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

Guillaume Pibre [a,b,c], Philippe Chaumont [a,b,c], Etienne Fleury [d], Philippe Cassagnau [a,b,c,*]

[a] *Université de Lyon, Lyon F-69003, France*
[b] *Université de Lyon 1, Lyon F-69003, France*
[c] *CNRS UMR5223, Ingénierie des Matériaux Polymères: Laboratoire des Matériaux Polymères et Biomatériaux, 17 Bvd Latarjet, F-69622 Villeurbanne, France*
[d] *Ingénierie des Matériaux Polymères: Laboratoire des Matériaux Macromoléculaires (IMP/LMM), UMR-CNRS 5223, INSA-Lyon,*
17 Avenue Jean Capelle, 69621 Villeurbanne cedex, France

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, tetra-alkylammonium 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

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octamethylcyclotetrasiloxane (D4, were 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 $(Et_4P^+ \approx Et_4N^+ \approx Cs^+ > Rb^+ > K^+ > Na^+ > Li^+)$ [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 hexapyrrolidinediphosphazenium 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 ε-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 ε-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 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'',N''-hexamethylphosphorimidic triamide ($P_1{}^t$Bu), N'-*tert*-octyl-N,N,N',N',N'',N''-hexamethyl-phosphorimidic triamide ($P_1{}^t$Oct), 1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-$2\Lambda^5,4\Lambda^5$-catenadi(phosphazene) ($P_2{}^t$Bu), 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-$2\Lambda^5,4\Lambda^5$-catenadi(phosphazene) ($P_4{}^t$Bu) and 1-*tert*-octyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]-$2\Lambda^5,4\Lambda^5$-catenadi(phosphazene) ($P_4{}^t$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 μL 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 preheated 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 $\omega = 10$ 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
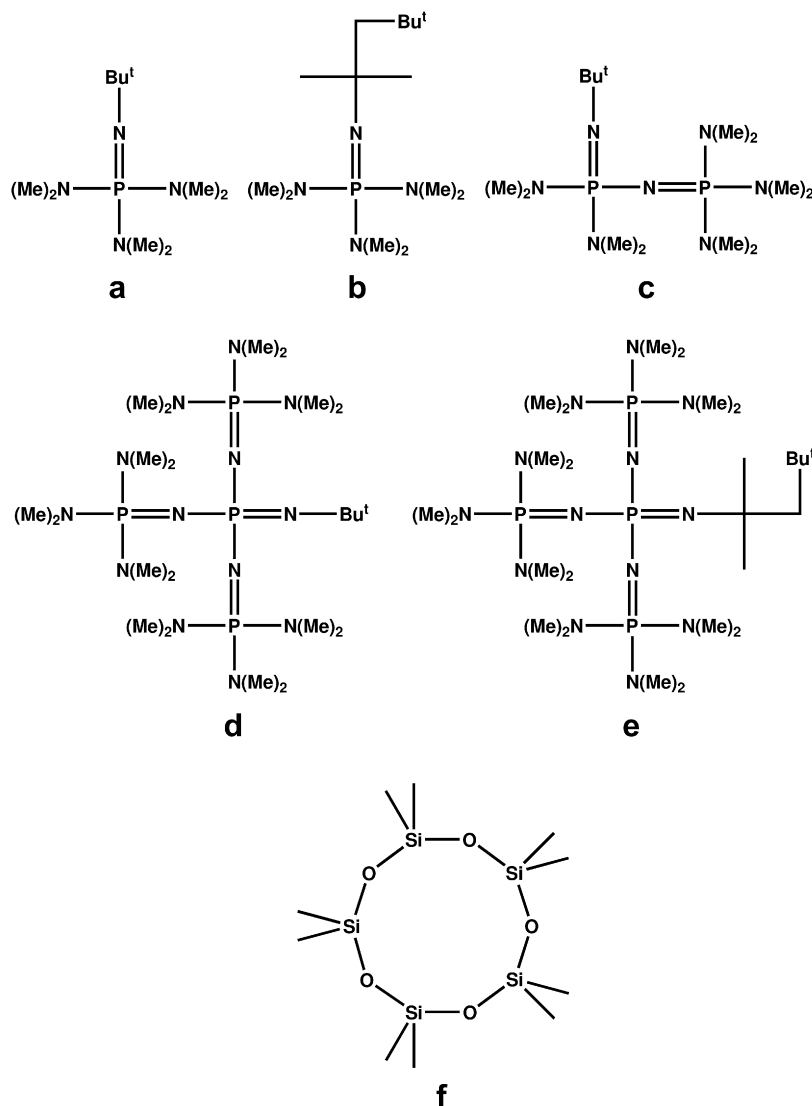
Fig. 1. Phosphazene bases and monomer used. a.: P_1^tBu; b.: P_1^tOct; c.: P_2^tBu; d.: P_4^tBu; e.: P_4^tOct, f.: decamethylcyclopentasiloxane (D5).

quenched into vials that contained an excess of chlorotrimethyl-silane and phosphoric acid diluted in toluene. The evolution of the monomer concentration has been followed by gas chroma-tography, using an Agilent 6890 Series GC system filled with an HP-5MS capillary column loaded with 95% poly(dimethyl-siloxane) and 5% poly(phenylmethylsiloxane); temperature programme: 50–310 °C with a 20 °C min^{-1} ramp, injection and flame ionization detection at 250 °C.

3. Results and discussion

3.1. Chemistry

Despite their high basicity and their solubility in apolar media, all the phosphazene bases implemented in the present study are not able to initiate the ring-opening polymerization of D5 with the same efficiency. In fact, even with high concen-tration (0.02 mol L^{-1}), the use of monomeric phosphazene bases P_1^tBu and P_1^tOct (MeCN pK_{BH^+}: 26.9 and 26.5, respec-tively) does not cause any increase of the viscosity of the reaction media. Furthermore, the dimeric phosphazene base used, P_2^tBu (MeCN pK_{BH^+}, 33.5), shows a very slow polymer-ization in catalytic conditions (2×10^{-3} mol L^{-1}). High vis-cous fluids are obtained only thanks to an overnight reaction that is not compatible with the kind of experiments performed in this study (i.e. short residence time of reaction media in the reactor). Only the two tetrameric phosphazene bases P_4^tBu and P_4^tOct (MeCN pK_{BH^+}: 41.9 and 42.7) are allowing a fast poly-merization process compatible with extrusive experimental conditions.

The phosphazene bases act like a catalyst in the polymeriza-tion of D5. Water trapped in the monomer is deprotonated by those catalysts and the formed hydroxyl initiates the AROP of D5. As previously discussed, such a fast reaction might be at-tributed to the large size of the counter-ion and the high level of dissociation of the ion pair, resulting from the formation of conjugated species of the base. Experiments performed at different temperatures with a constant amount of catalyst (1.75×10^{-4} mol L^{-1}) show that the kinetics of polymerization of D5 in bulk obeys a first order reaction in equilibrium

monomer concentration, so, the kinetic law can be expressed by Eq. (1) where [D5] and $[D5]_e$ are, respectively, the monomer concentration at the time t and when the equilibrium is reached and K_{app} is the reaction rate constant. The overall equilibrium concentration of the different cyclic species at the end of the reaction is 5% as shown in Fig. 2.

$$-\frac{d[D5]}{dt} = K_{app}\big([D5] - [D5]_e\big) \quad \text{with} \quad K_{app} = Ae^{-\frac{E_a}{RT}}[I_0] \qquad (1)$$

The same dependence is observed with the second tetrameric phosphazene base and the plot of $\ln(K_{app})$ versus $1/T$ shows (Fig. 3) that the ring-opening polymerization of D5 initiated by the two superbases follows the Arrhenius law. The calculated activation energy is $E_a = 110 \pm 2$ kJ mol^{-1} in both cases. Activation energies were measured for comparable AROP involving hexamethylcyclotrisiloxane and D4 [20]. Values are, respectively, 46 and 76 kJ mol^{-1}. Those results show that activation energy increases in a linear way with the number of siloxane units comprised in the cyclic species. Experiments performed at 100 °C with different amounts of P$_4^t$Bu allow checking the first external order in initiator concentration involved in this reaction, as presented in Fig. 4. This observation was already stressed out by Grzelka et al. [20] for the polymerization of D4 initiated by P$_2$Pyr$_6^+$OH$^-$. Chemical kinetics for the two initiator systems can be expressed by Eq. (1) with $A = 1.35 \times 10^{14}$ and $A = 8.23 \times 10^{12}$ s^{-1} when, respectively, P$_4^t$Bu or P$_4^t$Oct is used and where [I$_0$] stands for the initial catalyst concentration. Comparison of the value of the exponential front-factor obtained, thanks to Arrhenius law for the two tetrameric phosphazene bases in the same catalyst concentration and experimental conditions, shows that P$_4^t$Bu is more efficient than P$_4^t$Oct.

This difference can be intriguing compared to the basicity strength of the two compounds. The only difference between the two tetrameric phosphazene bases is the steric hindrance conferred by the different alkyl groups bonded to it. This means that the size of the counter-ion formed by the protonated species of P$_4^t$Oct is larger than the one with P$_4^t$Bu and then the

Fig. 3. Arrhenius plot for the polymerization of D5 in bulk (2.58 mol L^{-1}) initiated by P$_4^t$Bu -●- and P$_4^t$Oct -◇-, both in a concentration of 1.75×10^{-4} mol L^{-1}.

insertion of the monomer between the ion pair formed by the silanolate and its counter-ion may be more awkward with the first catalyst. The polymerization rate is then lower with this catalyst. Once this insertion complex is formed the monomer opening mechanism depends only on the silanolate and the monomer used like an intramolecular evolution of the system. That is why the temperature dependence of this reaction is the same with the two catalysts. This observation corroborates the study performed by Grzelka et al. [20]. This paper reveals the probable existence of a monomer insertion complex as an intermediate in the propagation step. The authors assumed that the interaction of the cyclic monomer with the propagating centers provokes the separation of ions by monomer as a loose ion pair.

3.2. Rheology

During the polymerization reaction the complex shear modulus ($G^*(\omega) = G'(\omega) + jG''(\omega)$) varies over about six decades within a few minutes as it can be seen in Fig. 5a. To perform an accurate monitoring of the viscoelastic functions during the polymerization process the time of measurement has to be lower than the characteristic evolution time of the system. This criterion was introduced for crosslinked systems by Winter and Mours [32] as the mutation number ($N_{mu} = t_{exp}\partial \ln(x)/\partial t$, $x = G'$, $x = G''$). In the present study, an angular
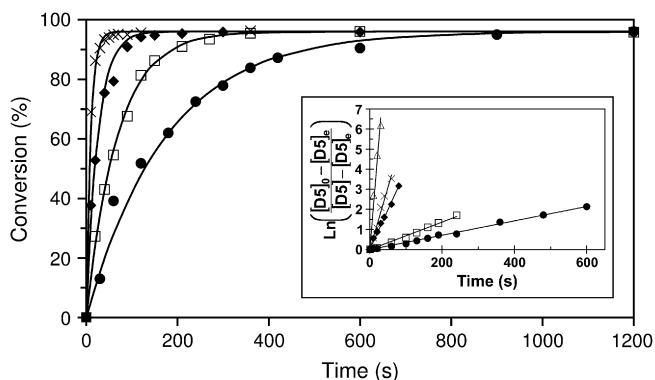

Fig. 2. Variation of the monomer conversion versus time for the polymerization of D5 in bulk initiated by P$_4^t$Bu for different temperatures. The initial concentrations in monomer and in initiator are 2.58 mol L^{-1}, 1.75×10^{-4} mol L^{-1}, respectively. In the bottom-right frame the dependence of the monomer conversion on time is plotted in the first order with the equilibrium monomer concentration. ●: 90 °C; □: 100 °C; ◆: 110 °C; ×: 120 °C; △: 130 °C.
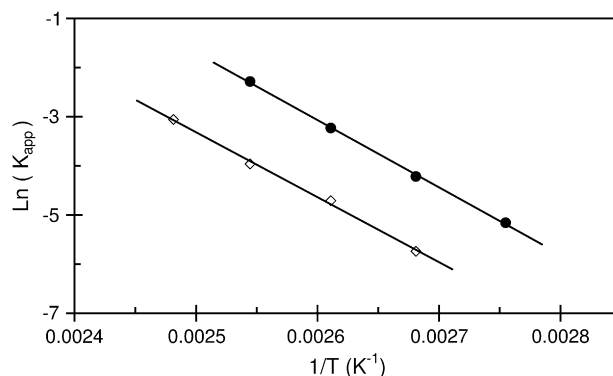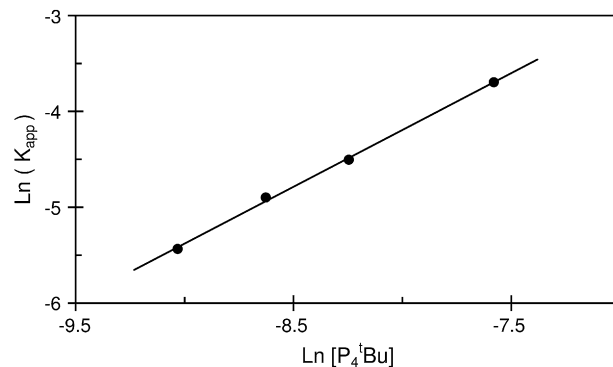

Fig. 4. Plot of K_{app} versus the initiator concentration in order to determine the external order of the initiator P$_4^t$Bu at $T = 100$ °C. Parameters of the linear regression are $\ln(K_{app}) = 1.1 \ln[P_4^tBu] + 5.3$.
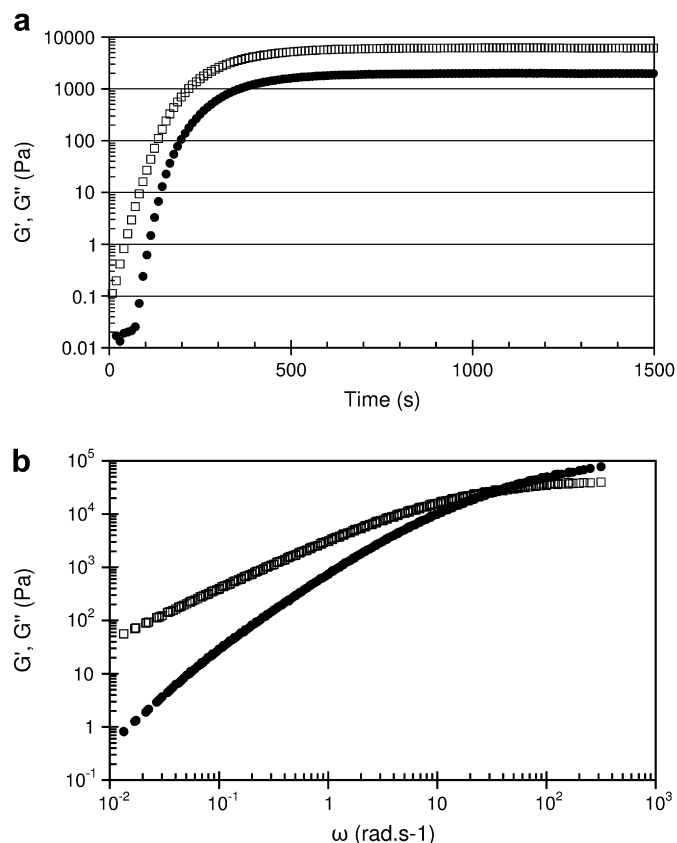
Fig. 5. In situ polymerization between the plates of the rheometer of D5 monomer by AROP reaction. (a) Typical variation of the storage ($\bullet$) and loss ($\square$) moduli versus reaction time. Catalyst: $P_4^t Bu$ (1.75×10^{-4} mol L^{-1}), $T = 90\,^\circ$C. (b) Master curve showing the variation of the storage ($\bullet$) and loss ($\square$) moduli versus the angular frequency of the polymer synthesized according to Fig. 5a. $T_0 = 90\,^\circ$C.
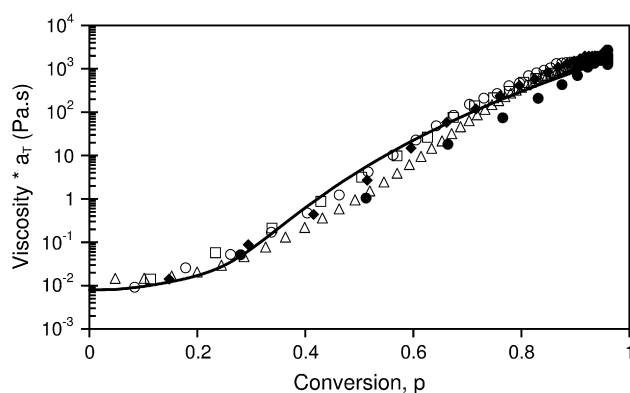

Fig. 6. Experimental master curve and model plotting the viscosity variation with the conversion in monomer for different temperatures and initiator systems. $P_4^t Bu$: $\triangle$: 90 °C, $\square$: 100 °C, $\bullet$: 110 °C and $P_4^t Oct$: $\bigcirc$: 110 °C, $\blacklozenge$: 120 °C.

frequency $\omega = 10$ rad.s^{-1} ($t_{exp} \approx 1$ s) was chosen to have a mutation number lower than 0.1 as recommended. At the end of the polymerization process frequency sweep experiments ($10^{-2} < \omega$ (rad.s^{-1}) $< 10^2$) were carried out in dynamic oscillatory mode at various temperatures ($80 < T$ (°C) < 110) in order to apply the time–temperature superposition principle (Fig. 5b). This type of curve allowed us to assess the main viscoelastic properties of PDMS samples once synthesized between the plates of the rheometer. Moreover, it can be assumed that the measurements are performed in a Newtonian domain until the end of the reaction. Consequently and for a convenient purpose, the modeling of the rheological kinetics was performed on the absolute complex shear modulus $|\eta^*(\omega)|$ which can be reduced to the zero shear viscosity.

By combining the chemical (Eq. (1)) and rheological kinetics (Fig. 5a) performed at different temperatures, a master curve plotting the viscosity versus monomer conversion (p) is generated as shown in Fig. 6. Actually, the viscosity was plotted at the reference temperature $T_0 = 90\,^\circ$C and a shift factor a_T ($a_T = e^{(E/R(1/T-1/T_0))}$) was calculated according to the flow activation energy of PDMS [33] ($E \approx 27$ kJ mol^{-1}).

From a chemical point of view, this result means that the polymerization process leads to comparable polymer chain length for the same monomer conversion because of the

same viscosity obtained. Actually, the behaviour of all the reactive media is identical whatever tetrameric phosphazene base is used, the only difference being obviously the polymerization rate as previously discussed.

In addition to the preceding chemical kinetic study, the monitoring of viscoelastic properties of reaction media during the polymerization allows the setting up of a model able to predict the variation of those properties with time at different temperatures. The main objective of the present study is to show how a simple predictive law on the zero shear viscosity variation during the bulk AROP can be built using rheological experiments in a few numbers.

In previous works on ε-caprolactone polymerization [26,31], we have developed a modeling strategy able to predict the variation of the rheological behaviour of reactive thermoplastic systems in the bulk at any reaction time and under any processing conditions of temperature, initiator concentration and shear rate. This modeling of the rheological kinetic law was based on modeling description of the viscoelastic properties of reaction media during the polymerization, i.e. the viscoelastic properties of a homogeneous solution of polymer in its monomer. The objective of the present work is to address a simple and efficient way of the modeling of the viscosity variation as our modeling is only focused on the variation of zero shear viscosity.

According to the type of reaction, the polymer concentration (φ) is the same as the polymer conversion (p):

$$\varphi \equiv p \tag{2}$$

Furthermore, Marin et al. [34] determined a unique model curve which correctly predicts the behaviour of the intrinsic zero shear viscosity of the solution of the two regimes (Rouse end entangled) as a function of the weight average molecular weight (M_w) and φ:

$$\eta_0(\varphi) = (1-\varphi)\eta_{0,m} + K\varphi a_\varphi M_w \left[1 + \left(\varphi^b \frac{M_w}{M_c} \right)^c \right] \tag{3}$$

From a theoretical point of view, the values used for the coefficients b and c should be, respectively, 1.25 and 2.4. These values come firstly from the power law concerning a Rouse

and entangled diluted system (respectively, $\eta_{0,\text{solution}} = \eta_{0,\text{bulk}}\varphi^1$, $\eta_{0,\text{solution}} = \eta_{0,\text{bulk}}\varphi^4$) and secondly from the viscosity power law dependence in Rouse and entangled regime ($\eta_0 \propto M_w^1$ and $\eta_0 \propto M_w^{c+1}$, respectively). According to the previous relations and Eq. (3) we have the following relationship $bc + 1 = 4$. a_φ is the free volume correction taking into account the change of the glass temperature with the dilution φ. In the case of the present study, the formed PDMS at the end of the polymerization is such a flexible polymer characterized by a very low T_g ($-125\,^\circ\text{C}$) that the correction factor can be neglected ($a_\varphi = 1$). Actually we assume that the polymer has the same T_g as the monomer. M_c is the critical molecular weight for the viscosity in bulk, from the literature [35,36] $M_c \approx 30{,}000\text{ g mol}^{-1}$. K is a constant which can be derived from the viscosity power law in bulk conditions ($\varphi \to 1$, $\eta_0 = KM_w(M_w/M_c)^c$). Furthermore K is temperature dependent ($K = K_0 e^{E/RT}$). The first term of Eq. (3) takes into account the viscosity of the monomer as $\eta_0(\varphi \to 0) = \eta_{0,\text{m}}$.

Also it can be reasonably assumed that the molecular weight grows linearly with respect to time ($M_w = k'\varphi$), so that Eq. (3) can be expressed as following:

$$\eta_0(\varphi) = (1-\varphi)\eta_{0,\text{m}} + Kk'\varphi^2\left[1 + \left(\frac{\varphi^{b+1}k'}{M_c}\right)^c\right] \quad (4)$$

The constant k' can be calculated from Fig. 6 itself according to the following equation [34] which expresses the critical molecular weight in solution $M_{c_{\text{solution}}}$ from M_c in bulk.

$$M_{c_{\text{solution}}} = M_{c_{\text{bulk}}}\varphi^{-1.25} \quad (5)$$

From Fig. 6, this transition occurs at the concentration $\varphi \approx 0.35$. Consequently the molecular weight of PDMS at this transition is $M_{c_{\text{solution}}} \approx 110{,}000\text{ g mol}^{-1}$ and finally $k' \approx 290{,}000\text{ g mol}^{-1}$.

The constants K and c were calculated from non-linear regression as the best fitting values of experimental values in Fig. 6. Then, the values obtained are $c = 4$ and $K = 9.8 \times 10^{-7}\text{ mol g}^{-1}\text{ Pa s}$. This result means that the dependence of the zero shear viscosity upon the molecular weight scales as $\eta_0 \propto M_w^5$ in bulk conditions. Nevertheless, it is well known that experimental data on the molecular weight dependence of η_0 generally support the power law $\eta_0 \propto M_w^{3.4}$ for narrow distribution samples, but results differ for broad distribution samples. For example, Montfort et al. [37] observed a power law $\eta_0 \propto M_w^{4.95}$ with polystyrene samples in a narrow range of M_w. In the same way, we observed [31] $\eta_0 \propto M_w^{4.6}$ for poly(ε-caprolactone) samples in situ polymerized between the plates of the rheometer according to an equivalent protocol as used in the present work.

As previously pointed out, the siloxane bonds are chemically identical whatever their localization in the monomer or even in the polymeric backbone may be. Thus, the active anionic species present in the polymerization media may attack monomers (leading to the awaited AROP) as well as polymeric chains, leading to disproportionation and back-biting reactions. Those kinds of side reactions provoke an increase of the polydispersity of the formed polymer in comparison

with conventional controlled polymerizations. For example, the steady-state compliance of PDMS samples at the end of the polymerization process is close to $J_e^0 \approx 3 \times 10^{-4}\text{ Pa}^{-1}$, whereas $J_e^0 \approx 1 \times 10^{-5}\text{ Pa}^{-1}$ for a narrow molecular weight PDMS. Finally, we can conclude that this drawback can be quoted to explain the value of 5 compared to the value of 3.4 obtained when narrow molecular weight samples are used.

However, the differences between theoretical and fitting values are high enough to ask for an experimental validation of the model. This verification can be performed using the model in order to predict the molecular weight value of the chains obtained at the end of the polymerization reaction. With a final viscosity of 2000 Pa s the model predicts a molecular weight of approximately 290,000 g mol^{-1}. Figures plotting the zero shear viscosity as a function of the weight average molecular weight found in the literature [35,36] show an average molecular weight of 300,000 g mol^{-1} for a viscosity of 2000 Pa s. The two values are close enough to validate the model, at least in such calculation.

Finally, Eq. (4) can be combined with Eqs. (1) and (2) to derive the prediction of the viscosity variation versus the reaction time. Examples of this prediction are given in Fig. 7a,b. Those examples reveal that the model predicts the viscosity well whatever the temperature and base used be.
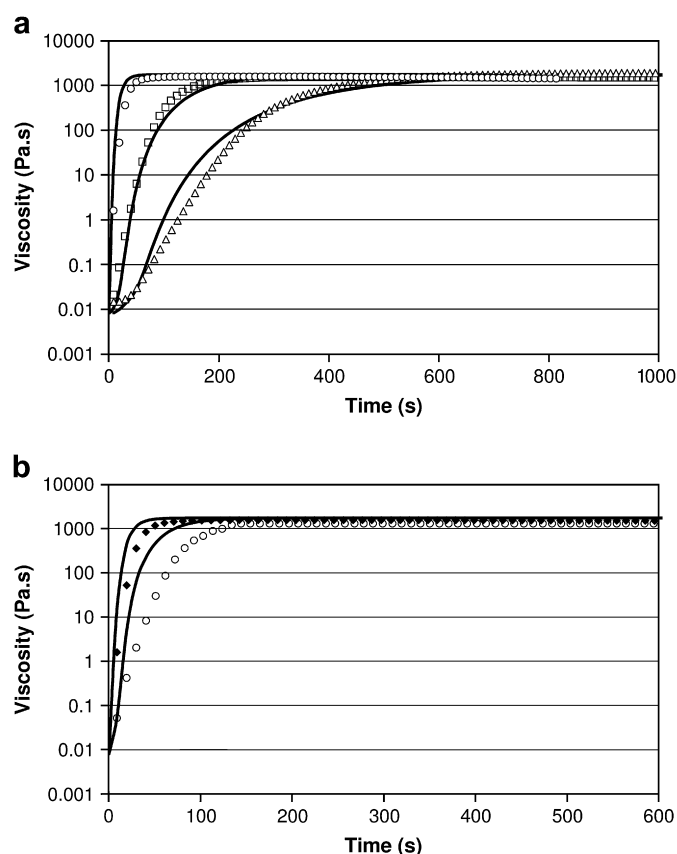

Fig. 7. Modeling of the variation of the absolute viscosity versus time ($\omega = 10\text{ rad s}^{-1}$). (a) Catalyst: $P_4^t\text{Bu}$ ($1.75 \times 10^{-4}\text{ mol L}^{-1}$) at $T = 90\,^\circ\text{C}$ ($\triangle$), $100\,^\circ\text{C}$ ($\square$) and $120\,^\circ\text{C}$ ($\bigcirc$). (b) Catalyst: $P_4^t\text{Oct}$ ($1.75 \times 10^{-4}\text{ mol L}^{-1}$) at $T = 110\,^\circ\text{C}$ ($\bigcirc$) and $120\,^\circ\text{C}$ ($\blacklozenge$).

4. Conclusion

The use of a rheometer as a chemical reactor allows us to monitor the anionic ring-opening polymerization of D5 initiated by phosphazene bases and water trapped in the monomer in bulk extrusive experimental conditions. In these conditions, all the phosphazene bases are not suitable for the AROP of D5. Only those having high basicity strength like P_4^tBu and P_4^tOct allowed us to reach high molecular weights within few minutes of reaction time. With such a procedure a full access to the chemical kinetics of this reaction has been possible. Thus the first orders in catalyst and in equilibrium monomer concentration have been confirmed. Besides, the activation energy concerning the AROP of D5 was determined to be about 110 kJ mol^{-1}.

The in situ monitoring of the complex shear modulus during the polymerization combined with the variation of the monomer conversion during the chemical reaction allowed us to build up a model able to predict the viscosity variation versus the reaction time. Actually, knowledge of the polymer concentration in its monomer when the transition between Rouse and entanglement regimes occurs, value of the critical weight and theoretical considerations about the evolution of viscoelastic properties in diluted systems are the relevant parameters of the model. Moreover, we admitted a linear increase of the chain's molecular weight with monomer conversion all along the polymerization reaction. This is checked by the existence of a master curve relating the zero shear viscosity to the monomer conversion. All of these lead to building up an efficient predictive model in order to control this polymerization process in extrusive conditions.

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