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COMMUNICATION

Zwitterionic Polymerization of Glycidyl Monomers to Cyclic Polyethers with $B(C_6F_5)_3$

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A new method of generating cyclic polyethers is reported. Glycidyl monomers react with $B(C_6F_5)_3$ to generate cyclic polyethers in anhydrous conditions. In the presence of water, linear chains are formed. A zwitterionic ring-opening polymerization mechanism is postulated based on experimental evidence and DFT calculations. The obtained cyclic polyethers can be considered a new family of crown ethers, where peripheral functional groups such as phenyls, fluorinated aliphatic chains or hydroxyls decorate the rings.

Cyclic polymers possess unique physico-chemical properties compared to their linear counterparts as a result of the absence of end-groups and the equivalence of all monomer units. These differences may be expressed in their hydrodynamic, rheological, optical and thermal properties.¹ In particular, cyclic polyethers have been recognized by their complexation with metal ions in a similar way to crown ethers.² An important area where these cyclic topologies have been gaining much interest is in supramolecular chemistry, where crown ether-based structures form complex architectures driven by noncovalent host-guest interactions.³

Cyclic polyethers have been mainly produced by cyclization of linear polyethers in dilute conditions. Synthetic approaches such as the reaction of poly(ethylene glycol) with either tosyl chloride or dichloromethane under alkaline conditions have been employed.⁴ The latter attains the ring closure via an acetal linkage, a method also used to produce cyclic poly(oxypropylene)⁵ as well as cyclic block copolyethers.⁶ One disadvantage of this ring-closure technique is the entropic penalty associated to coupling the chain ends, leading to cyclization yields of as little as 8%.⁷

Zwitterionic ring-opening polymerization (ZROP) has emerged in recent years as a strategy to generate cyclic polymers of high molecular weight.⁸ Important contributions to this area have been made in the ZROP of lactones with nucleophilic catalysts such as N-heterocyclic carbenes,^{9, 10} DBU¹¹ and imidazoles.¹² In these reactions, the nucleophiles are added to strained heterocyclic monomers generating macrozwitterions: polymer chains with a

positively and negatively charged group. Cyclization of the macrozwitterions occurs in appropriate conditions leading to the formation of cyclic polymers.

By analogy with nucleophilic catalysts, it is expected that catalysts with electrophilic character will also be able to promote ZROP. Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$), a Lewis acid of comparable acidity to BF_3 ,¹³ has been demonstrated to react with electron-rich species by forming stable Lewis acid-base adducts¹⁴ and catalyzing both organic¹⁵⁻¹⁷ and polymerization reactions.¹⁸⁻²² However, the catalytic activity of $B(C_6F_5)_3$ in the ZROP has not been proved yet despite its ability to form zwitterionic species by means of the ring-opening reaction of monomers such as THF,²³ dioxane, thioxane,²⁴ and lactones.²⁵ In these cases, a sterically hindered Lewis donor was also required to be present in the reaction in order to form what is called "frustrated Lewis pairs".²⁶ Attempts to ring-opening polymerization combining Al- and B-based Lewis acids and organic bases have been reported but with limited success.²⁷ Recently, well-defined high molecular weight cyclic polyesters have been synthesized using dual systems combining $Zn(C_6F_5)_2$ with an organic base (an amine or a phosphine) that promote the controlled ring-opening polymerization of lactide and ϵ -caprolactone.^{28, 29}

In this communication, we report that $B(C_6F_5)_3$ alone is able to catalyze the ring-opening polymerization of glycidyl monomers leading to the formation of cyclic polyethers, as determined by MALDI-TOF MS. We hypothesize that a ZROP mechanism is involved based on the formation of zwitterionic intermediates. The experimental work is complemented by a DFT study of the optimized structures of intermediates. The effects of solvent, water and monomer/catalyst ratio on the ZROP of glycidyl phenyl ether (GPE) to cyclic poly(GPE) are investigated in detail. Furthermore, ZROP of other glycidyl monomers, such as glycidol and glycidyl octafluoropentyl ether, to cyclic polyethers with $B(C_6F_5)_3$ is explored.

First, we investigated the ZROP of GPE with $B(C_6F_5)_3$ as a catalyst carried out in solution at a monomer/catalyst ratio of 10/1 (sample S1, Table 1). Fig. 1 revealed signals for Na-

complexed cyclic poly(GPE) separated by 150 mass units, where the peak at 773 m/z (corresponding to 5 GPE units) is the most intense of the spectrum. In agreement with these data, SEC of S1 showed a peak centered at 720 g/mol with the presence of a small shoulder at the high molecular weight (HMW) side (Fig. 2).

Table 1. Bulk (B) and solution (S) ring-opening polymerization of GPE with $B(C_6F_5)_3$ at room temperature.

Sample	$[GPE]_0/[B(C_6F_5)_3]_0^a$	Cond. ^b	<i>t</i> h	Yield wt% ^c	<i>M_p</i> g/mol ^d	PDI ^e
S1	10/1	CH ₂ Cl ₂	1	47	720	1.5
S2	943/1	CH ₂ Cl ₂	3	70	3100 ^f	1.9
S3	943/1	CH ₂ Cl ₂ /H ₂ O	24	5	960	1.6
B	943/1	Bulk	16	62	12000	1.9

^aMonomer to catalyst ratio. ^bReaction conditions. ^cYield of reaction, determined gravimetrically. ^dPeak molecular weight, determined by SEC with conventional PS calibration. ^ePDI = *M_w*/*M_n* determined by SEC. ^fHMW peak.

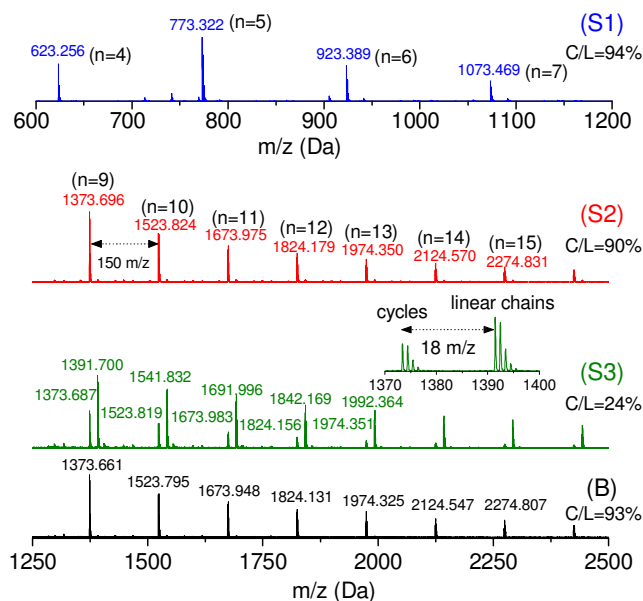


Fig. 1 MALDI-TOF spectra of samples reported in Table 1. C/L is the percentage ratio of cycles to linear chains.

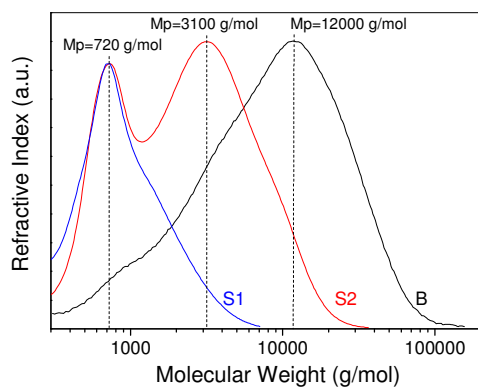


Fig. 2 SEC traces of samples S1, S2 and B in THF. The molecular weight at peak maximum (*M_p*) is indicated.

Next, to increase the molecular weight of cyclic poly(GPE), the monomer/catalyst ratio was adjusted to 943/1 (sample S2, Table 1). As a result, a bimodal molecular weight distribution was registered in the SEC experiment. The low molecular weight (LMW) peak appeared at 720 g/mol, at the same position where cycles of 5 GPE members were observed in sample S1, and the HMW peak emerged at 3100 g/mol. MALDI-TOF spectrum of S2 (Fig. 1) revealed ions corresponding to cyclic poly(GPE) in the whole molecular weight range. Assignment of ¹H NMR signals for S1 and S2 samples is shown in Fig. S1 of electronic supplementary information (ESI). The spectral differences found in both samples, especially in the region of aliphatic protons, can be attributed to the differences in the chain conformation imposed by the ring size.

To explore whether water affects the formation of cyclic structures or not, sample S3 was prepared in similar conditions to that for obtaining S2 but with the addition of 0.1 mL of water. MALDI-TOF spectrum of S3 (Fig. 1) revealed signals for Na-complexed cyclic poly(GPE) separated by 150 mass units along with considerable amounts of Na-complexed linear poly(GPE) terminated with OH groups. The latter signals are separated by 18 m/z from those corresponding to the cyclic chains. Kinetics experiments, in which the monomer conversion was monitored as a function of time by means of ¹H NMR measurements (Fig. S2 of ESI), revealed that the presence of water causes a significant reduction of the monomer conversion to about 5 % in stark contrast to 98% found in the dry solvent. These experiments demonstrate that the addition of water to the reaction was neither necessary nor useful to initiate the ring-opening polymerization unlike in the cationic vinyl polymerization initiated by Lewis acids.³⁰ Therefore, a direct reaction between GPE and $B(C_6F_5)_3$ must occur by forming a zwitterionic GPE-borane intermediate (zwitterion Z1, Fig. 3). This intermediate propagates upon nucleophilic attack of other GPE molecules forming the macrozwitterions Zn. Cyclization occurs by the nucleophilic attack of the oxygen next to borane on the electron-deficient α -carbon of the oxonium ion and the subsequent regeneration of the initiator. In the presence of water, the water molecules compete with GPE for the α -carbon next to the oxonium ions leading to the formation of linear chains terminated in OH and the release of $B(C_6F_5)_3$. The borane released would either react with water to form mono-, di- and trihydrate species¹⁴ or initiate new polymer chains. By changing solvent polarity from polar dichloromethane (dielectric constant, $\epsilon=8.93$) to relatively nonpolar benzene ($\epsilon=2.28$) we did not observe important effects on the molecular weight, although the reaction yield decreased noticeably in solvents with lower ϵ (Table S1). Additionally, the molecular weight distribution was bimodal in all cases (Fig. S3 of ESI). When solvents were cyclic ethers such as 1,4-dioxane or THF, we observed the formation of copolymers of GPE with these molecules. However, homopolymerization of 1,4-dioxane or THF does not proceed in the absence of GPE, indicating that these solvent molecules are reactive towards the zwitterionic $(GPE)_n-B(C_6F_5)_3$ species. In the case of using electron-donor solvents such as DMF, DMSO or acetonitrile, polymerization of GPE did not occur.

The molecular weights of the poly(GPE) obtained with a low monomer to catalyst ratio (i.e. 10/1, sample S1), correlate well to the $[GPE]_0/[B(C_6F_5)_3]_0$ values, implying that one cyclic chain per initiator is formed. However, when the monomer to catalyst ratio is relatively high (i.e. 943/1, sample S2) this correlation is no longer achieved. In this case the chains do not grow sufficiently and only cycles of 5 and 20 GPE members are formed. Although transfer reactions are likely to occur affecting the growing chain, the release of $B(C_6F_5)_3$ during cyclization and reinitiation (Fig. 3) will certainly favor the formation of cycles with a lower degree of polymerization, X_n , than that described by the equation $X_n = p[GPE]_0/[B(C_6F_5)_3]_0$, where *p* is the fractional conversion of the monomer. If both

processes, the release of $B(C_6F_5)_3$ and reinitiation, are favored by the diffusion of the liberated catalyst, it is then expected that cyclization in absence of solvent leads to longer cyclic chains. In fact, SEC data of sample B (Fig. 2), which was synthesized in bulk conditions by using a monomer to catalyst ratio of 943/1 (Table 1), revealed the formation of poly(GPE) of higher molecular weight than that obtained in its counterpart S2 sample. MALDI-TOF spectrum of B in Fig. 1 (see also Fig. S4 in ESI) revealed ions corresponding to cyclic poly(GPE), confirming the formation of high molecular weight cycles in bulk conditions. Surprisingly, rings of 5 GPE members are also detected by SEC and MALDI-TOF MS in the B sample. These results and the fact that the rings of 5 GPE units were also found from the very beginning of the polymerization reaction along with larger cycles in all the solvents studied suggest that cyclic poly(GPE) of 5 GPE units is the most thermodynamically stable ring.

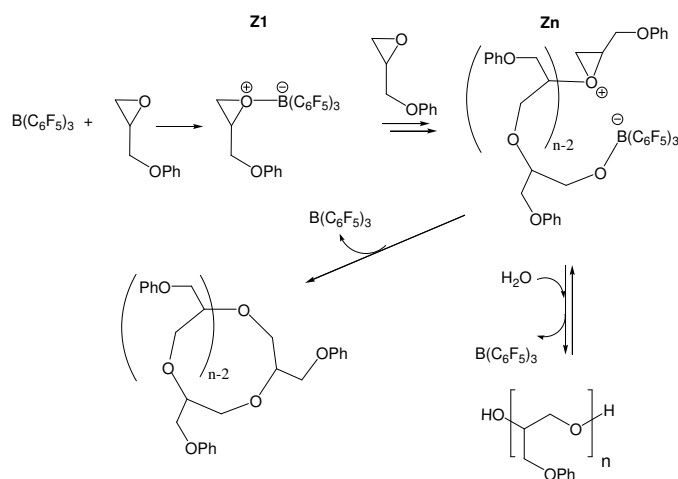


Fig. 3 Proposed mechanism for the zwitterionic ring-opening polymerization (ZROP) of GPE with $B(C_6F_5)_3$.

If we assume, as an approximation, that the ionization probabilities for both linear and cyclic chains are similar in the MALDI-TOF experiments, the percentage ratio of cycles to linear chains (C/L) can be calculated from the intensities of the corresponding signals in the spectra. The C/L data (see Fig. 1) revealed that in anhydrous conditions >90% of cyclic poly(GPE) chains are formed and that in the presence of water, this amount decreases to 24%. Also, the longer the chains are, the greater the increase in the fraction of linear chains (see Fig. S4 of ESI). We surmise that the presence of linear chains in the polyethers synthesized in anhydrous conditions stem from transfer reactions. As the molecular weight increases, the reaction between the zwitterionic chain ends belonging to the same chain becomes less probable. Therefore, these reactive species stay for a longer time in the reaction increasing the probability of abstracting protons from the surrounding medium. Another possibility is that the life of macrozwitterions is sufficiently long that they are still present during purification and react with water molecules contained in the solvents used for precipitation. However, it can be verified that this is not the case by deliberately adding water at the end of the reaction when all the monomer has been consumed. We checked that addition of water upon the reaction completion gave similar results to those obtained when adding dry methanol or dry acetonitrile at the end of the reaction.

DFT calculations were performed to support the proposed ZROP mechanism. Optimized structures were calculated using Gaussian 09³¹ at the B3LYP level of theory in CPCM solvent model ($CHCl_3$).

Relative energies were calculated using single-point M06³²/6-311G+(d,p) level of theory (see ESI for computational details). DFT calculations reveal the formation of the zwitterion Z1, for which a local minima was located at $\Delta H_{298.15} = -11.65$ kcal/mol (Fig. S5 of ESI). Subsequent addition of a GPE molecule leads to the formation of the zwitterion Z2 with $\Delta H_{298.15} = -16.14$ kcal/mol.

Cyclic poly(GPE) with $M_p = 3100$ g/mol (sample S2) exhibited an onset glass transition temperature at 7.6 °C, which is 4 °C higher than that of linear poly(GPE) of similar molecular weight (Fig. S6 of ESI). This result is consistent with theoretical predictions and experimental observations in a number of cyclic polymers.^{33, 34} The versatility of the synthesis approach reported here was corroborated by using other glycidyl monomers carrying a hydroxyl group (i.e. glycidol) and a fluorinated aliphatic chain (i.e. glycidyl octafluoropentyl ether). As a result, cyclic polyethers were obtained as determined by MALDI-TOF MS (Fig. S7).

In conclusion, ring-opening polymerization of GPE to give cyclic poly(GPE) occurs readily in the presence of the Lewis acid $B(C_6F_5)_3$ and the absence of water. In the presence of water, linear poly(GPE) chains terminated in OH groups are also formed. DFT calculations provide support for the formation of zwitterionic intermediates, and, therefore, for a ZROP mechanism. The versatility of the method is illustrated by the synthesis of cyclic polyethers carrying either a hydrophilic or a hydrophobic group, such as those obtained from glycidol or glycidyl octafluoropentyl ether, respectively. This new family of cyclic polyethers containing pendant functional groups promise to be useful in supramolecular chemistry.

Notes and references

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- Electronic Supplementary Information (ESI) available: Experimental details, computation and supporting figures. See DOI: 10.1039/c000000x/

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