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High molecular weight functionalized poly(ethylene oxide)

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Dedicated to Professor Roderic P. Quirk with best wishes on the occasion of his 60th birthday

Abstract

Novel high molecular weight copolymers of ethylene oxide (EO) and glycidol or ethoxy ethyl glycidyl ether (EEGE) were obtained via suspension anionic coordination polymerization using calcium amide-alkoxide initiating system. ^{1}H and ^{13}C NMR spectroscopy were used for the structural characterization of the copolymers as well as for the determination of the molar content (up to 2 mol%) of the functional monomers incorporated into the PEO backbone. SEC measurements of the copolymers determined $\bar{M}_n$ in the range of $(2-11)\times 10^5$ g/mol. Surprisingly low polydispersity values of average $\bar{M}_w/\bar{M}_n = 1.5$ were obtained for the EO/EEGE copolymers. The calcium amide-alkoxide initiated polymerization of EEGE resulted in high molecular weight polymers with relatively broad polydispersity values ($\bar{M}_n = (0.8-1.5)\times 10^5$ g/mol, $\bar{M}_w/\bar{M}_n \le 4.2$). EO/glycidol copolymers and polyglycidol were obtained after cleavage of the acetal protecting group of the EEGE units.

Polymers with hydrophilic backbone bearing hydrophobic stearyl moieties were obtained after modification of EO/glycidol copolymers with stearic acid. Their associating properties in aqueous solution were studied. Increasing either temperature or polymer concentration induces aggregate formation. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ethylene oxide/glycidol and ethylene oxide/ethoxy ethyl glycidyl ether copolymers; Associating properties; Calcium amide-alkoxide

1. Introduction

High molecular weight copolymers of ethylene oxide (EO) and oxiranes bearing polar functional groups have not been reported in the scientific literature. The latter undergo various side reactions involving either cationic or anionic polymerization, which makes the propagation process complex and hard to control [1–3]. Interesting novel materials would be obtained provided that various functional groups could be incorporated into a common high molecular weight PEO. These novel materials would display most of the characteristic properties of the PEO and in addition they could be designed through a selective chemical modification to meet various requirements in controlled drug delivery systems, nanoparticle formation, and rheology modifiers.

Glycidol (2,3-epoxypropanol-1) and 2,3-epoxypropyl 1-ethoxy ethyl ether (ethoxy ethyl glycidyl ether, EEGE) are found suitable for anionic initiated copolymerizations with EO.

Glycidol is a highly reactive monomer bearing both epoxy and hydroxyl functional groups. Its composition and structure favor the primary to secondary transitions of the alkoxide active sites, as well as the intermolecular transfers during base-initiated polymerization [4]. The propagation may evoke side reactions. Generally both the anionic [4] and cationic [5,6] polymerizations of glycidol lead to well-defined hyperbranched oligomers with numerous hydroxyl end groups. Frey et al. [7] reported on EO/glycidol multiarm star copolymers obtained by anionic mechanism.

On the other hand, ethoxy ethyl glycidyl ether (glycidol with protected hydroxyl group) is more stable than glycidol in basic media [8]. EEGE is easily obtained from glycidol and ethyl vinyl ether [9]. The lack of intramolecular transitions and side reactions during its anionic initiated polymerization favors the choice of this monomer for the anionic initiated synthesis of poly(EEGE) as well as EO/EEGE copolymers [8,10]. The acetal group is readily cleaved with acids, which makes poly(EEGE) and EO/EEGE copolymers suitable precursors for linear polyglycidol and EO/glycidol copolymers [8,10].

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This work reports on the copolymerizations of EO with glycidol, or with protected glycidol, done in heptane via an anionic coordination suspension mechanism provided by calcium amide-alkoxide [11]. Hence, very high molecular weight polymers were obtained.

2. Experimental

2.1. Materials

All solvents were purified by standard methods. Glycidol (Aldrich) was distilled under reduced pressure prior to use. The protection of glycidol with ethyl vinyl ether was done by the procedure described by Fitton et al. [9]. EO (Clariant), PhNCO and stearic acid (Aldrich) were used as received.

2.2. Polymerization procedure

2.2.1. Initiating system

The anionic precipitation polymerization of ethylene oxide and EEGE or glycidol, as well as the homopolymerization of EEGE was initiated by calcium amide-alkoxide [11]. The calcium amide-alkoxide catalyst was synthesized directly in the reaction vessel equipped with mechanical stirrer and an argon line. Ca 0.5 g was reacted with 0.8 ml of acetonitrile/propylene oxide (v/v, 2:3) in 75 ml liquid NH_3. After evaporation of NH_3, 40 ml of heptane was added followed by thermal treatment of the catalyst suspension at 90 °C for 1 h.

2.2.2. Poly(ethylene oxide-co-glycidol)

Copolymerizations were done in 80 ml of heptane for 5 h. After 15 min of slow bubbling of EO through the suspension formed by the modified Ca catalyst, a certain amount (1–2.5 ml) of glycidol was added dropwise for 2–4 h, while the bubbling of EO continued.

2.2.3. Poly(ethylene oxide-block-glycidol)

Diblock copolymers were made by sequential anionic polymerization of EO and glycidol in 80 ml of heptane. At zero time, EO was bubbled for 0.5–4 h through the catalyst suspension to obtain the first high molecular weight block of PEO, followed by slow addition of 0.5–4 ml glycidol for 0.5–6 h.

Polymer precipitates were filtered, washed several times with hexane and dried. The low molecular weight fractions (1–5 wt%) within both the random and diblock copolymers were separated by dialysis in distilled water with a cellulose membrane having a cut-off value of 12,000 (D-9527, Sigma).

2.2.4. Poly(ethoxy ethyl glycidyl ether)

Polymerizations of EEGE were done at 10–40 °C in 40 ml of heptane for 48 h with an initial monomer concentration of 1.3 mol/l. The opaque polymer solution was filtered and precipitated by adding a small amount of acetic acid. After ultracentrifugation the residue was dissolved in toluene, filtered and precipitated again. The polymer was washed several times with cold hexane (0 °C) and dried under reduced pressure for 12 h.

2.2.5. Poly(ethylene oxide-co-ethoxy ethyl glycidyl ether)

5 ml of EEGE was added to the suspension of the catalyst in heptane. At zero time, EO was bubbled through the reaction mixture, with stirring for 1–3 h at 20–60 °C.

2.2.6. Poly(ethylene oxide-block-ethoxy ethyl glycidyl ether)

Diblock copolymers were made by sequential anionic polymerization of EO and EEGE. The first HMW PEO block was made by bubbling EO for 0.5 h. The reaction mixture was left for 0.5 h to complete the EO polymerization. Then 5 ml of EEGE was introduced. The formation of the second block continued for 24 h.

The copolymers were filtered, dried and extracted with hexane to eliminate traces of unreacted EEGE as well as poly(EEGE), a possible by-product.

2.3. Chemical modification of the polymers

2.3.1. Synthesis of poly(glycidyl tosylate)

Ten millilitres of 1 M solution of *p*-toluenesulfonic acid in acetonitrile was added to another 10 ml of acetonitrile solution of 0.4 g poly(EEGE). A white precipitate of poly(glycidyl tosylate) was formed. It was filtered, washed several times with acetonitrile and dried in vacuo.

2.3.2. Deprotection of acetal groups of the polymers

One gram of EO/EEGE copolymer was dissolved in 20 ml of formic acid (98%) at room temperature. After dissolution, formic acid was evaporated under reduced pressure at room temperature. The polymer residue was then dissolved in 35 ml of dioxane–methanol mixture (1:1), and the solution was alkalized with 1N KOH (pH 10) and then refluxed for 24 h. The mixture was filtered then neutralized with 3% HCl. The solvent was evaporated and the residue was dissolved in water and extracted with $CHCl_3$.

Acetal groups of poly(EEGE) were removed by hydrolysis of the homopolymer in THF, with equimolar amount of hydrochloric acid.

2.3.3. Modification with PhNCO

To a magnetically stirred solution of EO/glycidol copolymer (0.5 g) in $CHCl_3$ (30 ml), while maintaining anhydrous conditions, phenyl isocyanate (five times molar excess) was added at 0 °C. The mixture was incubated at 40 °C for 16 h. Two thirds of the solvent was evaporated, and the polymer was precipitated by diethyl ether followed by drying.

2.3.4. Modification with stearic acid

EO/glycidol copolymer (1 g) was dissolved in CH_2Cl_2 (30 ml). Separately *N*,*N*′-dicyclohexylcarbodiimide (DCC), dimethylaminopyridine (DMAP) and stearic acid were dissolved in the same solvent and then added. The mole ratio of the reagents was $C_{17}H_{35}COOH$/[G]/DMAP/DCC = 2:1:0.5:4.4. The reaction continued for 24 h at room temperature. The solution was precipitated in freshly distilled dry diethyl ether, dried under reduced pressure, dissolved in acetone at 50 °C and precipitated by cooling to -30 °C.

2.4. Measurements

2.4.1. NMR

The ^{1}H and ^{13}C NMR spectra were recorded at 250 MHz on a Bruker WM 250 at room temperature, using $CDCl_3$ or (methyl sulfoxide)-d_6 as solvent.

2.4.2. Molecular weight characteristics

Molecular weights and polydispersities of EO/glycidol copolymer samples were measured by SEC using double detection on a chromatography line consisting of a M510 pump, a U6K injector, two Ultrahydrogel columns with pore size of 120 and 250 Å, a differential refractive index detector M 410, and a tunable absorbance detector M 486 (Waters Chromatography Division). Measurements were done in MeOH/H_2O (15/85, v/v) solvent at 20 °C with a nominal flow rate of 0.8 ml/min. Molecular weights were calculated according to calibration with PEO and polyethylene glycol narrow molecular weight standards.

$\bar{M}_w$, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ values of EEGE homopolymers and EO/EEGE copolymers were determined by SEC using 3 × PlGel Mixed C 30 cm plus guard columns with a Schambeck 2000 differential refractive index detector and a DAWN EOS multiangle light scattering detector from Wyatt Technologies. Measurements were done in THF at 40 °C with a nominal flow rate of 1 ml/min. Results were evaluated using the ASTRA software from Wyatt Technologies.

Refractive index increments in THF were determined independent to 0.063 for PEO and to 0.080 for polyEEGE. For EO/EEGE copolymers, 0.063 was used.

2.4.3. DSC

The DSC plots were obtained with a Perkin–Elmer DSC-7 thermal analysis system at a standard heating and cooling rate of 10 °C/min. Samples of 10 mg were run in an argon atmosphere over a temperature range of -50 to 150 °C. Indium ($T_m = 156.6$ °C) was used for temperature calibration. Copolymer crystallinity was estimated as the ratio between the experimentally determined enthalpy of melting (ΔH_m) and enthalpy of melting of a 100% crystalline PEO ($\Delta H_{m^0} = 8276$ J/mol [12]).

2.4.4. Viscosimetry

Viscosity measurements were done with a Ubbelohde type viscometer equipped with a capillary of 0.45 mm diameter and thermostated at 30 °C. The solvent (distilled water) and the solutions were filtered prior to the measurement. $\bar{M}_v$ was determined using the constants for pure PEO—$K = 1.25 \times 10^{-4}$ and $\alpha = 0.78$ [13].

2.4.5. Rheological measurements

Rheological measurements of 5 wt% copolymer solutions in distilled water were made on a Brabender Rheotron 1.8 rheometer with a P_7/B system having a cone diameter of 50 mm, plate diameter of 52 mm, and cone angle of 0.3°. Working shear rates ranged from 0.1 to 100 s^{-1}.

2.4.6. Dye solubilization

Aqueous solutions (2 ml) of a hydrophobically modified copolymer in the concentration range from 0.1 to 3.5 g/l were prepared. Two microlitres of a 0.4 mM solution of 1,6-diphenyl-1,3,5-hexatriene (DPH) in methanol were added to each of the copolymer solution. Solutions were incubated in the dark for 16 h. Absorbance spectra in the range $\lambda = 300$–500 nm were recorded on a Specord UV–vis spectrometer (Carl Zeiss, Jena) at a room temperature. The main absorption peak, characteristic of DPH solubilized in a hydrophobic domain was at 356 nm [14–16].

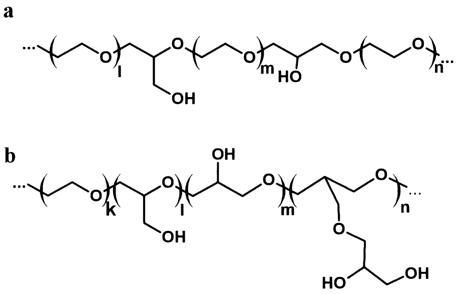
3. Results and discussion

3.1. Polymerization

Polymerization of EO by an alkaline earth compound gives a polymer of extremely high molecular weight. Polymerizations induced by these catalysts are considered to follow a ‘coordinate anionic mechanism’ in which the monomeric oxirane is coordinated to the catalyst by an unshared electron pair of the oxygen atom from the epoxy ring. Calcium amide-alkoxide initiators are very active below the polyether melting point, which is very important for their industrial application. The reaction produces a polymer that is not soluble in the reaction medium, hence it remains in a granular form. Therefore, the granular polymer can be recovered by filtration and used without further processing.

3.1.1. Copolymerization of EO and glycidol

Anionic suspension copolymerization of EO and glycidol in hydrocarbon media initiated by calcium amide-alkoxide would provide us with a simple procedure for the industrial preparation of high molecular weight PEO with pendant hydroxyl groups in the main chain. Precipitation polymerization systems differ significantly from the pattern established for homogenous polymerization. Alkoxide active sites are incorporated within the polymer particles, thus monomer diffusion into the particle plays a very



Scheme 1. EO/glycidol copolymers: (a) poly(ethylene oxide-*co*-glycidol), (b) poly(ethylene oxide-*block*-glycidol).

important role. The active centers are ‘living’—the reaction ceases when the supply of monomer is interrupted. The reaction resumes when another portion of epoxide monomer is introduced. It is possible that one of the monomers may polymerize with little or no incorporation of the other one and the percentage of the functional monomer may vary substantially in the polymer fractions formed at different time intervals. The expected structures of EO/glycidol copolymers are illustrated in Scheme 1.

The hydroxyl group of the glycidol units has been transformed to an urethane group after reacting dialyzed EO/glycidol copolymers with phenylisocyanate. Thus, the molar content of glycidol units has been calculated using UV and ^{1}H NMR spectroscopy based on characteristic peaks of the phenyl residue. Results from the copolymerizations are presented in Tables 1 and 2. The molar content values of glycidol determined by UV spectroscopy correlate with those of the ^{1}H NMR data. Incorporation of functional monomer into the PEO backbone is higher when 1.5–1.7 ml of glycidol is added during the simultaneous copolymerization. For sequential block copolymerization, the molar amount of glycidol units increases with the increased quantity of the glycidol added. Generally the molar amount of glycidol units is equal or smaller than 2.5%, which allows comparison of the intrinsic viscosity of EO/glycidol copolymers with that of pure PEO. As expected the copolymer polydispersity values are very broad, which is typical for suspension anionic coordination polymerization. SEC analyses of non-dialyzed copolymers showed bimodal distribution presented by an additional less intense peak assigned to oligomeric products. After dialysis, the low molecular weight fractions were removed and isolated. Their NMR spectra reveal a predominance of glycidol units.

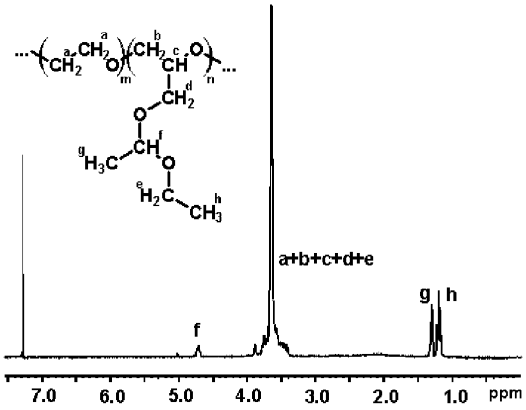


Fig. 1. ^{1}H NMR spectra of high molecular weight poly(EO-*co*-EEGE) (PRE2) in $CDCl_3$.

3.1.2. Polymerization of EEGE

Polymerizations of EEGE in heptane using calcium amide-alkoxide initiating system results in rubber-like high molecular weight polymers with average yields of 50%. Polymerization conditions and the molecular weight data of poly(EEGE) are summarized in Table 3.

Despite different polymerization temperatures, polymer yields and molecular weight characteristics do not differ significantly.

3.1.3. Copolymerization of EO and EEGE

Studies on the anionic suspension polymerization of EO and EEGE by using calcium amide-alkoxide initiators have shown clearly that high molecular weight copolymers can be obtained easily (Tables 4 and 5). According to the ^{1}H and ^{13}C NMR (Figs. 1 and 2) spectral data, the copolymers possess a linear structure, which is better defined in comparison to that of the EO/glycidol copolymers (Scheme 2).

SEC analyses show monomodal distribution. However, some of the results are rather difficult to rationalize. The apparent molecular weight distributions are surprisingly

Table 1
Poly(ethylene oxide-*co*-glycidol) polymers after dialysis. Polymerization conditions: 0.5 g Ca, 80 ml heptane, reaction temperature 40 °C

No	Added G (ml)	EO/G feeding (h)	Yield (g)	G (mol%)		$[\eta]_{H_2O}$ 30 °C	$\bar{M}_v \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
				UV	^{1}H NMR				
PRG1	1	2	24	1.0	0.4	3.6	5.2	9.3	9.0
PRG2	1	2	27	1.5	0.6	4.3	6.5		
PRG3	1.5	4	22	3.0	2.5	6.4	11.0	5.0	13.0
PRG4	1.7	4	21	2.2	1.3	2.9	4.0	1.6	3.0
PRG5	2.5	4	32	0.7	0.7	6.9	12.0	4.50	3.0
PRG6[a]	3	4	21	0.5	0.4	3.7	5.4	–	–

[a] Reaction temperature 15 °C.

Table 2
Poly(ethylene oxide-*block*-glycidol) polymers after dialysis. Polymerization conditions: 0.5 g Ca, 80 ml heptane, reaction temperature 40 °C

No	Added G (ml)	EO feeding	G Feeding (h)	Yield (g)	G (mol%)		$[\eta]_{H_2O}$ 30 °C	$\bar{M}_v \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
					UV	^{1}H NMR				
PBG1	0.5	4 h	0.5	39	3.0	2.0	3.9	6.0	2.1	9.0
PBG2	1.5	2.5 h	1.5	50	1.0	0.4	7.6	14.0	3.0	7.4
PBG3	2.5	2 h	2.5	60	2.5	2.0	6.4	11.0	4.2	4.0
PBG4	4.3	10 min	6	19	2.3	2.0	2.5	3.4	2.5	3.5

Table 3
Poly(EEGE). Polymerization conditions: 0.5 g Ca, 40 ml heptane, monomer concentration—1.3 mol/l

No	Reaction temperature (°C)	Reaction time (h)	Conv. in %	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
PH1	10	48	50	0.87	4.5
PH2	20	48	52	1.8	3.4
PH3	40	48	52	1.3	4.5
PH4	40	29	29	1.5	4.2

Table 4
Poly(EO-*co*-EEGE). Polymerization conditions: 0.5 g Ca, 100 ml heptane, 5 ml added EEGE, EO feeding—3 h, reaction time—6 h

No	T (°C)	Yield (g)	EEGE[a] (mol%)	$[\eta]_{H_2O}$ 30 °C	$\bar{M}_v \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	T_m (°C)	χ[b] (%)
PRE1	20	50	2.3	6.0	10.2	11.4	1.1	63.3	58.4
PRE2	30	57	1.7	10.1	19.6	9.6	1.2	60.7	55.3
PRE3	40	43	1.8	8.4	15.5	7.8	1.3	60.2	54.4
PRE4	60	34	2.0	3.6	5.0	0.7	1.7	60.1	56.7

[a] Determined by ^{1}H NMR analysis.
[b] Degree of crystallinity.

Table 5
Poly(EO-*block*-EEGE). Polymerization conditions: 0.5 g Ca, 100 ml heptane, 5 ml added EEGE, 0.5 h EO feeding, reaction time—24 h

No	T (°C)	Yield (g)	EEGE[a] (mol%)	$[\eta]_{H_2O}$ 30°C	$\bar{M}_v \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	T_m(°C)	χ[b] (%)
PBE1	10	20	0.9	3.7	5.4			68.9	67.2
PBE2	20	33	0.8	5.2	8.3	7.3	1.15	67.6	61.9
PBE3	30	13	1.7	1.8	2.1	3.0	1.56	66.2	62.3
PBE4	30	19	1.8	2.0	2.5	4.2	1.35	66.7	61.7
PBE5	40	21	1.5	3.9	5.8			67.9	67.0

[a] Determined by ^{1}H NMR analysis.
[b] Degree of crystallinity.

narrow for the heterogenous suspension polymerization. In some cases, the necessary relation $\bar{M}_n < \bar{M}_v < \bar{M}_w$ is disturbed. One possible explanation is that $\bar{M}_v$ is determined with the aid of K and α constants from the Mark–Houwink equation for pure PEO. Although the applied multiangle light scattering detection yields absolute $\bar{M}_w$ values for the samples, for the proper determination of $\bar{M}_n$ an ideal chromatographic separation is necessary (assumption of monodisperse slices). As seen in Fig. 3, there is some non-linearity when plotting the molar mass versus elution time, which may indicate an imperfect chromatographic separation. Further studies are under way to resolve this discrepancy.

Reaction temperatures in the interval of 20–40 °C are preferred. Fig. 1 shows the ^{1}H NMR spectrum of poly(EO-*co*-EEGE). The molar content of EEGE has been determined by calculating the peak ratios between the acetal group protons at 1.18, 1.30, and 4.70 ppm and the EO and the glycidyl units protons in the range of 3.4–3.9 ppm. DSC analysis shows a lower T_m and a lower degree of crystallinity (χ) of the random copolymers. Obviously the random distribution of

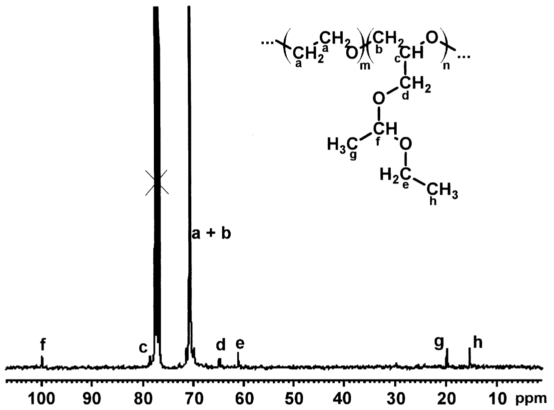
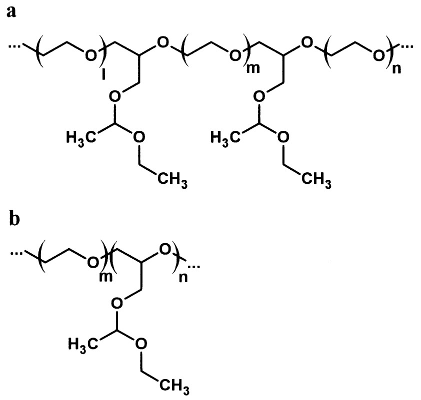


Fig. 2. ^{13}C NMR spectrum of poly(EO-*co*-EEGE) (PRE1) in $CDCl_3$.



Scheme 2. EO/EEGE copolymers: (a) poly(ethylene oxide-*co*-ethoxy ethyl glycidyl ether), (b) poly(ethylene oxide-*block*-ethoxy ethyl glycidyl ether).

EEGE units within the PEO backbone results in the formation of a more defective crystalline lattice compared to one formed by the block copolymers.

3.2. Chemical modification of the polymers

3.2.1. Deprotection of acetal groups of EEGE units

Linear polyglycidol has been obtained after the deprotection reaction of poly(EEGE) with dilute hydrochloric acid. The polymer structure has been confirmed by ^{13}C NMR. Fig. 4 shows the presence of one type repeating monomer unit. Treatment of EO/EEGE copolymers with formic acid followed by successive saponification leads directly to linear EO/glycidol copolymers comprising up to 2 mol% of reactive hydroxyl groups. The transition of an acetal group to a hydroxyl group is shown in Fig. 5. The data indicates that the deprotection reactions are quantitative.

The ethoxy ethyl protecting group on EEGE monomer units has been transformed into a tosylate group by reacting poly(EEGE) with *p*-toluenesulfonic acid (Fig. 6). Other functional groups can be obtained easily from tosylate groups via further chemical modification of poly(glycidyl tosylate).

3.2.2. Hydrophobization of EO/glycidol copolymers: rheological properties

Great interest has been generated in self-associating polymers because of a substantial enhancement of viscosity due to hydrophobic group association. Thus, these 'viscosity builders' have many important applications, especially as coatings, and also in the cosmetics industry, as well as for preparing polymer nanoparticles from aqueous polymer solutions.

EO/glycidol copolymers have been reacted with stearic acid by using the DCC/DMAP method [17], which is a further illustration of useful modification of functional hydroxyl groups provided by glycidol units within the polymer chain. Thus, polymers with a hydrophilic backbone bearing hydrophobic stearyl moieties have been obtained. The dye solubilization method has been used for the determination of critical aggregation concentration [14–16]. A typical plot of DPH absorbance at 356 nm versus the concentration of aqueous solutions of hydrophobically modified poly(ethylene oxide-*co*-glycidol) (PRG4) is shown in Fig. 7. The sharp increase in absorbance shows that polymer aggregates are formed at concentrations higher than 1.3 g/l.

Rheological studies on aqueous solutions of the hydrophobically modified derivatives at concentrations higher than the overlapping concentration, $C^{*} = 1/[\eta]$, have been done at 20 and 40 °C. The effect of changing shear rate is shown in Fig. 8. Considerable increase of viscosity (more than 150 times) as a function of shear rate compared to that of unmodified copolymers at 40 °C was observed. Shear rate

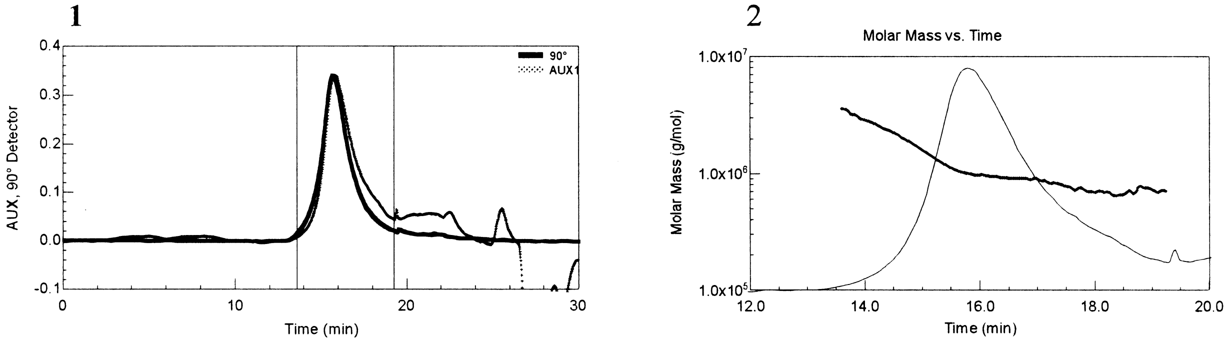


Fig. 3. SEC of poly(EO-*co*-EEGE) (entry PRE3 in Table 4): (1) RI and 90° light scattering traces, (2) plot of the molecular weight versus elution time.

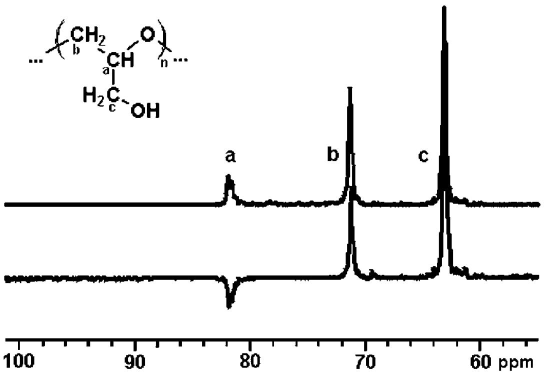


Fig. 4. ^{13}C and DEPT NMR spectra of linear polyglycidol obtained after hydrolysis of PH4. CD_3OD solvent, $T = 50$ °C.

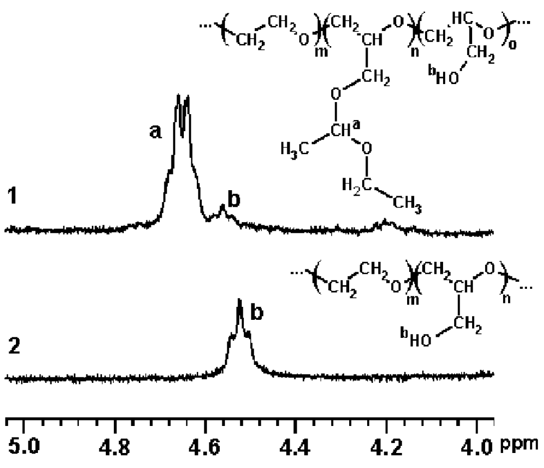


Fig. 5. ^1H NMR spectrum of EO/EEGE copolymer; solvent—(methyl sulfoxide)-d_6: (1) Partially deprotected poly(EO-*co*-EEGE) (PRE4) after a two-week dialysis; (2) Poly(ethylene oxide-*co*-glycidol) obtained by a two step deprotection reaction of poly(EO-*co*-EEGE) with formic acid and KOH.

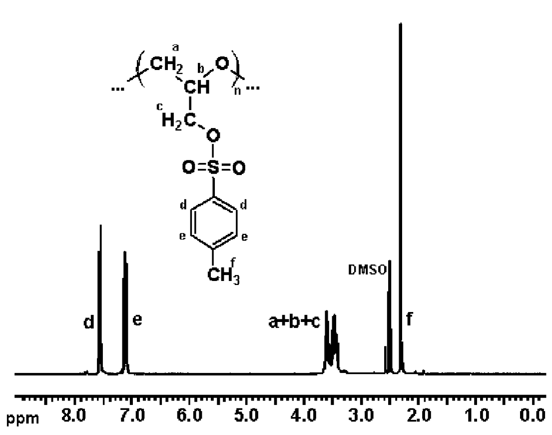


Fig. 6. ^1H NMR spectrum of poly(glycidyl tosylate) (PH4 precursor) taken in (methyl sulfoxide)-d_6.

at 20 °C does not have a significant effect upon the viscosity curve. The hydrophobicity of stearyl moieties became higher with increasing temperature due to the unique hydrogen-bond breaking process.

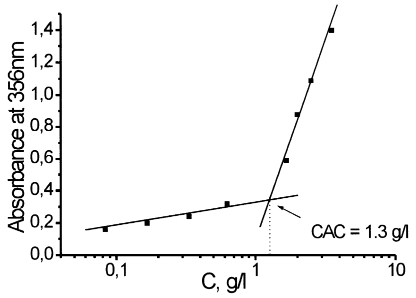


Fig. 7. Variation of the absorbance of DPH at 356 nm as a function of concentration in aqueous solution of poly(ethylene oxide-*co*-glycidyl stearate) (PRG4 precursor, 0.42 mol% incorporated hydrophobe).

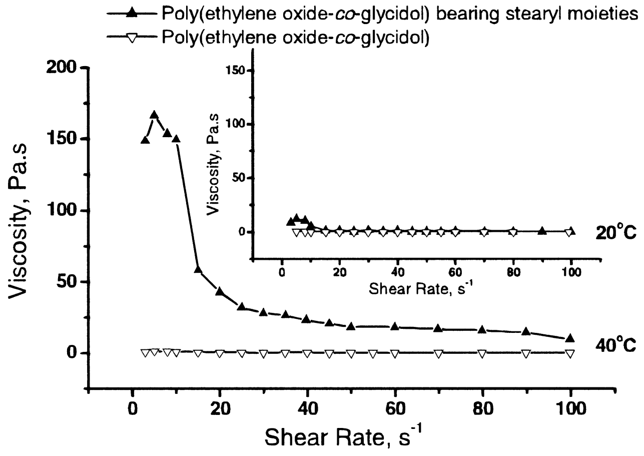


Fig. 8. Rheological properties of poly(ethylene oxide-*co*-glycidol) precursor (PRG4) and poly(ethylene oxide-*co*-glycidyl stearate), 0.42 mol% incorporated hydrophobe. Polymer concentration—5 wt%.

4. Conclusions

In this study, we report the synthesis of novel high molecular weight copolymers of ethylene oxide with glycidol as a second monomer via an anionic suspension mechanism using a calcium amide-alkoxide initiating system. Thus, PEO-bearing hydroxyl groups were obtained by a one-pot procedure that can be easily adopted for industrial purposes.

It was possible to synthesize well-defined EO/ethoxy ethyl glycidyl ether copolymers under mild conditions, with significantly reduced side reactions.

Simple modification of the hydroxyl groups on EO/glycidol copolymers by stearyl moieties brought a significant change in the rheological properties of aqueous polymer solutions. Hydrophobically modified PEO underwent self-aggregation at a critical aggregation concentration of 1.3 g/l.

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