

# Ring-opening polymerization of decamethylcyclopentasiloxane initiated by a superbases: Kinetics and rheology

Guillaume Pibre<sup>a,b,c</sup>, Philippe Chaumont<sup>a,b,c</sup>, Etienne Fleury<sup>d</sup>, Philippe Cassagnau<sup>a,b,c,\*</sup>

<sup>a</sup> Université de Lyon, Lyon F-69003, France

<sup>b</sup> Université de Lyon 1, Lyon F-69003, France

<sup>c</sup> CNRS UMR5223, Ingénierie des Matériaux Polymères: Laboratoire des Matériaux Polymères et Biomatériaux, 17 Bvd Latarjet, F-69622 Villeurbanne, France

<sup>d</sup> Ingénierie des Matériaux Polymères: Laboratoire des Matériaux Macromoléculaires (IMP/LMM), UMR-CNRS 5223, INSA-Lyon, 17 Avenue Jean Capelle, 69621 Villeurbanne cedex, France

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## Abstract

The use of phosphazene bases in combination with water was proved to be efficient in order to obtain polysiloxane polymers from cyclic monomers. Only a few minutes are necessary to obtain polymer chains with a monomer concentration of 5% at the equilibrium. For that purpose the space which is between a rheometer's plates is the most convenient device to monitor this reaction concerning a chemical and viscoelastic point of view. Therefore, here is proposed a chemo-rheology study that leads in the same time to the chemical kinetics equations and to the variation of the viscoelastic functions during the polymerization. In this way different catalysts are used and their efficiencies are compared as a function of their "basicity tank". Whatever the experimental conditions involved are, viscosity versus polymer concentration or conversion shows a master curve for catalysts suitable to be used under extrusive conditions. Thus, only a few experiments are needed in order to develop a model which can be used to foresee the variation of the viscosity during the reaction.

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## 1. Introduction

Polyorganosiloxanes are among the most interesting polymer classes, as they show both organic and inorganic behaviours [1]. Several processes are allowing the synthesis of linear polysiloxanes, like the ring-opening polymerization of cyclic monomers through siloxane bond dissociation. Such a route seems to be the most useful to obtain high molecular weight polymers. Because of the thermodynamical equality of siloxane bonds located in monomers, as well as in formed polymers, this kind of synthesis is essentially an entropy-driven process. Anionic ring-opening polymerization of low molecular

weight cyclosiloxanes is a well-known reaction that can be carried out in presence of a wide variety of strong bases, such as hydroxides, alcoholates, silanolates of alkali metals, tetraalkylammonium and tetraalkylphosphonium [2]. Those techniques are well known, but among their major drawbacks is the frequent low compatibility of the catalyst in the bulk monomer at low temperatures and also the abundant catalyst residue.

Twenty years ago, Schwesinger and Schlemper [3,4] described very strong, sterically hindered and non-charged bases generated by nitrogen atoms doubly bonded to a pentavalent phosphorous. In such compounds, named phosphazene bases, the basicity is increased with the oligomerization of the peralkylated triaminoiminophosphorane. Since 1987, many routes allowing to prepare different phosphazene bases [5] and their high basic activity [6,7] have been discussed. Ten years ago, Molenberg and Möller [8] used for the first time a tetrameric phosphazene base in association with methanol in order to initiate the anionic ring-opening polymerization (AROP) of

\* Corresponding author. CNRS UMR5223, Ingénierie des Matériaux Polymères: Laboratoire des Matériaux Polymères et Biomatériaux, 17 Bvd Latarjet, F-69622 Villeurbanne, France. Tel.: +33 4 72446208; fax: +33 4 72431249.

E-mail address: [philippe.cassagnau@univ-lyon1.fr](mailto:philippe.cassagnau@univ-lyon1.fr) (P. Cassagnau).

octamethylcyclotetrasiloxane (D4, where D symbolizes a dimethylsiloxane bond). As it had been previously investigated, the rate of the AROP of cyclic siloxanes increases with the size of the counter-ion ( $\text{Et}_4\text{P}^+ \approx \text{Et}_4\text{N}^+ \approx \text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ ) [2,9]. Thus, the very large soft counter-ion formed by deprotonation of methanol by the phosphazene superbase involves a fast AROP of cyclosiloxanes. Furthermore, this counter-ion shows a good solubility in non-polar solvents like bulk cyclosiloxanes. The phosphazene superbases are so efficient that they allow the AROP of cyclosiloxanes even at room temperature [8]. Recently, Dow Corning patented different ways to prepare high molecular weight polydimethylsiloxane (PDMS) and functionalized PDMS in an industrial scale, using phosphazene base/water [10–13] or an ionic form of a phosphazene base [14–18] as an initiator for AROP of cyclosiloxane. These processes have been reviewed by Hupfield and Taylor [19] who showed that water and silanols contained in the monomers can act as activators, producing in situ the hydroxide or the corresponding silanolate. Recently Grzelka et al. [20] showed that the polymerization of D4 initiated with hexapyrrolidinediphosphazanium hydroxide in toluene proceeds to a well-known equilibrium monomer concentration with first order kinetics and an external first order in initiator concentration. Moreover, functionalized monomers like tetraphenyltetramethylcyclotetrasiloxane were also used by Van Dyke and Clarson [21], and 2,2,4,4,6,6-hexamethyl-8,8-divinylcyclotetrasiloxane [22] and 2,2,4,4,6,6-hexamethyl-8,8-diphenylcyclotetrasiloxane [23] by Teng et al. Concerning the polymerization of D4, the authors report such a fast reaction that its monitoring is hardly possible in bulk system even at low temperature.

However, such bulk systems may be monitored thanks to the measurement of the viscosity of reactive media because the flow behaviour is strongly coupled up with both the increase of molecular weight and the concentration of formed polymer. Since rheology is sensitive to small variation of molecular weight, it can be used for monitoring the polymerization kinetics [24]. Thus, such methods have been used in order to monitor rheo-chemistry or rheo-kinetics of polymerization of linear polymeric species, as in the case of both urethane and  $\epsilon$ -caprolactone. The first review concerning the understanding of the viscosity variation during polymerization processes is attributed to Cioffi et al. [25]. Empirical developments discussed in this review showed that viscosity increase and kinetic constants could be predicted from rheo-kinetic experiments. Recently, Cassagnau et al. [26] described the setting up of a model able to predict the evolution of the viscoelastic behaviour during the reactive processing of  $\epsilon$ -caprolactone initiated by titanium *n*-propoxide, in bulk, at any time, under any processing conditions of temperature, initiator concentration and shear rate. From the point of view of rheo-chemical modeling, the most frequently described linear polymerization is the case of urethane performed by polyaddition reaction between diisocyanate and diols [27–30]. The authors assumed that the number average molecular weight increases linearly with the reaction time. In this kind of polymerization the monomer disappears at the very beginning of the reaction. This behaviour is quite different in the case of ring-opening polymerizations

where monomers remain in the bulk until the end of the reaction [31].

As discussed in the previous section, the use of a rheometer as a chemical reactor enables the monitoring of the chemical reaction and the measuring of the viscoelastic behaviour of the mixture while the polymerization occurs. Then, with experiments of that kind, the first goal of this work is to compare the efficiency of different phosphazene bases in respect with both the number of  $\text{PN}_3$  “basicity battery cells” and the alkyl chain contained in the chemical structure. Then chemical kinetics will be deduced in extrusive reaction conditions. The second goal of this study is to build a predictive law of the viscoelastic behaviour of polydimethylsiloxane during the AROP of decamethylcyclopentasiloxane (D5) initiated by phosphazene bases in bulk.

## 2. Experimental section

Decamethylcyclopentasiloxane has been used as received, and purity has been checked by gas chromatography. Water content in the monomer (250 ppm) has been quantified by the Karl Fisher titration method. HPLC grade toluene, phosphoric acid, pentadecane (Acros), trimethylchlorosilane (ABCR) have been used as received. Five different phosphazene bases *N'*-*tert*-butyl-*N,N,N',N'',N'''*-hexamethylphosphorimidic triamide ( $\text{P}_1^t\text{Bu}$ ), *N'*-*tert*-octyl-*N,N,N',N'',N'''*-hexamethylphosphorimidic triamide ( $\text{P}_1^t\text{Oct}$ ), 1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)- $2\Lambda^5,4\Lambda^5$ -catenadi(phosphazene) ( $\text{P}_2^t\text{Bu}$ ), 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]- $2\Lambda^5,4\Lambda^5$ -catenadi(phosphazene) ( $\text{P}_4^t\text{Bu}$ ) and 1-*tert*-octyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]- $2\Lambda^5,4\Lambda^5$ -catenadi(phosphazene) ( $\text{P}_4^t\text{Oct}$ ), pure or in their solvents have been supplied by Fluka (chemical structures of those bases are shown in Fig. 1). Appropriate dilutions have been performed with extra-dry *n*-heptane under argon before use.

Polymerizations were performed in a rheometer (AR2000 TA Instruments) within a temperature domain from 90 °C to 130 °C. Correct amount of catalyst precursor was added with a micropipette into a syringe containing 2 g of D5 and 50  $\mu\text{L}$  of pentadecane (used as internal standard) which had been previously degassed under argon for 1 h, in order to remove any carbon dioxide dissolved into the cyclic monomers. Then the reaction mixture was instantaneously shaken, and quickly introduced with a needle into the 1 mm gap set between the pre-heated parallel plate geometry of the rheometer (40 mm diameter). Thus, the exchange surface between the polymerization medium and the area is small in comparison with the volume, limiting the loss of D5 by evaporation. Variation of the storage and loss moduli during the polymerization step have been monitored by time sweep oscillatory experiments under a shear stress of 8 Pa and an angular frequency  $\omega = 10 \text{ rad s}^{-1}$ . The chemical kinetics were performed similarly, using the parallel plate of the rheometer as chemical reactor, in order to have the same experimental conditions of polymerization. For that purpose, samples have been collected during the reaction from the mixture with a needle and they have been immediately

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