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# Controlled Polymerization of Glycidyl Methyl Ether Initiated by Onium Salt/Triisobutylaluminum and Investigation of the Polymer LCST

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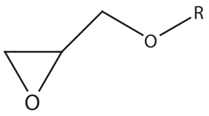
**Summary:** New initiating systems developed for monomer activated anionic polymerization of propylene oxide, i.e. onium salt/triisobutylaluminum, were applied to the polymerization of glycidyl methyl ether. At low to medium temperature they yield fast polymerization and allow the synthesis of poly(glycidyl methyl ether) with high molar masses in a controlled way. Poly(glycidyl methyl ether) exhibits a critical solubility temperature (LCST) in water which is influenced by the polymer molar masses. Surprizingly Poly(glycidyl methyl ether)s show also some tendency to crystallize in water at low temperature, which perturb their solubility characteristics and behaviour in water.

**Keywords:** anionic polymerization; glycidyl methyl ether; onium salt; triisobutylaluminum; thermal properties

## Introduction

Glycidyl ethers represent an interesting family of monomers because of the great diversity of the corresponding polymer materials which can be potentially obtained by varying the nature of the alkoxide group (OR). This allows the preparation of polymers with tunable properties such as glass transition, hydrophilic to hydrophobic balance, LCST, etc…



Various types of initiating species have been used to polymerize glycidyl ethers but their polymerization was subjected to important side reactions. Nucleophilic species such as tertiary amines,[1–3] potassium or sodium hydroxides or alkoxides[4] are commonly used although they show limitations in the control of the polymerization and only allow the formation of oligomers due to transfer reactions[5–7] to monomer and solvent (Figure 1).

Polymerization by coordination was also reported. However the most commonly studied system $(i\text{-PrO})_3Al + ZnCl_2$[8–10] is not able to control the polymerization of glycidyl ethers and yields polydisperse materials with only low molar masses (<15 000 g/mol). Glycidyl ethers present an other interest in the preparation of epoxy-networks from multifunctional monomers. Accordingly, latent thermal initiators and photoinitiators were developed. Latent thermal initiators such as sulfonium,[11] pyridinium[12] and phosphonium[13,14] salts were first used to initiate bulk ring opening polymerization of multifunctional glycidyl ether derivatives at high temperature. Non-ionic species such as hydroxylamides,[15] aminimides,[16] esterified phosphonic acids[17] or amides[18] were also used as latent initiators in similar

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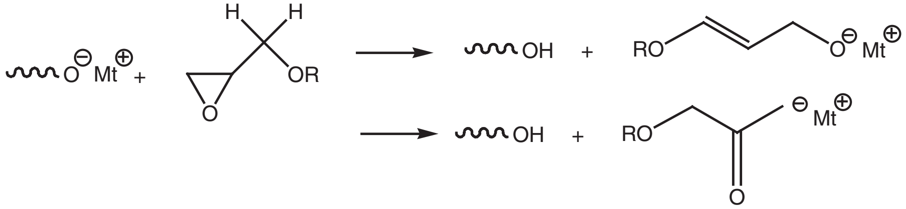


***Figure 1.***
Transfer reactions to the monomer in anionic polymerization of glycidyl ethers.[6]

conditions. However, when used with phenyl glycicyl ether as model monomer of epoxy network precursors, all these systems yield only low molar masses oligomers (5 000 g/mol). Dialkyliodonium and trialkylsulfonium salts were also developed as cationic photoinitiators for the polymerization of glycidyl ether type monomers;[19–21] kinetic behaviors were investigated but no mention was made about obtained polymer molar masses.

We have found recently that the association of trialkylaluminum to alkali metal alkoxides[22] or ammonium salts[23,24] allows the controlled high speed anionic polymerization of propylene oxide and ethylene oxide at low to moderate temperatures. This presentation deals with the use of these initiating systems for the polymerization of glycidyl methyl ether (GME) and with a study of the LSCT properties of the corresponding poly(glycidyl methyl ether) as a function of their molar masses.

## Experimental Part

Triisobutylaluminum ($i$–$Bu_3Al$, 1 M in toluene), tetraoctylammonium bromide ($NOct_4Br$, 98%) were purchased from Aldrich. $i$–$Bu_3Al$ was used without further purification, $NOct_4Br$ was dried under dynamic vacuum for 2 hours and then solubilized in toluene to the desired concentration. Glycidyl methyl ether (GME, >85%, TCI) was first distilled, dried over $CaH_2$, then distilled under vacuum two times over trialkylaluminum and finally distilled under vacuum before use. Toluene (99%, J.T. Baker) was purified over polystyryllithium seeds and distilled under vacuum before use.

All polymerizations were performed at −30 °C, followed by a slow raise up to 20 °C, under argon in a glass reactor equipped with a magnetic stirrer, fitted with PTFE stopcocks and previously flamed under vacuum. Solvent, and monomer were successively introduced in the reactor under vacuum trough connected glass tubes. The polymerization was triggered by addition of onium salt and then $i$–$Bu_3Al$ via a syringe and under argon. Polymerizations were stopped with addition of EtOH. Conversions were determined gravimetrically after a complete drying of the polymer under vacuum at room temperature.

Poly(GME) molar masses were determined by SEC at 20 °C using THF as eluant on a Varian apparatus equipped with a JASCO HPLC-pump type 880-PU, a dual refractive index/UV Varian detector and fitted with three TSK columns HXL (2000, 3000, 4000) at an elution rate of 1ml/min. Polystyrene standards were used as reference.

The LCSTs of 1% wt aqueous polymer solutions in water were measured by monitoring UV-absorbance of a 500 nm light beam at increasing and decreasing temperatures.

Microscopy analysis was performed, with ×10 enlargement, on a Leitz (Laborlux-k) apparatus, equipped with a Metter Toledo oven.

DSC measurements were performed on a TA instrument (Q100), runs were done from −100 °C to + 130 °C and from +130 °C to −100 °C, at 10 °C/min.

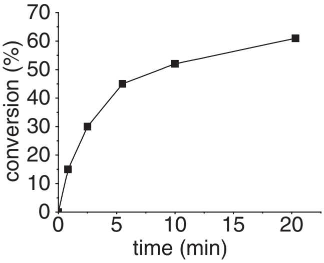


***Figure 2.***

Typical conversion versus time plot for GME polymerization initiated by $NOct_4Br$, activated by $i$-$Bu_3Al$ (1.5 eq), [GME]/[I] = 335, [GME] = 3 mol/l, 0 °C in toluene

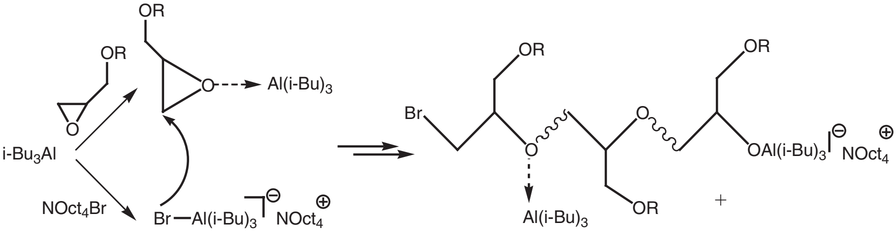
## Results and Discussion

As already reported for propylene oxide activated anionic polymerization,[23] to be active, the initiating system $i$-$Bu_3Al$/$NOct_4Br$ requires to work with a slight excess of aluminic compound with respect to the ammonium salt ([$i$-$Bu_3Al$]/[$NOct_4Br$]>1). In these polymerization conditions, at −30 °C in toluene, methyl glycidyl ether polymerization proceeds up to completion within minutes to few hours, depending on the targeted polymer molar mass. After a rapid monomer consumption, up to about 50%, a lowering of the polymerization rate is observed at high monomer conversion (Figure 2) up to final and quantitative GME conversion.

Fast polymerization of the oxirane monomer can be explained by the monomer activated mechanism. $i$-$Bu_3Al$ first coordinates to the tetraalkylammonium initiator to form a 1:1 [$i$-$Bu_3Al$]/[$NOct_4Br$] ''ate'' complex. Then, thanks to its coordination with the excess of $i$-$Bu_3Al$, a small fraction of the monomer is strongly activated towards nucleophiles, allowing its attack by the formed ''ate'' complex (Scheme 1). The presence of a bromo end group at the chain head confirms the nucleophilic initiation mechanism. After monomer insertion subsequent complexation of new monomer molecules by $i$-$Bu_3Al$ allows the propagation to proceed further. In agreement with this mechanism, activated polymerisation was shown to follow a zero order dependence with respect to monomer.[23] At high monomer conversion, the significant reduction of polymerization rate observed can be attributed to a competitive complexation of the polyether chain with $i$-$Bu_3Al$, decreasing thus the concentration of complexed monomer (see Scheme 1).

As shown in Table 1, experimental molar masses of the poly(methyl glycidyl ether)s are in agreement with theoretical ones assuming the formation of one chain per ammonium salt and molar mass distributions are narrow. High molar masses poly(GME) (up to 100 000 g/mol) can be achieved readily in mild conditions, which is a great improvement in comparison with previously reported systems for glycidyl ether polymerization that only allowed the synthesis of oligomers.

To confirm the controlled character of the polymerization, the evolution of poly (GME) molar masses versus conversion was followed for a polymerization experiment performed at 0 °C, see Figure 3. As may be seen the number-average molar masses increases linearly with increasing



***Scheme 1.***

Reaction mechanism involving monomer activation and trapping of $i$-$Bu_3Al$ by growing chain.

***Table 1.***

Glycidyl methyl ether (GME) polymerization initiated by $NOct_4Br$ (I) in the presence of $i$-$Bu_3Al$, [GME] = 3 mol/l, in toluene, −30 °C followed by slow temperature raise, up to 20 °C. Conversion : 100%.

| [Al]/[I] | Polym. time | $\overline{M}_{n_{th}}$ g · mol$^{-1}$ | $\overline{M}_{n_{exp.}}$ g · mol$^{-1}$ | PDI |
|---|---|---|---|---|
| 1.3 | 5h20 | 3 000 | 3 100 | 1.16 |
| 1.5 | 15h | 10 000 | 10 900 | 1.06 |
| 2.6 | 4h50 | 30 000 | 28 700 | 1.07 |
| 4.3 | 7h | 47 500 | 43 600 | 1.10 |
| 7 | 7h30 | 93 000 | 87 100 | 1.16 |

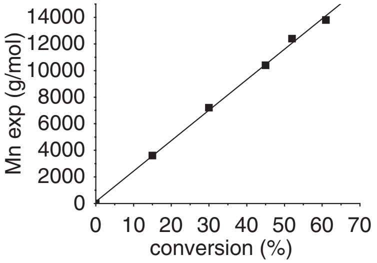


***Figure 3.***

$\overline{Mn}_{exp}$ versus conversion plot for GME polymerization initiated by $NOct_4Br$, activated by $i$-$Bu_3Al$ (1.5 eq), [GME]/[I] = 335, [GME] = 3 mol/l, 0 °C in toluene.

conversion, in agreement with a living-like polymerization.

Litterature makes reference to thermosensitive properties of poly(glycidyl ethers) in water and especially of poly(GME),[25] which oligomers have a critical solubility temperature (LCST) at 57.7 °C, beyond which the polymer is insoluble. Preliminary studies of poly(GME) LCST by monitoring UV-absorbance of a 1% wt aqueous polymer solution as a function of temperature confirm the LCST characteristics and critical solubility temperature (Tc) with some dependence on the polymer molar mass (Figure 4). Tc varies from 60.5 °C for $\overline{M}_n = 10\,900$ g/mol to 56.5 °C for $\overline{M}_n = 43\,600$ g/mol and 87 000 g/mol. Surprisingly, in the same conditions, chains with $\overline{M}_n = 3\,000$ g/mol are not fully soluble over the whole range of temperature examined, and yield already an opaque solution at 20 °C, which finally turns to white and opaque, in agreement with a Tc at 63 °C.

We can also notice in Figure 4, a slight increase of the UV-absorbance at low temperatures for the 10 900 g/mol sample. This phenomenon can be associated to the formation of bright poly(GME) particles after a few minutes of cooling of the solution.

Preliminary microscopy analysis of the polymer particles recovered from water after partial drying confirmed the formation of spherulitic structures, with an average size of about 200 μm (Figure 5a and 5b), suggesting a partial crystallization process of poly(GME) in the solution.

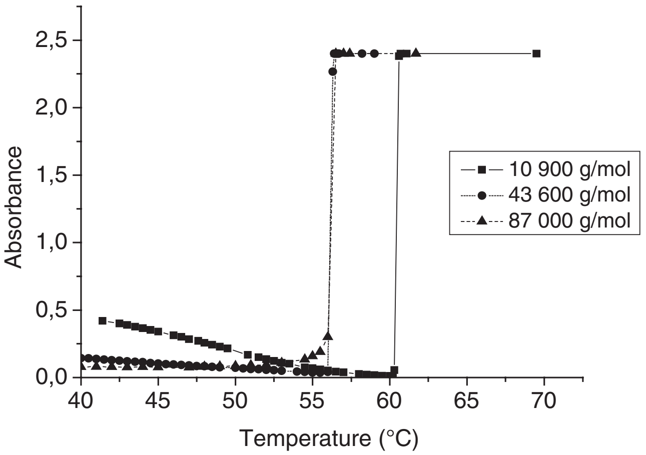


***Figure 4.***

LCST dependence on polymer molar mass for 1% wt aqueous poly(GME) solutions.

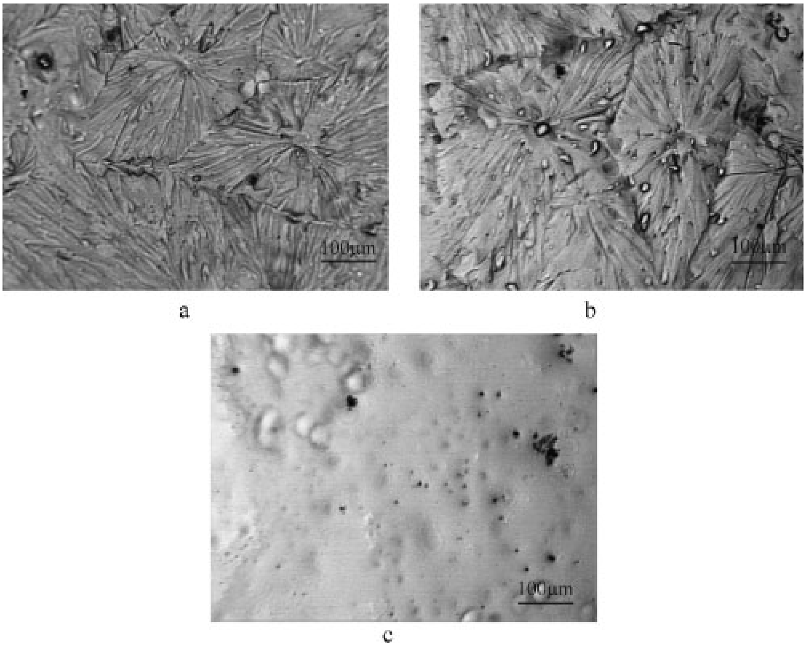


***Figure 5.***
Optical microscopy of poly(GME) morphology ($\overline{M}_n = 10\,900$ g/mol) observed at increasing temperature (×10) a) : room temperature; b) : 60 °C ; c) : 95 °C.

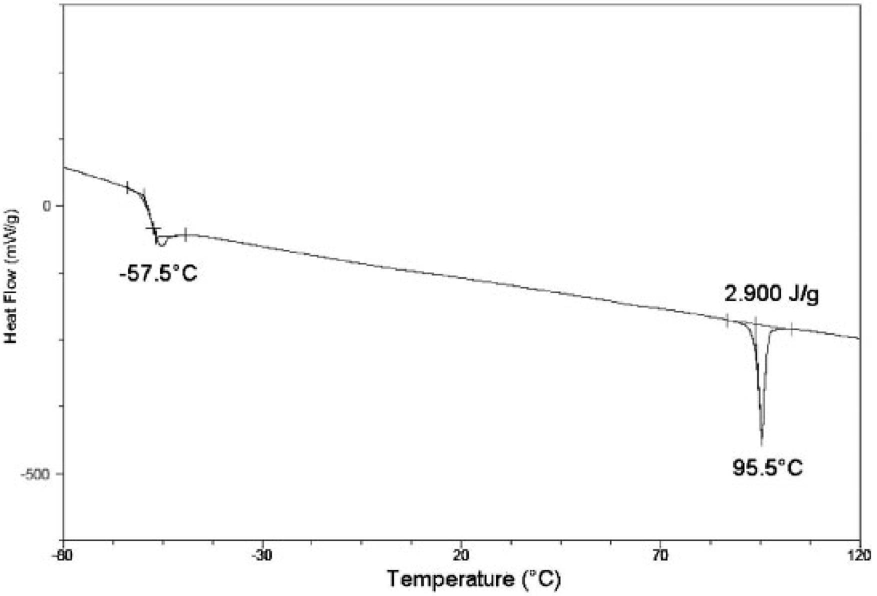


***Figure 6.***
DSC analysis of polyGME particules (8 400 g/mol), 3$^{rd}$ run : from −100 °C to +130 °C at 10 °C/min.

Further analysis of these spherulites at increasing temperatures indicates their melting from about 60 °C, Figure 5b, to 95 °C, Figure 5c. Decreasing the temperature results in their reformation between 80 and 70 °C.

These results were confirmed by DSC analysis of low molar mass (<10 000 g/mol) poly(GME) samples. As shown Figure 6 for the 8 400 g/mol PGME sample, the observed melting point at 95.5 °C and glass transition at -57.5 °C indicate the formation of semi crystalline polymers. This is also the case for PGME of 3000 g/mol. The crystalline properties of poly(GME) are quite surprising since the activated polymerization of other epoxides, i.e. propylene oxide, was found to yield amorphous atactic polypropylene oxide.

## Conclusions

It has been shown in this paper that the system $i\text{-Bu}_3\text{Al/NOct}_4\text{Br}$, in presence of a slight excess of trialkylaluminium, yields in mild reaction conditions, a fast and controlled polymerization of glycidyl methyl ether, and allows the preparation of poly (GME) of high molar masses, up to 100 000 g/mol, with narrow dispersity (<1.2).

We have shown that poly(GME) shows critical solubility temperature with a Tc which depends to some extent on polymer molar mass. Moreover, during this study and quite surprisingly, the poly(GME) of lower molar mass were found to crystallize in water. This specific behaviour is not yet fully understood and further works are in progress to determine the microstructure of the poly(GME) chains formed during the activated polymerization of GME initiated by the onium salt/$\text{AlR}_3$ systems.

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