homopolymer and Copolymers Prepared via Polymer Analogous Reaction with Numbers for NMR Assignment



^{1}H NMR (DMSO-d_6): δ = 1.70−1.82 (m, 2H, CH_2-6), 2.56−2.65 (m, 2 H, CH_2-5), 3.25−3.71 (m, CH_2-7, 8, 10; CH-9), 4.22 (s br, OH), 7.14−7.20 (m, 3 H, CH-1,3), 7.23−7.30 (m, 1 H, CH-2) ppm. ^{13}C NMR (DMSO-d_6): δ = 30.97 (C-6), 31.63 (C-5), 60.85 (C-10), 63.03 (C-10^E), 69.34 (C-8), 70.65, 70.74 (C-8^E, C-9^E), 79.98, 80.07 (C-9), 125.66 (C-1), 128.24, 128.29 (C-2, 3), 141.75 (C-4) ppm.

(b) Poly(allyl glycidyl ether-*co*-ethoxyethyl glycidyl ether) (2.013 g, 0.47 mmol) was dissolved in THF (200 mL), treated with aqueous HCl (32%, 11.5 mL), and stirred for 5 min at room temperature.

Table 2. Hydrolysis of Poly((allyl glycidyl ether)-*co*-(ethoxyethyl glycidyl ether)) (P(AGE)-co-P(EEGE) with Aqueous HCl in Tetrahydrofuran (THF): Reagents, Yields and Results Obtained by Size Exclusion Chromatography (SEC) (Number Average Molecular Weight (M_n) and Molecular Weight Distribution M_w/M_n))

					SEC	
polymer no.	P(AGE)-*co*-P(EEGE) [g (mmol acetal-r.u.)]	THF (mL)	HCl(aq,32%) (mL)	yield [g (%)]	M_n	M_w/M_n
4a	4.561 (16.9)	300	24	1.850 (55.4)	5400	1.08
4b	3.000 (11.1)	360	18	1.599 (72.8)	4700	1.12

Table 3. Pd-Catalyzed Removal of the Allyl Ether Protection Groups from Poly(*tert*-butyl glycidyl ether)-*co*-poly(allyl glycidyl ether), P(*t*BuGE)-*co*-P(AGE): Reagents, Yields, and Results Obtained by Size Exclusion Chromatography (SEC) (Number Average Molecular Weight (M_n) and Molecular Weight Distribution M_w/M_n))

polymer no.	P(tBuGE)-*co*-P(AGE) [g (mmol allyl-r.u.)[	methanol (mL)	Pd/C (mg)	*p*-TsOH [mg (mmol)]	yield [g (%)]	M_n SEC	M_w/M_n SEC
3a	3.013 (11.6)	20	528	180 (1.04)	1.137 (45)	n.b.	n.b.
3b	5.910 (22.8)	35	989	370 (2.14)	4.603 (92)	5900	1.12

The solution was neutralized with an aqueous solution of KOH (30%), KCl was filtered off, and the solution was dried over anhydrous Na_2CO_3 and filtered again. Then the solvent was removed in vacuum and the residue dried to give a yellow oil. Yield: 1.027 g (93%).

Synthesis of Poly(glycidyl trifluoroacetate) (2). P(*t*BuGE) (3.133 g, 0.73 mmol, 23.3 mmol *t*Bu-r.u., $P_n = 32$) were dissolved in TFA (8.5 mL, 111.5 mmol, 4.8 equiv) and stirred for 3 h at room temperature. TFA was distilled off in vacuum to yield an auburn oil (2.197 g, 0.61 mmol, 83%, 22 trifluoroacetate and 10 OH repeating units per chain). M_n(SEC) = 6400, $Q = 1.10$. For NMR assignment, see Scheme 2.

^{1}H NMR (DMSO-d_6): $\delta = 1.74-1.83$ (m, 2 H, CH_2-6), 2.61 (t, $^3J = 7.5$ Hz, 2 H, CH_2-5), 3.39−3.76 (m, 5 H, CH_2-7, 8, CH-9), 4.37 (br, 1 H, CH_2-10), 4.52 (br, 1 H, CH_2-10′), 7.14−7.19 (m, 3 H, CH-1, 3), 7.24−7.29 (m, 2 H, CH-2) ppm. ^{13}C NMR (DMSO-d_6): δ = 27.68 (C-6), 29.02 (C-5), 60.43 (C-10^{OH}), 60.78 (C-10^{OH,E}), 67.61 (C-10^{Fac}), 69.37, 69.44 (C-8), 76.16, 76.04(C-8^E, C-9^E), 79.93−80.28 (C-9), 114.19 (q, C-12, $|^1J(C, F)| = 285.0$ Hz), 125.63 (C-1), 128.18 (C-2, 3), 141.68 (C-4), 156.33 (q, C-11, $|^2J(C, F)| = 41.5$ Hz) ppm.

Synthesis of Poly(allyl glycidyl ether-*co*-glycidol) (4). P(AGE)-*co*-P(EEGE) (M_n(SEC) = 3300, $Q = 1.11$, 15 repeating units each) was dissolved in THF (120 mL per gram polymer) and treated with aqueous HCl (32%, 6 mL/g of polymer). After a few minutes, the reaction was complete, and the solution was neutralized with an equimolar amount of KOH (30% solution in water). The solution was filtered to remove KCl and dried over anhydrous sodium carbonate, and the solvent was removed by distillation in vacuum to give the product as yellow oil. For amounts of reagents, see Table 2; for NMR assignment, see Scheme 2.

^{1}H NMR (DMSO-d_6): $\delta = 1.71-1.80$ (m, 2 H, CH_2-6), 2.59−2.64 (m, 2 H, CH_2-6), 3.37−3.67 (m, 7 H, CH_2-7, 8, 10, CH-9), 3.94 (d, $^3J = 3.2$ Hz, 2 H, CH_2-11), 5.05 (s br, 1 H, OH), 5.19 (dd, $^2J = 33.8$ Hz, $^3J = 13.9$ Hz, 2 H, CH_2-13), 5.81−5.92 (m, 1 H, CH-12), 7.14−7.20 (m, 3 H, CH-1, 3), 7.25−7.30 (m, 2 H, CH-2) ppm. ^{13}C NMR (DMSO-d_6): $\delta = 29.02$ (C-6), 29.78 (C-5), 69.33−69.85 (C-8, 10), 71.36 (C-11), 78.24, 78.20 (C-9), 116.28 (C-13), 125.76 (C-1), 128.33, 128.36 (C-2, 3), 135.29 (C-12), 141.83 (C-4) ppm.

Synthesis of Poly(allyl glycidyl ether-*co*-glycidyl trifluoroacetate) (5). P(*t*BuGE)-*co*-P(AGE) (1.986 g, 0.39 mmol, 7.7 mmol *t*Bu-r.u., M_n(SEC) = 3800, $Q = 1.13$) was dissolved in TFA (3 mL, 38.8 mmol, 5 equiv) and stirred for 3 h. Removal of the acid by distillation in vacuum gave the product as brown oil.

For NMR assignment, see Scheme 2.

^{1}H NMR ($CDCl_3$): $\delta = 1.84-1.93$ (m, 2 H, CH_2-6), 2.67 (t, $^3J = 7.6$ Hz, 2 H, CH_2-5), 3.48−3.69 (m, 7 H, CH_2-7, 8, 10, CH-9), 3.98 (d, $^3J = 3$ Hz, 2 H, CH_2-11), 4.38 (br, 1 H, CH-14), 5.21 (dd, $^2J = 25.6$ Hz, $^3J = 13.2$ Hz, $^3J = 10.4$ Hz, 2 H, CH_2-13), 5.82−5.94 (m, 1 H, CH-12), 7.16−7.19 (m, 3 H, CH-1,3), 7.25−7.30 (m, 1 H, CH-2) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 31.21$ (C-6), 32.19 (C-5), 61.37 (C-10^{OH}), 67.31 (C-10^{FAc}), 68.65 (C-8), 69.71−70.25 (C-7, 10), 72.26 (C-11), 78.56−79.21 (C-8, C-9), 114.50 (quart, C-16, $|^1J(C,F)| = 284.3$ Hz), 117.03 (C-13), 125.79 (C-1), 128.33, 128.43 (C-2, 3), 134.37−134.70 (C-12), 157.86 (quart, C-15, $|^2J(C,F)| = 42.5$ Hz) ppm.

Synthesis of Poly(glycidol-*co*-*tert*-butyl glycidyl ether) (3). A solution of P(*t*BuGE)-*co*-P(AGE) in methanol was degassed with nitrogen; palladium on charcoal (Pd/C 5%, 40 mg per 1 mmol of allyl group) was added, followed by 10 mol % of *p*-toluenesulfonic acid (*p*-TsOH). After 5 days, the reaction mixture was filtered over neutral alumina, and rinsed with 200−300 mL of methanol. The filtrate was dried over anhydrous sodium carbonate, filtered again, and the solvent was removed by distillation in vacuum to yield the polymer as colorless oil. For amounts of reagents, see Table 3; for NMR assignment, see Scheme 2.

^{1}H NMR ($CDCl_3$): $\delta = 1.18$ (s br, 9 H, CH_3-12), 1.85−1.93 (m, 2 H, CH_2-6), 2.68 (t, $^3J = 7.4$ Hz, 2 H, CH_2-5), 3.34−3.71 (m, 8 H, CH_2-7, 8, 10, CH-9, OH), 7.18−7.20 (m, 3 H, CH-1, 3), 7.25−7.30 (m, 2 H, CH-2) ppm. Because of the low solubility, no ^{13}C NMR spectrum could be measured.

Synthesis of Poly(glycidyl propargyl ether-*co*-glycidol) (6). Polyglycidol (**1**) (0.955 g, 12.2 mmol of OH-r.u.) was dissolved in dimethylformamide (10 mL), and solid KOH (684 mg, 12.2 mmol) and propargyl bromide (1.45 mg, 12.2 mmol) were added. After the reaction was stirred for 3 d at room temperature, the solids were removed by filtration and the product was precipitated in water (110 mL). The mixture water/product was centrifuged, the water decanted and the polymer was dried in vacuo to yield a brownish oil (148 mg, yield = 11%, degree of substitution: 81%). M_n (SEC) = 5600, $Q = 1.09$. For NMR assignment, see Scheme 3.

^{1}H NMR ($CDCl_3$): $\delta = 1.83-1.94$ (m, 2 H, CH_2-6), 2.50 (s br, 1 H, CH_2-13), 2.61−2.71 (m, 2 H, CH_2-5), 3.54−3.65 (m, 8 H, CH-9, CH_2-7, 8, 10, OH), 4.18 (s, 2 H, CH_2-11), 7.16−7.20 (m, 3 H, CH-1, 3), 7.24−7.31 (m, 2 H, CH-2) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 32.25$ (C-6), 36.49 (C-5), 58.55 (C-11), 69.73 (C-8), 74.74 (C-13), 77.38 (C-12), 78.58 (C-9^E), 79.87 (C-9), 125.78 (C-1), 128.33, 128.46 (C-2, 3) ppm.

Synthesis of Poly(glycidyl propargyl ether-*co*-glycidol-co-*tert*-butyl glycidyl ether) (7). A solution of poly(glycidol-*co*-*tert*-butyl glycidyl ether) (**3**) in 15 mL dichloromethane was treated with KOH powder (1.5 equiv). A solution of propargyl bromide (PropBr) in toluene (80% g/g) was added dropwise; the solution was stirred intensively for 3 h. Then insoluble materials were removed by filtration and the solvent was removed in vacuum to yield a yellow oil. For amounts of reagents, see Table 4; for NMR assignment, see Scheme 3.

^{1}H NMR ($CDCl_3$): $\delta = 1.17$ (s br, 9 H, CH_3-12), 1.84−1.95 (m, 2 H, CH_2-6), 2.47 (s, 1 H, CH-15), 2.65−2.70 (m, 2 H, CH_2-5), 3.39−3.65 (m, 7 H, CH_2-7, 8, 10, CH-9, OH), 4.18 (s, 2 H, CH_2-13), 7.13−7.20 (m, 3 H, CH-1, 3), 7.23−7.30 (m, 2 H, CH-1) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 27.54$ (C-12), 58.54 (C-13), 62.03 (C-10), 69.65−69.99 (C-8), 70.46 (C-10^E), 72.84 (C-11), 74.63 (C-15), 78.56 (C-14), 79.25 (C-9), 125.29 (C-1), 128.47, 128.32 (C-2, 3), 137.85 (C-4) ppm.

Scheme 3. Structure of Copolymers with Propargyl Ether Side Groups with Numbers for NMR Assignment

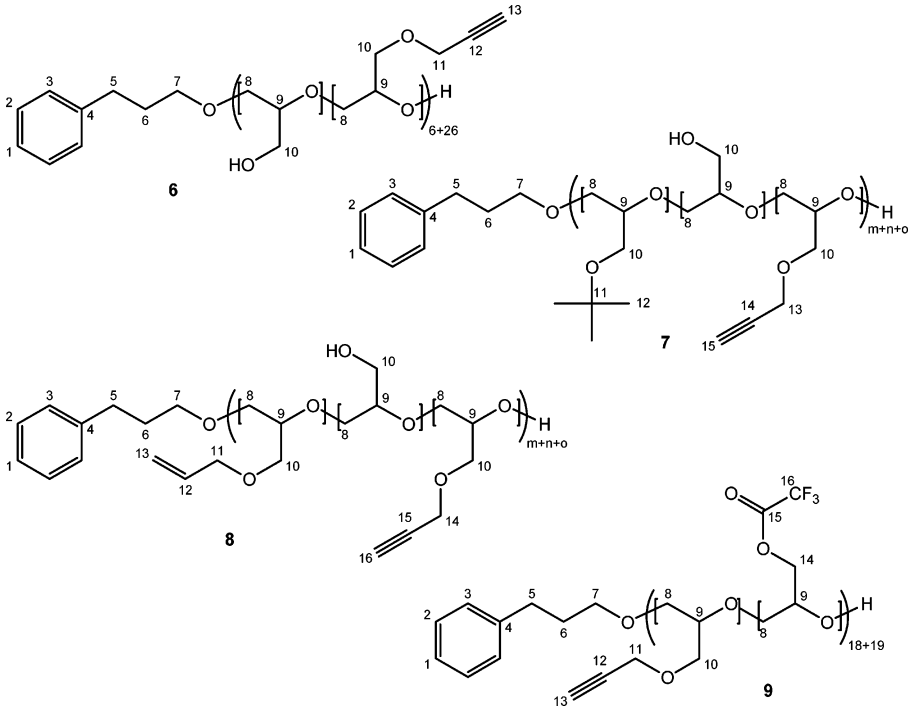


Table 4. Polymer Analogous Reaction of Polymer 3 with Propargyl Bromide:[a] Reagents, Yields

		starting material[b]					product[b]			
polymer no.	no.	*m*	*n*	amount [g (mmol OH-r.u.)]	KOH [mg (mmol)]	PropBr[c] [g (mmol)]	*m*	*n*	*o*	yield [g (%)]
7a	**3a**	20	20	1.137 (5.4)	470 (8.4)	1.472 (12.4)	19[a]	5	15	0.935 (73)
7b	**3b**	18	19	1.376 (6.3)	529 (9.4)	1.149 (9.7)	18	6	13	1.245 (77)

[a] Solvent: dichloromethane. Time: 3 h at room temperature. [b] (*m*) Number of *tert*-butyl glycidyl repeating units, (*n*) number of glycidol repeating units, and (*o*) number of propargyl glycidyl repeating units. *m*, *n*, *o* were determined via ^{1}H NMR analysis. [c] Propargyl bromide.

Table 5. Polymer Analogous Reaction of Polymer 4 with Propargyl Bromide:[a] Reagents, Yields

		starting material[b]			KOH		product[b)]			
polymer	no.	*m*	*n*	amount [g (mmol OH-r.u.)]	KOH [mg (mmol)]	PropBr[c] [g (mmol)]	*m*	*n*	*o*	yield [g (%)]
8a	**4a**	20	20	1.227 (6.3)	540 (9.6)	1.488 (12.5)	16.6	5.5	9.5	0.649 (69)
8b	**4b**	15	15	0.922 (4.7)	395 (7.0)	1.688 (14.2)	10	4	11	0.810 (92)
8c	**4b**	15	15	1.017 (5.1)	430 (7.7)	3.028 (25.5)	12	2	11	0.819 (84)

[a] Solvent: dichloromethane. Time: 3 h at room temperature. [b] (*m*) Number of allyl glycidyl repeating units, (*n*) number of glycidol repeating units, and (*o*) number of propargyl glycidyl repeating units; *m*, *n*, *o* were determined via ^{1}H NMR analysis. [c] Propargyl bromide.

Synthesis of Poly(allyl glycidyl ether-*co*-glycidol-*co*-propargyl glycidyl ether) (8). Polymer **4** was dissolved in 15 mL dichloromethane. Solid KOH and propargyl bromide were added. After stirring for 3 h, the solids were removed by filtration and the solvent was removed in vacuo to give a yellow oil. For amounts of reagents, see Table 5; for NMR assignment, see Scheme 3.

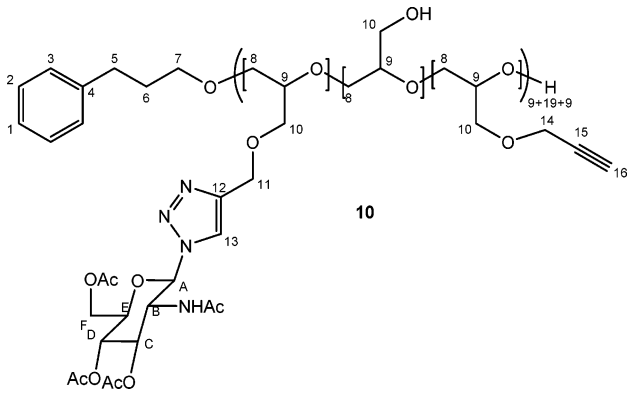
^{1}H NMR ($CDCl_3$): δ = 1.82−1.93 (m, 2 H, CH_2-6), 2.49 (s br, 1 H, CH-16), 2.66−2.70 (m, 2 H, CH_2-5), 3.54−3.65 (m, 8 H, CH-9, CH_2-7, 8, 10, OH), 3.98 (d, ^4J = 3 MHz, 2 H, CH_2-11), 4.17 (s br, 2 H, CH_2-14), 5.15−5.29 (dd, ^2J = 33 MHz, ^3J = 18 MHz, ^3J = 9 MHz, 2 H, CH_2-13), 5.84−5.93 (m, 1 H, CH-12), 7.15−7.21 (m, 3 H, CH-1, 3), 7.24−7.30 (m, 2 H, CH-2) ppm. ^{13}C NMR ($CDCl_3$): δ = 31.25 (C-6), 32.26 (C-5), 58.54 (C-14), 69.71, 69.80 (C-8), 70.06, 70.10 (C-10), 72.25 (C-11), 74.83 (C-16), 78.65 (C-9), 79.71 (C-9^E), 116.83 (C-13), 125.77 (C-1), 128.32, 128.46 (C-2, 3), 134.77 (C-12) ppm.

Synthesis of Poly(glycidyl propargyl ether-*co*-glycidyl trifluoroacetate) (9). **7a** (1.032 g, 4.5 mmol of *t*Bu-r.u.) was dissolved in TFA (2.670 g, 22.4 mmol, 5 equiv) and stirred for 3 h. After removal of TFA by distillation, **9** was obtained as a brown material in a yield of 960 mg (0.18 mmol, 80%). M_n(SEC) = 6100, Q (SEC) = 1.08. For NMR assignment, see Scheme 3.

^{1}H NMR ($CDCl_3$): δ = 1.84−1.93 (m, 2 H, CH_2-6), 2.67 (t, ^3J = 7.6 Hz, 2 H, CH_2-5), 3.34−3.65 (m, 7 H, CH_2-7, 8, 10, CH-9), 4.16 (br, 2 H, CH_2-11), 4.40 (br, 1 H, CH_2-14), 4.56 (br, 1H, CH_2-14′), 7.16−7.21 (m, 3 H, CH-1, 3), 7.26−7.31 (m, 2 H, CH-2) ppm. ^{13}C NMR ($CDCl_3$): δ = 27.79 (C-6), 32.18 (C-6), 58.47 (C-11), 68.57−69.80 (C-8), 74.83 (C-10), 78.22 (C-8^E, 9^E), 79.31−79.52 (C-9), 114.44 (quart, C-16, $|^1J$(C, F)| = 284.9 Hz), 117.35 (C-13), 125.85 (C-1), 128.34. 128.38 (C-2, 3), 157.19 (quart, C-15, $|^2J$(C, F)| = 40.6 Hz) ppm.

Synthesis of Poly(glycidol-*co*-glycidyl propargyl ether-*co*-glycidyl triazolyl sugar) (10). Poly(glycidyl propargyl ether-*co*-glycidol) (504 mg, 2.5 mmol of propargylic r.u.) was dissolved in 10 mL of water/*t*BuOH (1:1 v/v). CuCl (3 mg, 0.03 mmol), sodium L-ascorbate (63 mg, 0.27 mmol) and the azido sugar (460 mg, 1.25 mmol) were added. After being stirred for 21 h at room temperature, the solution was diluted with water (30 mL) and extracted with dichloromethane (3 × 50 mL). The organic phase was dried over anhydrous sodium carbonate and filtered, and the product was isolated by distillation of the solvent in vacuum to yield a golden powder (631 mg, 90 μmol, 65%). M_n(SEC, DMAc) = 11 700, Q = 1.09. For NMR assignment, see Scheme 4.

Scheme 4. Structure of 10 with Numbers for NMR Assignment



^{1}H NMR ($CDCl_3$): δ = 1.99 (s, 12 H, sugar-CH_3), 2.60 (m, 2 H, CH_2-5), 3.52 (br, 7 H, CH_2-7, 8, 10, CH-9), 4.10 (br, 3 H, CH_2-11, CH-*B*), 4.25 (br, CH-*C*), 4.52−4.55 (br, 3 H, CH-*A*, *F*), 5.21 (br, 1 H, CH-*E*), 5.51 (br, 1 H, CH-*D*), 6.20 (br, 1 H, NH), 7.10−7.12 (m, 3 H, CH-1, 3), 7.18−7.21 (m, 2 H, CH-2), 7.98−8.01 (br, CH-13) ppm. ^{13}C NMR ($CDCl_3$): δ = 19.65 (CH_3-acetate), 21.72 (CH_3-acetamido), 28.67 (C-6), 31.20 (C-5), 52.43 (C-*C*), 60.78, 60.89 (C-10), 62.98 (C-*F*), 67.22 (C-*E*), 68.43−68.98 (C-8), 71.29 (C-*D*), 78.56 (C-7), 84.45, 84.54 (C-9), 89.49 (C-*A*), 124.68 (C-1), 127.35, 127.44 (C-2, 3), 143.76 (C-1), 154.36 (C-13), 155.69 (C-12), 168.49, 169.46, 169.71 (sugar carboxyl groups) ppm.

3. Results and Discussion

Ring-opening polymerization of the protected glycidols EEGE, *t*BuGE, and AGE was performed under nitrogen atmosphere in dry diglyme with 3-phenylpropan-1-ol/potassium 3-phenylpropenolate (Scheme 5).[11]

In order to have a controlled polymerization, the alcohol to potassium alcoholate ratio was chosen to be 9:1. For homopolymerization and copolymerization the total monomer to initiator ratio was chosen to be between 20 and 40. Copolymerization were prepared from an equimolar mixture of monomers. Polymerizations were performed at 120 °C for ca. 20 h. Table 6 shows (i) that the number-average molecular weight determined by end group analysis corresponds to the expected value and (ii) the molecular weight distribution is rather narrow as expected for living polymerization conditions.

Kinetic Measurements. The time−conversion dependence for the polymerization of the protected glycidols was determined in diglyme as solvent at 120 °C. Data indicate that full conversion is reached within 3−5 h.

Table 6. Protected Poly(glycidol)s Obtained by Ring-Opening Polymerization[a]

			polymer		
polymer[b]	M_1	M_2	M_1/M_2[c]	M_n[d]	Q[d]
P(*t*BuGE)	*t*BuGE		32	2800	1.12
P(AGE)	AGE		21[e]	2400	1.27
P(EEGE)	EEGE		32	3300	1.12
P(*t*BuGE)-*co*-P(AGE)-1	*t*BuGE	AGE	19.5/20.5[f]	3800	1.13
P(*t*BuGE)-*co*-P(AGE)-2	*t*BuGE	AGE	11.2/15.0[g]	2800	1.09
P(*t*BuGE)-*co*-P(EEGE)-1	*t*BuGE	EEGE	13.3/12.6[g]	2500	1.12
P(*t*BuGE)-*co*-P(EEGE)-2	*t*BuGE	EEGE	16.0/13.0[g]	3100	1.10
P(AGE)-*co*-P(EEGE)-1	AGE	EEGE	15.1/15.1[g]	3300	1.11
P(AGE)-*co*-P(EEGE)-2	AGE	EEGE	15.0/15.0[g]	3400	1.11

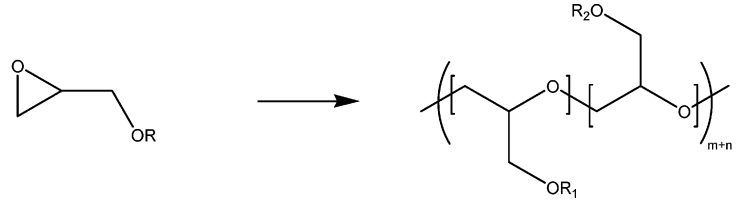
[a] Polymerization conditions: dry diglyme, 10% active chains, 120 °C, 20 h; $(M_1 + M_2)$/initiator = 32/1. [b] *t*BuGE: *tert*-butyl glycidyl ether. AGE: allyl glycidyl ether. EEGE: ethoxyethyl glycidyl ether. [c] The number of repeating units of monomer 1 and monomer 2 was determined by end group analysis from ^{1}H NMR spectra. [d] Determined by SEC measurements in *N*,*N*′-dimethylacetamide/LiCl. [e] Monomer conversion ca. 70%. [f] $(M_1 + M_2)$/initiator = 40/1. [g] $(M_1 + M_2)$/initiator = 30/1.

Applying first-order kinetics (Figure 1) it can be observed that the polymerization rate of the three monomers decreases in the order EEGE > AGE > *t*BuGE. Some observations should be noted: (i) Homopolymerization of EEGE shows a straight line in the first-order plot up to high conversion, consistent with a living polymerization. (ii) With *t*BuGE, an induction period is clearly observed. (iii) With AGE, polymerization is controlled up to a conversion of ca. 80%. At this stage we believe that with decreasing monomer concentration a side reaction occurs by proton/hydrogen abstraction from the allyl position, leading to chain termination. Furthermore, poly(allyl glycidyl ether) forms a gel on standing at room temperature for several days. Whether this cross-linking reaction occurs according to a radical or ionic mechanism is still under investigation.

The dependence of the number-average of molecular weight on conversion as determined by SEC is linear up to high conversion (Figure 2). The values are almost identical for all the three monomers investigated, this is a sign that all three polymers are linear and branching of the P(AGE) does not occur during polymerization. Polydispersity ($Q = M_w/M_n$) indices approach a value of Q = 1.1, as expected for a Poisson distribution (Figure 2). Because of the induction phase, the dependence of Q for the polymerization of *t*BuGE shows first an increase up to a conversion of ca. 40%, before Q approaches a small value as expected for a Poisson distribution.

The copolymerization kinetics were studied under the same conditions as described for the homopolymerizations, with equimolar mixtures of monomers. The first-order plots

Scheme 5. Ring-Opening Polymerization of Protected Glycidols[a]



tBuGE: R = -$C(CH_3)_3$
AGE: R = -CH_2-CH=CH_2
EEGE: R = -$CH(CH_3)$-O-CH_2CH_3

P(*t*BuGE): $R_1 = R_2$ = -$C(CH_3)_3$
P(AGE): $R_1 = R_2$ = -CH_2-CH=CH_2
P(EEGE): $R_1 = R_2$ = -$CH(CH_3)$-O-CH_2CH_3

P(*t*BuGE)-*co*-P(AGE): R_1 = -$C(CH_3)_3$; R_2 = -CH_2-CH=CH_2
P(*t*BuGE)-*co*-P(EEGE): R_1 = -$C(CH_3)_3$; R_2 = -$CH(CH_3)$-O-CH_2CH_3
P(AGE)-*co*-P(EEGE): R_1 = -CH_2-CH=CH_2; R_2 = -$CH(CH_3)$-O-CH_2CH_3

[a] Reaction conditions: nitrogen atmosphere, dry diglyme, 3-phenylpropan-1-ol (10% activated using a potassium alcoholate), 120 °C, 20 h.

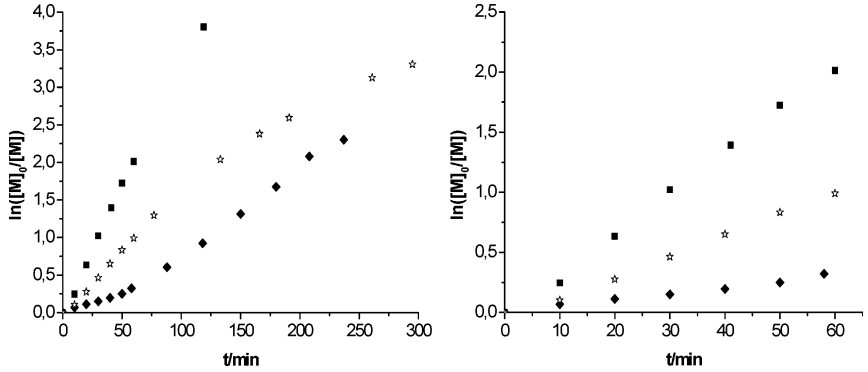


Figure 1. First-order-plot in the homopolymerization of ethyoxyethyl glycidyl ether (EEGE) (■), *tert*-butyl glycidyl ether (*t*BuGE) (☆), and allyl glycidyl ether (AGE) (◆) at 120 °C. Monomer/initiator = 32: with 10% active chains (left) and zoom for the first 60 min (right). ln([M]$_0$/[M]): natural logarithm of starting ([M]$_0$) and actual ([M]) monomer concentration; determined via ^{1}H NMR spectroscopy.

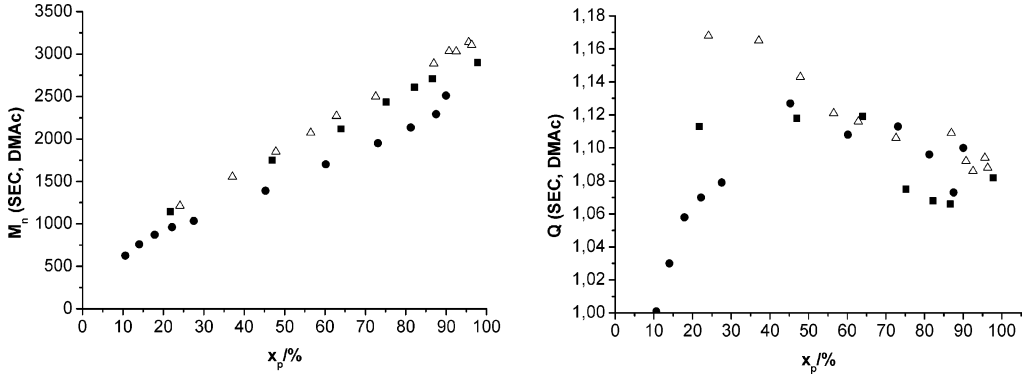


Figure 2. Dependence of the molecular weight (M_n) on conversion (x_p) for the polymerization of ethoxy ethyl glycidyl ether (EEGE) (■),*tert*-butyl glycidyl ether (*t*BuGE) (●), and allyl glycidyl ether (AGE) (△) (left) and dependence of the polydispersity (Q) on conversion for the same reaction (right). (Monomer/initiator = 32; with 10% active chains.)

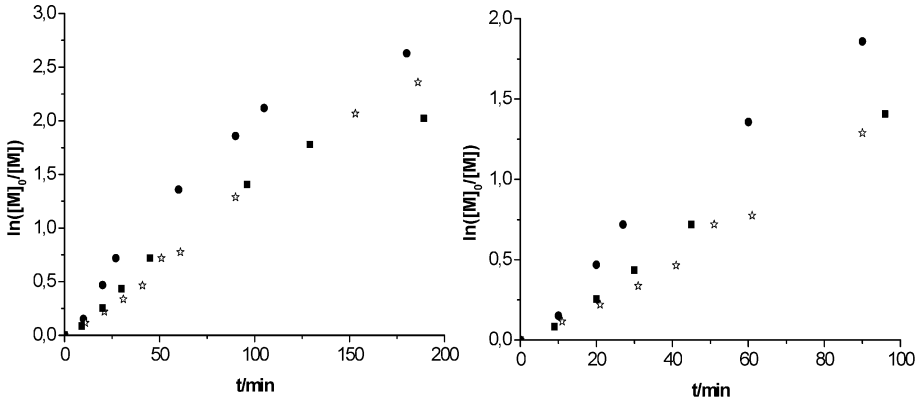


Figure 3. First-order-plot for the copolymerization of AGE/*t*BuGE (●), EEGE/*t*BuGE (☆), and AGE/EEGE (■) (left), zoom for the first 100 min (right).

(Figure 3) indicate that for each combination of monomers, the polymerization rate is the same. Irrespective of the results of the homopolymerization, indicating that the combination of EEGE and AGE to be the one with the highest rate.

The dependence of M_n (determined by SEC in DMAc) on conversion (Figure 4) is linear for all copolymerization studied; however, the maximum molecular weight obtained is different. The monomer combination AGE/*t*BuGE lead to the highest molecular weights. The two systems with EEGE as one component show nearly the same dependence, independent of the second monomer. Our explanation for this result refers to the different structure of the repeating units leading to different hydrodynamic volumes in the GPC solvent DMAc/LiCl. The conversion dependence of M_w/M_n shows a similar behavior as found in the homopolymerization. For copolymers with *t*BuGE the M_w/M_n values first increase up to a certain conversion and decrease afterward as was observed in the homopolymerization of *t*BuGE. Irrespective of the fact that an induction period was hardly detected in the copolymerization.

Removal of protection groups by polymer analogous reactions is summarized in Figure 5 and Table 7. The acetal group of poly(ethoxyethyl glycidyl ether) was cleaved quickly and completely in THF with an aqueous solution of hydrochloric acid (32%).[11] Polyglycidol (**1**) was obtained in good yields (81%).

The *t*Bu ether group was removed by treatment of poly(*tert*-butyl glycidyl ether) with trifluoroacetic acid (TFA).[14,23] It was observed by ^{1}H NMR spectroscopy that all *tert*-butyl groups were removed; however, beside free hydroxyl groups trifluoroacetate groups are formed. The ratio of free hydroxymethyl

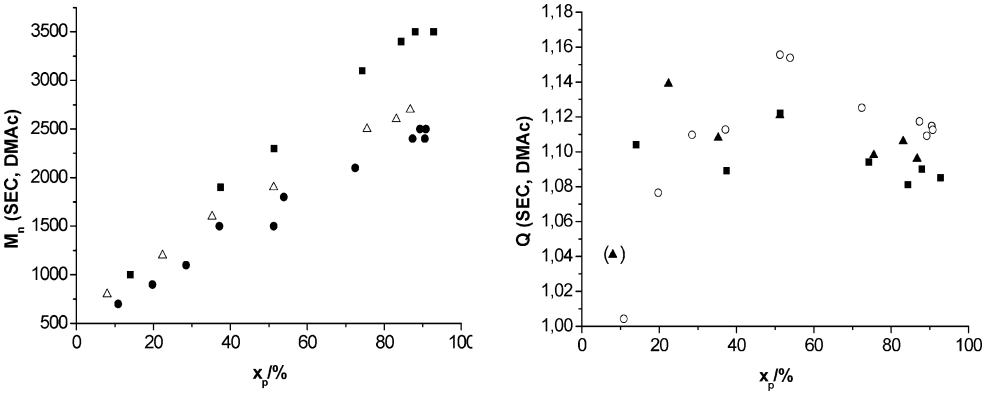


Figure 4. Dependence of the molecular weight (M_n) on conversion (x_p) for the copolymerization of AGE/*t*BuGE (■), EEGE/*t*BuGE (●), and EEGE/AGE (△) (left) and dependence of the polydispersity (Q) on conversion of the same reaction (right) (monomer/initiator = 32; with 10% active chains).

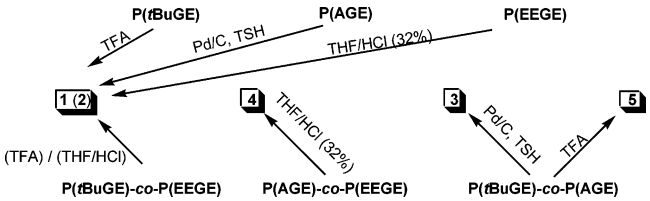


Figure 5. Removal of protection groups from protected polyglycidols. TSH = *p*-toluenesulfonic acid.

groups and trifluoroacetate groups in the copolymer **2** was easily determined from ^{1}H NMR spectra since the $\mathbf{CH_2}$-$OCOCF_3$ groups appear well resolved at $\delta = 4.2$ and 4.4 ppm. In several experiments performed under the same reaction conditions variable ratios of trifluoroacetate/hydroxyl groups were obtained. This is related to the water content in the reaction medium. At this point, it should be mentioned that the trifluoroacetate groups are easily converted to hydroxyl groups in contact with water.

Hydrolysis of the *tert*-butyl ether groups in P(*t*BuGE) with aqueous HCl failed under the same reaction conditions used for the cleavage of the acetal group within the same reaction time.

For the removal of allyl ether groups from poly(allyl glycidyl ether) two procedures were applied: (i) $Pd(PPh_3)_4$ in dichloromethane with sodium *p*-toluenesulfinate in methanol[17] and (ii) Pd(0)/charcoal/*p*-toluenesulfonic acid,[18] respectively. In both procedures, the deprotection was successful; however, isolation and purification of the poly(glycidol) by removal of *p*-toluenesulfinate and residual Pd/C, respectively, was troublesome, as during filtration procedure, the polymer was stuck to the filtration material.

To remove the acetal protection group from the copolymers P(AGE)-*co*-P(EEGE) and P(*t*BuGE)-*co*-P(EEGE) both copolymers were treated with aqueous HCl (32%) in THF under the conditions reported for poly(ethoxyethyl glycidyl ether), however, no precipitate was observed. Therefore, the work up procedure was modified: the solution was neutralized with an aqueous KOH solution (30%). From P(AGE)-*co*-P(EEGE) poly(allyl glycidyl ether-*co*-glycidol) (**4**) was obtained proving that the allyl ether group is stable under these conditions of hydrolysis. However, from P(*t*BuGE)-*co*-P(EEGE) no poly(*tert*-butyl glycidyl ether-*co*-glycidol) (**3**) was obtained; instead complete deprotection occurred leading to polyglycidol (**1**) which was soluble in the solvent mixture (H_2O, THF, *t*BuOH, EtOH, CH_3CHO). ^{1}H NMR analysis confirmed the removal of both protection groups from P(*t*BuGE)-*co*-P(EEGE) within a few minutes. Treatment of P(*t*BuGE)-*co*-P(AGE) with aqueous HCl in THF showed no conversion; under the reaction conditions neither the *tert*-butyl ether nor the allyl ether group were removed. From these results we conclude the *tert*-butyl ether group cannot be hydrolyzed by aqueous HCl in THF unless free OH-groups formed during hydrolysis of the acetal groups—as is possible in P(*t*BuGE)-*co*-P(EEGE)—catalyze the removal of the *tert*-butyl ether protection groups.

Experiments with P(*t*BuGE)-*co*-P(EEGE) as substrate showed that also TFA cleaves both protective groups with formation of free hydroxyl groups and trifluoroacetate groups resulting in partially trifluoroacetylated polyglycidol **2**—as was shown for the homopolymer P(*t*BuGE).

It was, however, possible to selectively remove the *tert*-butyl group in P(*t*BuGE)-*co*-P(AGE) by treatment with TFA; poly(allyl glycidyl ether-*co*-glycidol) (**5**) was obtained. All *t*Bu-groups were removed; however, beside free hydroxyl groups again trifluoroacetate groups are observed in the NMR spectrum.

To cleave the allyl group of P(*t*BuGE)-*co*-P(AGE) and P(AGE)-*co*-P(EEGE) selectively, we found that palladium on charcoal in combination with *p*-toluenesulfonic acid is a useful reagent. After degassing a polymer solution of P(*t*BuGE)-*co*-P(AGE) or P(AGE)-*co*-P(EEGE) in methanol with nitrogen, these two reagents have been added in a catalytic amounts and reacted for several days. Starting with polymer P(*t*BuGE)-*co*-P(AGE) the allyl ether group was successfully removed, leaving the *tert*-butyl ether groups unchanged. Poly(glycidol-*co*-*tert*-butyl glycidyl ether) (**3**) was obtained in good yield. Starting with polymer P(AGE)-*co*-P(EEGE), the allyl ether group was also successfully removed; however, under the action of the acidic catalyst and traces of water more than 50% of the acetal groups were converted, too. In dry THF as solvent, no conversion of the allyl ether groups was observed. In conclusion, a protic solvent with traces of water are necessary for the removal of the allyl ether protection group.

Some characteristics of the polymers obtained upon deprotection are shown in Table 7. Most important is the observation that, according to the backbone signals in ^{1}H NMR spectra, the polymer did not degrade upon removal of the protection groups and that the polydispersity of the obtained polymers is quite unchanged from the one of the starting material. The increasing number-average molecular mass (M_n) of deprotected polymers let us assume a formation of aggregates in the used solvent, *N*,*N*′-dimethylacetamide.

Propargylation of Glycidol Repeating Units by Polymer Analogous Reaction. Polymers with propargyl groups in the side chain are of interest because of their efficient (2 + 3)

Table 7. Poly(glycidyl ether) Copolymers Obtained by Removal of the Protective Groups

			P_n[a]		SEC	
polymer	reagent	product	initial	after conversion	M_n[b]	Q[b]
P(EEGE)	HCl/THF	P(glycidol)	32	32	6300	1.09
P(*t*BuGE)-*co*-P(EEGE)	HCl/THF	P(glycidol)	32	32	n.d.	n.d.
P(*t*BuGE)	TFA	P(glycidol)/TFAc[c]	32	10/22	6400	1.10
P(*t*BuGE)-*co*-P(EEGE)	TFA	P(glycidol)/TFAc[c]	29	2/27	n.d.	n.d.
P(*t*BuGE)-*co*-P(AGE)	Pd/C, TSH	P(glycidol)-*co*-P(*t*BuGE)	40	18/19	5900	1.12
P(AGE)-*co*-P(EEGE)	HCl/THF	P(AGE)-*co*-P(glycidol)	30	15/15	5400	1.08
P(*t*BuGE)-*co*-P(AGE)	TFA	P(AGE)/TFAc[c]	40	15/15	5400	1.11

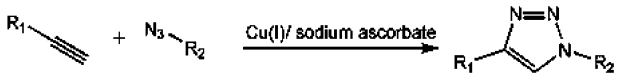
[a] Determined by ^{1}H NMR spectroscopy. [b] Measured with *N*,*N*′-dimethylacetamide as eluent. [c] Trifluoroacetyl.

Table 8. Functionalization of Free Hydroxyl Groups in Poly(glycidyl ether) Copolymers with Propargyl Bromide (PpgBr), Trifluoroacetic Acid (TFA), and the Azido Sugar via Polymer Analogous Reactions

			P_n[a]		SEC	
polymer	reagent	product	initial	after conversion	M_n[b]	Q[b]
P(glycidol)	PpgBr	P(GPE)-*co*-P(glycidol)	32	26/6	5600	1.09
P(glycidol)-*co*-P(*t*BuGE)	PpgBr	P(GPE)-*co*-P(glycidol)-*co*-P(*t*BuGE)	18/19	15/5/19	4900	1.10
P(AGE)-*co*-P(glycidol)	PpgBr	P(AGE)-*co*-P(glycidol)-*co*-P(GPE)	15/15	12/2/11	5300	1.09
P(GPE)-*co*-P(glycidol)-*co*-P(*t*BuGE)	TFA	P(GPE)[d]/TFAc[c]	15/5/19	18/19	6100	1.08
P(GPE)-*co*-P(glycidol)	azido sugar	P(GSTM)[e]-*co*-P(GPE)[d]-*co*-P(glycidol)	18/19	9/9/19	11 700	1.09

[a] Determined by ^{1}H NMR spectroscopy. [b] Measured with *N*,*N*′-dimethylacetamide as eluent. [c] Trifluoroacetyl. [d] GPE = glycidyl propargyl ether. [e] GSTM = glycidyl sugar triazolyl methyl ether.

Scheme 6. Huisgen (2 + 3) Dipolar Cycloaddtion Controlled by Cu(I) Species, To Yield Only 1,4-Triazolyl Rings



dipolar cycloaddition reaction with azide derivatives ($R-N_3$) and formation of 1,4- and/or 1,5-substituted triazolyl rings (Scheme 6).[20] To yield exclusively the 1,4-substituted triazolyl derivative, a Cu(I) species was added to the reaction mixture to control the regioselectivity and in addition sodium-L-ascorbate was added to prevent the oxidation of the Cu(I) species. If the R group in the azide is for example a glucopyranosil derivative, the resulting polymers are of interest for biomedical applications.

We have studied the propargylation reaction of polyglycidol (**1**), poly(glycidol-*co*-*tert*-butyl glycidyl ether) (**3**), and poly(glycidol-*co*-allyl glycidyl ether) (**4**) by using propargyl bromide and potassium hydroxide as reagents (Table 8). For polyglycidol (**1**) the propargylation reaction was performed in DMF-solution for 3 days at room temperature. After aqueous workup the water insoluble polymer **6** (11 wt %) showed a degree of substitution of ca. 81%. Obviously polymers with a lower degree of substitution are still soluble in water/DMF. The propargylation of poly(glycidol-*co*-*tert*-butyl glycidyl ether) (**3**) and poly(glycidol-*co*-allyl glycidyl ether) (**4**) was performed in methylene chloride solution using propargyl bromide and potassium hydroxide as reagents. The polymers obtained are the terpolymers poly(glycidol-*co*-*tert*-butyl glycidyl ether-*co*-propargyl glycidyl ether) (**7**) and poly(glycidol-*co*-allyl glycidyl ether-*co*-propargyl glycidyl ether) (**8**). For these polymers yields of ca. 70−90 wt % were obtained with a degree of substitution between 63 and 84%. Polymer **7** was subjected to further polymer analogous reactions. Dissolution of the polymer in TFA yielded after 3 h stirring at room temperature complete removal of the *tert*-butyl protection group and formation of poly(propargyl glycidyl ether-*co*-glycidyl trifluoroacetate) (**9**). This polymer was subjected to a Huisgen (2 + 3) cycloaddition using an azido sugar derivative (2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosylazide, GlcNAc) as reagent. The resulting polymer poly(glycidol-*co*-glycidyl propargyl ether-*co*-glycidyl triazolyl sugar) (**10**) was obtained in 65% yield as a golden powder.

In conclusion, with *tert*-butyl ether or trifluoroacetate groups, as protective group beside propargyl groups the click reaction was performed with excellent conversion and in good yield, however, if allyl groups are present beside propargyl groups the click reaction is not selective any more, Azides react with both triple and double bonds, double bonds being more reactive toward azides. In consequence, with propargyl and allyl ether groups in the polymer side chain, the formation of 4,5-dihydro-1*H*-1,2,3-triazole derivatives is preferred.[22]

All polymers prepared were analyzed by ^{1}H NMR and GPC (Table 8). During the polymer analogous reactions, the polydispersity increased only marginally, so that a uniform conversion, meaning a uniform distribution of converted functional groups can be assumed. The original Q values were in a region of 1.08 to 1.10, and the highest Q value found after modification was around 1.16.

4. Conclusions

Protected polyglycidols with two different protective groups were successfully prepared via anionic ring-opening polymerization of two differently protected glycidol monomers. The degree of polymerization as determined by ^{1}H NMR spectroscopy, corresponds to the theoretical value determined by the monomer to initiator ratio and conversion. SEC analysis showed that all polymers have a low polydispersity, as expected for a controlled anionic polymerization.

Poly(glycidyl ether)s with a combination of allyl and *tert*-butyl or allyl and acetal protection groups were selectively deprotected to obtain: (i) poly(glycidyl ether)s **3** with free hydroxymethyl and *tert*-butyloxymethyl groups, (ii) poly(glycidyl ether)s **4** with free hydroxymethyl and allyloxymethyl groups, and (iii) poly(glycidyl ether)s **5** with trifluoroacetoxymethyl and alloxymethyl groups. The poly(glycidyl ether)s **3** and **4** were propargylated in a polymer analogous reaction and poly(glycidyl ether)s **7** was successfully converted to a triazolyl sugar derivative by reaction with an azido sugar. In consequence, we have shown that starting with differently protected polyglycidols, specific and multiple functionalization of polyethers is possible.

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