Bis(trifluoromethane)sulfonimide initiated ring-opening polymerization of octamethylcyclotetrasiloxane

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Abstract

Polymerization of octamethylcyclotetrasiloxane in the presence of hexamethyldisiloxane and catalytic amounts of bis(trifluoromethane)sulfonimide (TFSI-H) under dry conditions at 25 or 100 °C gave α,ω-bis(trimethylsilyl)-polydimethylsiloxanes (PDMS) of a low molecular weight ($\bar{M}_n < 13\,000$ g mol^{-1}). The polymers are very similar to those obtained in the presence of trifluoromethane sulfonic acid as initiator but the polymerization initiated by TFSI-H was faster. Addition of the sufficient quantity of tributylamine to neutralize completely any acid suppressed the polymerization. No polymerization was observed in the presence of triflic anhydride (TfA), trimethylsilyl-bis(trifluoromethane)sulfonimide, trimethylsilyltriflate or the lithium salt of bis(trifluoromethanesulfonyl)imide. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The growing use of polysiloxanes in macromolecular engineering has led to numerous studies of the polymerization of cyclosiloxanes and the polycondensation of silanols. Both reactions require the use of a catalyst. The catalytic system (acidic or basic, homogeneous or heterogeneous) has been selected according to the desired material [1–4].

Anionic polymerization of cyclic monomers has been commonly used for the preparation of polysiloxane. In some cases, this reaction is quite close to living polymerization and gives a high yield of polymer. The cationic polymerization of cyclosiloxanes presents, however, some advantages over the anionic route. With some initiators it takes place very rapidly at room temperature and the initiator can be easily removed from the polymer. Moreover, the reaction can be performed with cyclosiloxane monomers bearing functional groups (e.g. SiH or SiCH$_2$Cl) which are unstable under the conditions of the anionic process.
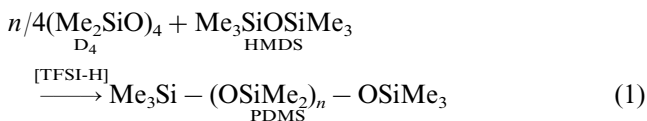
Acid-initiated ring opening polymerization of cyclosiloxanes has been extensively used both in the laboratory and in the industry. Mechanisms are complex and still unclear. Most studies reported in the literature deal with polymerizations of hexamethylcyclotrisiloxane (D$_3$) or octamethylcyclotetrasiloxane (D$_4$) initiated by strong protic acids such as H$_2$SO$_4$ and HClO$_4$ or by Lewis acids. Among those, trifluoromethanesulfonic acid (triflic acid) has been extensively investigated [1–49]. More recently, catalytic systems derived from triflic acid or perfluorohomologues have been reported to polymerize cyclosiloxane monomers, in particular those containing fluorine substituents. Typical examples are perfluoroalkylsulfonic acids (C$_n$F$_{2n+1}$SO$_3$H) [5–8], trimethylsilyltriflate (CF$_3$SO$_3$SiMe$_3$, TMST) [9–13] or benzyldimethylsilyltriflate (BDMST) associated with a selective proton trap (e.g. triethylamine, tri-n-butylamine, pyridine) or a quaternary ammonium triflate such as t-Bu$_4$N$^+$CF$_3$SO$_3^-$. TMST associated with triflic acid was also successively used for the polymerization

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of 1,1-diphenyl-3,3,5,5-tetramethylcyclotrisiloxane [9]. The addition of TMST or triflic anhydride (TfA) was expected to reduce the formation of cyclic oligomers resulting from an end-to-end ring closure mechanism and to decrease the amount of condensation reactions resulting in chain coupling. TMST alone did not catalyze the polymerization of D_3 [14].

Herein, we describe the ring opening polymerization of D_4 in the presence of bis(trifluoromethane)-sulfonimide $(CF_3SO_2)_2NH$, (TFSI-H) as initiator and hexamethyldisiloxane $(Me_3SiOSiMe_3$, HMDS) as a chain end blocker. The aim was to prepare a low-molecular weight α,ω-bis(trimethylsilyl)-polydimethyl-siloxane (PDMS) according to Eq. (1).

$$n/4\underset{D_4}{(Me_2SiO)_4} + \underset{HMDS}{Me_3SiOSiMe_3}$$

$$\xrightarrow{\text{[TFSI-H]}} Me_3Si-\underset{PDMS}{(OSiMe_2)_n}-OSiMe_3 \qquad (1)$$

For comparison we have also studied the same polymerization reaction in the presence of triflic acid as initiator. Other potential initiators have also been examined, e.g. TfA, TMST, trimethylsilyl-bis(trifluoromethane)sulfonimide $((CF_3SO_2)_2 NSiMe_3$, TMSS) or the lithium salt of TFSI-H. Also the effect of added tri-n-butylamine on the polymerization reaction will be discussed.

2. Experimental

2.1. Materials

Octamethyltetracyclosiloxane and hexamethyldisiloxane are Rhodia Silicones products (purity > 99.9% by NMR) which were dried for 24 h over magnesium sulfate and kept for several days over 4 Å molecular sieves under argon atmosphere. Triflic acid, trimethylsilyl-bis(trifluoromethane)sulfonimide, triflic acid anhydride and trimethylsilyltriflate were also coming from Rhodia (purity > 99% by NMR). TFSI-H was bought from Sigma (purity > 97% by NMR) and its lithium salt came from Fluka (purity > 99% by NMR). N-Trimethylsilyl-bis(trifluoromethane)sulfonimide was prepared from allyl trimethylsilane following the described procedure [50]. Its purity (> 98%) was assessed by NMR. The initiators were kept away from moisture and used without further purification. Tributylamine (Fluka, purity > 99% by GC) was dried over calcium hydride.

2.2. Methods

Polymers were analyzed by gel permeation chromatography (GPC) in trichloroethylene using a Spectra Physics Isochrom chromatograph equipped with a Perkin–Elmer 1320 infrared detector and 10^5, 2×5.10^4, 100 Å PL columns. Average molecular weights $\bar{M}_w$ and $\bar{M}_n$ are given in polystyrene standards equivalents.

^{29}Si-NMR spectra (59 MHz, gated decoupling with addition of Fe(acac)$_3$, TMS as internal reference) and ^{1}H-NMR spectra (300 MHz, HMDS as internal references) were taken in CHCl$_3$ with a Bruker AMX 300 spectrometer. Polymerization kinetics was followed by viscosimetry in a 25 °C thermostatic bath.

The determination of the trimethylsilyl group content was done by GC after ethoxylation of PDMS.

2.3. General procedure for polymerization

Polymerizations were performed under argon in a 250 ml three-necked flask equipped with a magnetic stirrer and a temperature regulating system. All glassware was flame-dried under vacuum. The flask was filled with a mixture of D_4 (100 g, 0.337 mol) and HMDS (1.35 g, 0.0083 mol). The initiator (4% molar with respect to D_4) and, in some cases, the freshly dried and filtered amine (0.31 g, 0.0017 mol) were added at 23–25 °C under continuous stirring. Polymerizations were conducted at 25 °C or the mixture was brought up quickly (10 min) and kept for 5 h at 100 °C.

The reaction was monitored by measuring the viscosity of the reaction mixture. If necessary, the polymerization could be stopped by stirring the mixture for 1 h with sodium bicarbonate in excess with respect to the initiator. Filtration yielded a transparent oil. The viscosity of the various samples was measured without further purification.

When the polymerization was completed, residual monomer, end-capping agent and some low-molecular weight cyclic or linear oligomers were distilled off (270 °C, 15 mbar with a stream of 50 l h^{-1} of nitrogen) and the residue was analyzed.

3. Results and discussion

3.1. Polymerization catalyzed by TFSI-H or TfOH

For the ring-opening polymerizations of D_4 in the presence of HMDS at 25 or 100 °C readily proceeded in the presence of TFSI-H or TfOH we have chosen to synthesize an PDMS with low molecular weights (Table 1).

As shown by following the change of viscosity with time, the polymerization was quite fast, even at 25 °C. In the case of TFSI-H, the polymerization was essentially completed after 1 h. With TfOH as initiator the reaction was slower.

After removal of the volatile products, polymer yields were in the range of 88–92% for both initiators. Byproducts were cyclosiloxanes including unreacted D_4,

Table 1
Polymerization of D$_4$ with HMDS and synthesis of PDMS initiated by TfOH and TFSI-H at 25 or 100 °C

Runs number	1	2	3	4
Initiator	TfOH	TfOH	TFSI-H	TFSI-H
Mcata. (g) [a]	0.203	0.203	0.380	0.380
$T_{\text{Polymerization}}$ (°C)	25	100	25	100
V25 $_{1/2\,h}$ [b]	211	222	258	291
V25 $_{1\,h}$ [b]	268	255	295	298
V25 $_{3\,h}$ [b]	290	265	298	306
V25 $_{5\,h}$ [b]	300	285	304	308
$GPC_{(crude\ product)}$ [c]				
$\bar{M}_n$	13 360	11 740	11 570	11 460
$\bar{M}_w$	24 310	23 360	22 810	22 790
I_p	1.82	2	2	2
Yield (%) [d]	88.4	87.8	91.9	91.9
V25$_{(final\ PDMS)}$ [d]	449	441	467	458
$GPC_{(final\ PDMS)}$ [d]				
$\bar{M}_n$	12 310	12 900	11 275	12 455
$\bar{M}_w$	24 835	24 720	24 150	23 935
I_p	2	1.9	2.15	1.9
D_{Pn} [d,e]				
By GPC	164	172	154	153
By ^{29}Si-NMR	144	165	165	165
By ethoxylation	149	149	138	135
M [f]	11 188	11 188	10 374	10 152

[a] 0.013 mol (4‰ in mol to D$_4$).

[b] Viscosity (mm^2 s^{-1}) at 25 °C after x h of reaction for a PDMS before distillation of the volatiles.

[c] Analysis before distillation (without elimination of low-molecular compounds).

[d] Analysis after distillation (elimination of low-molecular compounds).

[e] Theoretical $D_{Pn} = 4\ [D_4]/[HMDS] = 162$.

[f] M (real mass of PDMS with the following structure Me$_3$SiO–(Me$_2$SiO)$_{D_{Pn}}$–SiMe$_3$) is calculated from the D_{Pn} after ethoxylation.
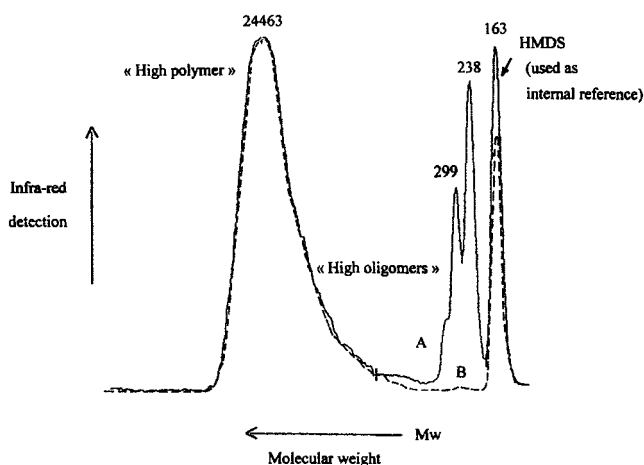

Fig. 1. Polymerization of D$_4$ with HMDS and synthesis of PDMS initiated by TFSI-H 100 °C (Run number 4, see Table 1). GPC chromatograms of the crude product (A) and of the final polymer (B). We made stated by NMR analysis that the quantity of HMDS remained after the reaction was negligible.

residual but negligible HMDS and some very low molecular weight linear PDMS.

GPC of the crude reaction mixture indicated the formation of two main components. There was a peak corresponding to a polymer ($\bar{M}_w \sim 24\,000$ g mol^{-1}, in polystyrene equivalents) with a shoulder corresponding to 'high' oligomers (cyclosiloxanes, macrocycles, linear compounds) and a zone of several peaks corresponding to low oligomers, residual D$_4$ and HMDS. Polydispersity ($I_p = \bar{M}_w/\bar{M}_n$) of the polymer was typically between 1.9 and 2.1. After purification (stripping and evaporation), only the first peak was present ($\bar{M}_n = 11\,000$–13 000, $\bar{M}_w = 24\,000$–25 000) and the shoulder had also disappeared. Fig. 1 shows two GPC chromatograms resulting from run 4. The first chromatogram A corresponds to the crude material, the second, B, corresponds to the product obtained after distillation and stripping with nitrogen. As can be seen from Table 1, both initiators gave similar results.

^{1}H- and ^{29}Si-NMR spectra of purified polymers indicated the presence of the expected dimethylsiloxy chain groups and trimethylsilyl end groups. The surface ratio between these signals allowed the calculation of the D_{Pn} and the real $\bar{M}_n$ of the PDMS. The results were in complete agreement with the ethoxylation–GC method measuring trimethylsilyl group ratios: $D_{Pn} \sim 135$–150 and $M \sim 10\,000$–11 000 (Fig. 1). These numbers are, as expected, lower than those found by GPC, because of the non-exact fitting of the structure of PDMS to polystyrene standards used for the calibration of the columns of the GPC equipment.

3.2. Polymerization with TFSI-H and TfOH in the presence of TBA

We then effected the ring-opening polymerization of D$_4$ under the experimental conditions of Table 1 but in the presence of enough TBA to ensure the absence of adventitious protic acid. The amine acts as a proton scavenger and allows to avoid initiation by a 'simple' Brönsted acid. In these conditions, there is no polymerization. We can therefore conclude that, in the case of TFSI-H or TfOH the initiation is due to the protons of TFSI-H or TfOH (see the results in Table 2).

3.3. Polymerization with initiators derived from triflic acid with or without TBA

Table 2 shows the results obtained for the polymerization catalyzed by triflic acid derivatives such as TfA, TMSS, TMST and TMSS lithium salt.

In some cases TBA was added to avoid the catalysis by triflic acid which would be accidentally introduced in the mixture. As before, there was no significant change of viscosity with time indicating that there was no polymerization.

Table 2
Polymerization of D_4 with HMDS and synthesis of α,ω-bis(trimethylsilyl)-polydimethylsiloxane initiated by various triflic acid-derivatives at 25 or 100 °C

Initiator[a]	TfOH or TFSI-H				$CF_3SO_2SiMe_3$				$(CF_3SO_2)_2O$				$(CF_3SO_2)NSiMe_3$				$(CF_3SO_2)_2N^-Li^+$			
With (+) or without (−) TBA	+		−		+		−		+		−		−		+		−		+	
$T^{polymerization}$ (°C)	25	100	25	100	25	100	25	100	25	100	25	100	100	25	100	25	25	100	25	100
$V25_{5\,h}$[b]	10	15	4	5	7	16	5	7	11	17	9	7	2	2	2	2	2	2	2	2

[a] 0.013 mol (4‰ in mol to D_4).
[b] Viscosity ($mm^2\ s^{-1}$) measured at 25 °C after 5 h of reaction before distillation.
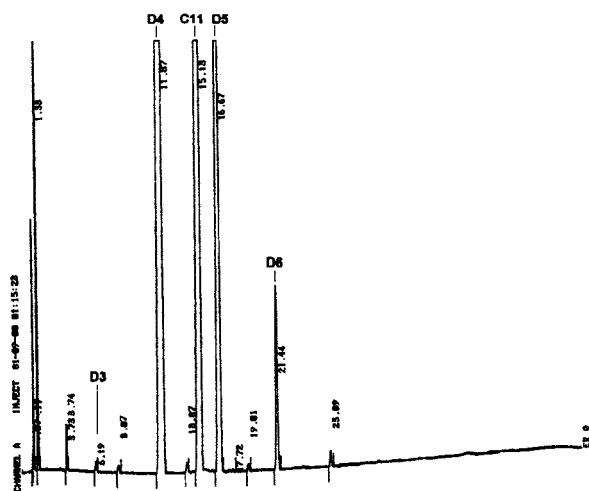
Fig. 2. GC of the reaction at 50 °C of the volatiles of the final product.

3.4. Kinetic studies of the polymerization of D_4 and HMDS with TFSI-H

To determine the kinetic values of the polymerization of D_4 with HMDS catalyzed by TFSI-H, we have carried out kinetic studies. The starting polymerization mixture was the same as used before (D_4: 100 g, 0.337 mol, HMDS: 1.35 g, 0.0083 mol). The mixture was heated (50 and 100 °C) and the catalyst (TFSI: 3.95 g or 4% molar with respect to D_4) added when the selected temperature was reached. Aliquots were neutralized with TBA and distilled (120 °C/20 min/2–5 Torr/ $\sim$ 5 g product) to separate the volatiles from the polymer. These volatiles were analyzed by calibrated GC to quantify the composition of its cyclosiloxanes D_n with $n = 3$, 4, 5 and 6 (Fig. 2).

Fig. 3 shows the concentration of the volatiles and the polymer in function of reaction time.

One can see that the statistical equilibrium for the redistribution at 50 °C was reached after $\sim$ 100 min and at 100 °C after $\sim$ 75 min. As expected, the main product of the volatiles was the D_4 species. In both cases, the yield of the PDMS polymer was about 91% (w/w) considering the product, which had not been distilled under the used, conditions as the PDMS polymer.

The formation of cyclosiloxanes other than D_4 can be explained by the mechanism of this cationic ring opening polymerization (CROP). One step of the mechanism describes an intra-molecular reaction of the reactive end-group of the PDMS ('back-biting' [1,51]).

The decreasing amount of the cyclics is in the order of $D_4 > D_5 > D_6 > D_3$. The reactivity of D_3 is much higher than for D_n ($n \geq 4$), due to its high ring strain, which favors the opening of this ring. Decreasing formation of the higher cyclics was explained by the

decreasing probability of the back-biting reaction with the size of the ring [51].

To find out the kinetic law for the D_4 polymerization, we measured the substrate half-life time ($t^{1/2}$) determination (Fig. 4).

Fig. 4 shows the substrate half-life determination from different initial concentration of D_4 and its substrate graphical exploitation.

The exploitation of the given datas shows that the polymerization of D_4 is of 2nd order with respect to monomer (Fig. 5).

Fig. 5 shows the comparison of k of the polymerization of D_4 with HMDS at 50 and 100 °C.

Rate constants of the polymerization for the D_4 are: k (323 K) = 18.4 (mol^{-1} s^{-1}) and k (373 K) = 19.2 (mol^{-1} s^{-1}). The calculated activation energy, was ca. 0.8 kJ mol^{-1}.

Chojnowski published the E_a value for the CROP of D_4, catalyzed with TfOH, as 24 kJ mol^{-1} [1]. The addition of water, which acts as an inhibitor for TfOH, can increase E_a up to 72 kJ mol^{-1}. The lower activation energy for TFSI-H for the polymerization of D_4 seems to confirm our observation that under the used conditions TFSI-H could be a more powerful initiator than TfOH for the CROP of D_4.

4. Conclusion

CROP of octamethyltetracyclosiloxane was shown to occur in the presence of TFSI-H as initiator and hexamethyldisiloxane (HMDS) as terminating agent. In the chosen example of a PDMS with a low molecular weight ($\bar{M}_n < 1300$ g mol^{-1}) the reaction afforded α,ω-bis(trimethylsilyl)-polydimethylsiloxane at 25 and 100 °C in high yield ($\sim$ 90%).

This method has thus potential utility for the synthesis of PDMS polymers. The material has very close properties with that produced in the presence of triflic acid but the polymerization reaction is much faster.

Ring opening polymerization of octamethyltetracyclosiloxane in the presence of hexamethyldisiloxane as termination agent by TFSI-H at even room temperature (25 °C), in mild conditions or at higher temperature (100 °C) has given, as expected, PDMS in relatively high yield ($\sim$ 90%). The process has a potential utility for the synthesis of such material. Although, this material is very close to those synthesized with triflic acid as initiator, the polymerization with TFSI-H is beneficial, as it goes faster.

The reaction in the same experimental conditions and with the same initiators, but in the presence of enough tributylamine to ensure the neutralizing of any protic acid, gives no polymerization. No catalytic activity was found for the polymerization of D_4 with triflic acid anhydride, trimethylsilyltriflate sulfonimide, trimethylsilyltriflate, and TFSI-H lithium salt.
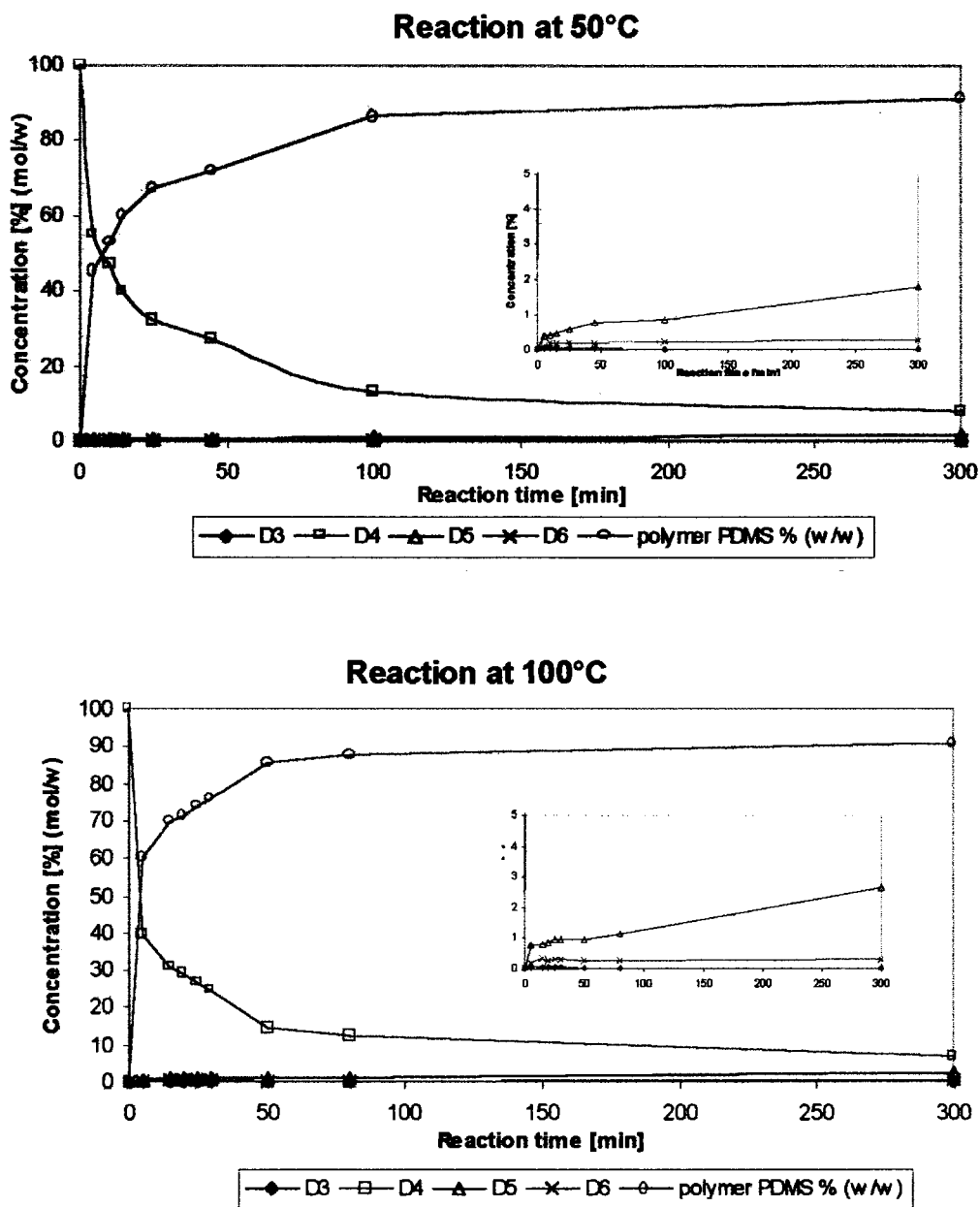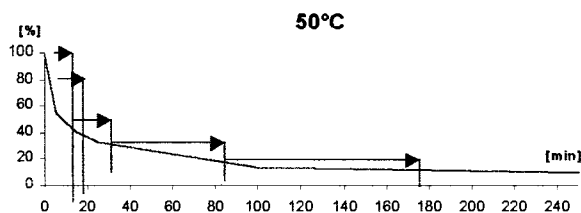
Reaction at 50°C

Reaction at 100°C

Fig. 3. Concentration of PDMS and its volatiles, splitted of in its cyclosiloxanes D_n for the polymerization of D_4 with HMDS at 50 and 100 °C after 5 h of reaction.

E.g. Grapic shown for 50°C

D4(initial) [%] (-p) (mol/weight)	t½ [min] (50°C)	t½ [min] (100°C)
100	9	4.5
80	12.5	4.5
60	30	14
40	57	42.5
20	138	125

Fig. 4. Half-life determination from different initial concentration of D_4 and its graphical exploitation.
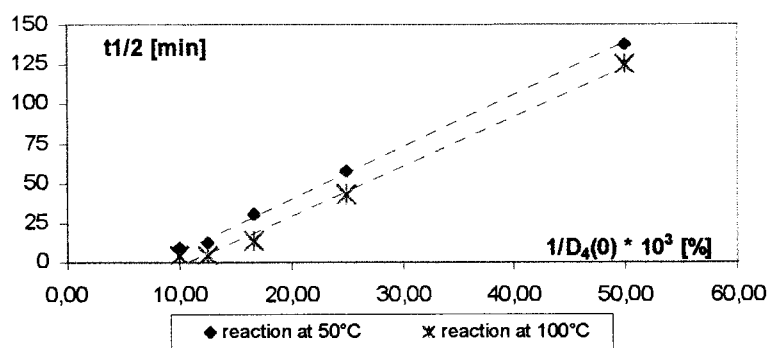
Fig. 5. Comparison of k of the polymerization of D_4 with HMDS at 50 and 100 °C.

Kinetic investigations seem to indicate a lower activation energy for TFSI-H for the polymerization of D_4 than for TfOH. It strengthens our observation that under used conditions TFSI-H is a more powerful initiator for the CROP of D_4 than TfOH.

Acknowledgements

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