

## Controlled polymerization of glycidyl methyl ether initiated by onium salt/triisobutylaluminum and investigation of polymer LCST.

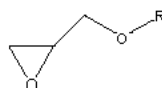
Amélie Labbé<sup>1</sup>, Stéphane Carlotti<sup>1</sup>, Alain Deffieux<sup>1</sup>, Akira Hirao<sup>2</sup>, Takashi Ishizone<sup>2</sup>

Laboratoire de Chimie des Polymères Organiques, Université Bordeaux-1, ENSCPB-CNRS, 16 Av. Pey Berland, 33607 Pessac, France- deffieux@enscpb.fr

Polymeric and Organic Materials department, graduate School of Science and engineering, Tokyo Institute of Technology, 2-12-1, H-127, Ohokayama, Meguro-Ku, Tokyo 152-8552, Japan

### 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), thus allowing the preparation of polymers with hydrophilic to hydrophobic chains, tunable LCST, etc.



Various types of initiating species have been used to polymerize glycidyl ethers but their polymerization was subjected to important side reactions. Latent initiators such as sulfonium<sup>1</sup>, pyridinium<sup>2</sup> and phosphonium<sup>3,4</sup> salts were used for glycidyl ethers polymerization at high temperature. Non-ionic species such as hydroxylamides<sup>5</sup>, aminimides<sup>6</sup>, esterified phosphonic acids<sup>7</sup> or amides<sup>8</sup> were also used as initiators. All these systems yield only low molar masses oligomers (5000 g/mol).

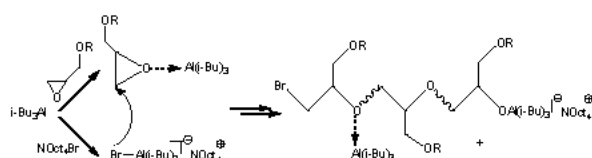
Nucleophilic species such as potassium or sodium hydroxides or alkoxides<sup>9</sup> are also commonly used although they show limitations in the control of the polymerization and only allow the formation of oligomers due to transfer reactions<sup>10,11,12</sup> to monomer and solvent.

We have found recently that the association of trialkylaluminum to alkali metal alkoxides or ammonium salts allows the controlled high speed anionic polymerization of propylene oxide and ethylene oxide<sup>13</sup>. This presentation deals with the use of these initiating systems for the polymerization of glycidyl methyl ether (GME) and a study of the LCST properties of the polymers as a function of their molar masses.

### Results and discussion

To be active the initiating system *i*-Bu<sub>3</sub>Al/NOct<sub>4</sub>Br requires to work with a slight excess of aluminic compound with respect to the ammonium salt. In these polymerization conditions, at -30°C in toluene, methyl glycidyl ether polymerization proceeds up to completion although a lowering of the polymerization rate is observed at high monomer conversion. Polymerization can be explained by the monomer activated mechanism in which each monomer molecule is activated by *i*-Bu<sub>3</sub>Al before the nucleophilic attack of the 1:1 [*i*-Bu<sub>3</sub>Al][NOct<sub>4</sub>Br] "ate" complex (Scheme 1). Beside reduction of polymerization rate is attributed to competitive complexation of *i*-Bu<sub>3</sub>Al by the polyether chain.

Experimental molar masses of the poly(methyl glycidyl ether)s are in agreement with theoretical molar masses assuming the formation of one chain per ammonium salt and molar mass distributions are narrow (Table 1). Indeed, MALDI-TOF analysis of poly(glycidyl ether) samples allow to confirm an initiation mechanism involving the bromide anion.



**Scheme 1** - Reaction mechanism involving monomer activation and trapping of *i*-Bu<sub>3</sub>Al by growing chain.

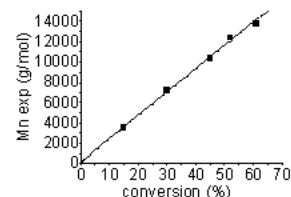
The evolution of polymer molar masses versus conversion during a polymerization experiment performed at 0°C is shown in Figure 1. As may be seen the number-average molar masses increases

linearly with increasing conversion in good agreement with a living-type polymerization.

**Table 1** - Glycidyl methyl ether (GME) polymerization initiated by NOct<sub>4</sub>Br (I) in the presence of *i*-Bu<sub>3</sub>Al, in toluene. Conversion; 100%

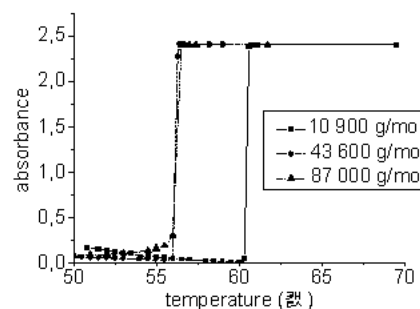
[GME] (mol/l)	[Al]/[I]	T <sup>a)</sup> (°C)	time	$\overline{M}_n$ th. (g/mol)	$\overline{M}_n$ exp. (g/mol)	PDI
3	1.3	-30	5h20	3 000	3 100	1.16
	1.5	-30	15h	10 000	10 900	1.06
3	2.6	-30	4h50	30 000	28 700	1.07
3	4.3	-30	7h	47 500	43 600	1.10
3	7	-30	7h30	93 000	87 100	1.16

a) Initiation temperature followed by slow raise up to 20°C



**Figure 1** -  $\overline{M}_n$  exp versus conversion plots for GME polymerization initiated by NOct<sub>4</sub>Br, activated by *i*-Bu<sub>3</sub>Al (1.5 eq), [GME]/[I] = 335, [GME] = 3 mol/l, 0°C in toluene

Preliminary studies of polyGME in aqueous solution allowed us to confirm the LCST characteristics of the polymer and to show the dependence of the critical solubility temperature T<sub>c</sub> on the polymer molar mass (Figure 2). T<sub>c</sub> varies from 60,5°C for  $\overline{M}_n$  = 10 000 g/mol to 56,5°C for  $\overline{M}_n$  = 43 600 and 87 000 g/mol. Surprisingly chains with  $\overline{M}_n$  = 3000 g/mol are not soluble over the whole range of temperature examined. Further work is in progress in this area to understand these findings.



**Figure 2** - LCST dependence on polymer molar mass for 1%wt aqueous polyGME solutions

### References

- O. Shimomura, I. Tomita, T. Endo, *J. of Polym. Sci. Part A: Polym. Chem.*, 2000, 38, 18
- S-B. Lee, T. Takata, T. Endo, *Macromolecules*, 1991, 24, 2689
- K. Takuma, T. Takata, T. Endo, *Macromolecules*, 1993, 26, 862
- T. Toneri, F. Sanda, T. Endo, *J. Polym. Sci. Polym. Chem.*, 1998, 36, 1957
- F. Sanda, T. Kaizuka, A. Sudo, T. Endo, *Macromolecules*, 2003, 36, 967
- S-D. Lee, F. Sanda, T. Endo, *J. Polym. Sci. Polym. Chem.*, 1997, 35, 689
- M. Kim, F. Sanda, T. Endo, *Macromolecules*, 1999, 32, 8291
- M. Kim, F. Sanda, T. Endo, *Macromolecules*, 2000, 33, 3499
- S. Boileau, in *Comprehensive polymer science, chain polymerization*, 1989; Vol 3, part I, 467
- P. Banks, R.H. Peters, *J. Polym. Sci. Part A. 1.*, 1970, 8, 2595
- A. Stolarzewicz, *Makromol. Chem.*, 1986, 187, 745
- A. Stolarzewicz, Z. Grobelny, *Makromol. Chem.*, 1992, 193, 531
- Results to publish