ELSEVIER

Polymer 42 (2001) 7239–7246

polymer

www.elsevier.nl/locate/polymer

Anionic polymerization of octamethylcyclotetrasiloxane in miniemulsion II. Molar mass analyses and mechanism scheme[☆]

M. Barrère, F. Ganachaud*, D. Bendejacq, M.-A. Dourges, C. Maitre, P. Hémery

Laboratoire de Chimie des Polymères, UMR 7610 CNRS/Université, Pierre et Marie Curie, T44 E1, 4 Place Jussieu, 75252 Paris Cedex 05, France

Received 10 January 2001; received in revised form 5 March 2001; accepted 14 March 2001

Abstract

Hydroxyl α,ω-functionalized polydimethylsiloxane (PDMS) standards have been synthesized by ring-opening anionic polymerization of octamethylcyclotetrasiloxane (D_4)[1] in miniemulsion. Their absolute molar masses as well as Mark–Houwink–Sakurada parameters were then estimated in toluene at 30°C by triple detection size exclusion chromatography (SEC^3). MALDI-TOF confirmed the SEC^3 results in addition to providing several clues on chain microstructure and evidence of redistribution reactions. Trimethyl and vinyl α,ω-terminated PDMS oligomers were similarly synthesized in miniemulsion in the presence of functional transfer agents and used together with small dihydroxylated PDMS standards to compare the effect of substituents on the SEC calibration curve. Precise measurement of average molecular weights showed that the existing kinetics model could not account solely for mass control below 70% conversion. A thermodynamic explanation is then proposed where the molar mass control is exerted by the surface activity of the chains which drives their reactivity. Small chains rapidly propagate and backbite at the interface. Once the chains reach a critical DP corresponding to their loss of surface tension activity, they penetrate into the particles where side reactions such as redistribution and condensation hardly occur. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Functionalized PDMS; Anionic polymerization; Miniemulsion

1. Introduction

Silicones of various microstructure and architecture are widely used in industry mainly because of their absence of toxicity, high chain flexibility and low surface energy. For instance, emulsions based on silicones have been prepared for use in drug vectorisation or personal care products [2].

A very simple process to synthesize well-defined α,ω-dihydroxylated polydimethylsiloxane (PDMS) consists of polymerizing the monomer directly in emulsion. Few fundamental studies of this process were reported in literature (see Ref. [1] and references therein). It is, however, currently used as a tool for synthesizing PDMS seeds from which particles with an outer-shell are grown by radical polymerization of various vinyl monomers [3–5].

As part of a research project on ionic polymerization in emulsion (IPE), the ring-opening anionic polymerization of octamethylcyclotetrasiloxane (D_4) in miniemulsion has been previously studied in our group [1,6]. Benefits in pre-emulsifying the system is that all the monomer is scattered in small droplets that should act as independent bulk 'mini-reactors'. However, different features appeared in polymerization rate, molar mass distribution, and cycle amounts between bulk and miniemulsion D_4 polymerization. Specifically, the latter system led to narrow PDMS molar mass distributions up to 70% conversion without much low cycle production (less than 10%). It was then postulated that all reactions were taking place at the interface, without ruling out possible 'bulk' reactions [1,6]. Kinetic simulations taking into account relative rates of initiation, propagation and condensation appeared to reasonably fit the experimental data [1].

Molar mass distributions are generally closely related to polymerization mechanism. For instance, transfer and termination rate constants can be derived from the full molar mass distribution as shown in free radical polymerization of styrene in emulsion [7]. Similar measurements of polymers obtained by the IPE process should gain valuable information.

Nowadays, triple detection SEC (i.e. equipped with a refractometer, a light scattering and viscometer detectors)

[☆] First part of this series: see Ref. [1].

* Corresponding author. Tel.: +33-1-44-27-55-01; fax: +33-1-44-27-70-89.

E-mail address: ganachau@ccr.jussieu.fr (F. Ganachaud).

[1] The notation for the siloxane oligomers throughout the paper is the following: M holds for $(CH_3)_3SiO_{1/2}-$, M^v for $CH_2{=}CHSi(CH_3)_2O_{1/2}-$, M^{OH} for $HOSi(CH_3)_2O_{1/2}-$ and D for $-Si(CH_3)_2O-$.

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00207-5

is a convenient tool to measure absolute molar mass [8,9]. In addition, it provides Mark–Houwink–Sakurada (MHS) parameters [10] theoretically from a single broad polymer sample, from which a universal calibration curve can be constructed [11]. To our knowledge, multi-detection SEC has not been applied to the characterization of PDMS. Emergent techniques such as mass spectrometry (MALDI-TOF [12–15] or electrospray ionization [16]) have likely been used for better characterizing PDMS samples. For instance, MALDI-TOF together with SEC [17] can bring about useful information on the chemistry of the polymerization reaction itself by looking at chain-ends, thus confirming the overall structure of the polymer or stressing out possible side-reactions (transfer, recombination, etc).

The purpose of the present study is to measure with greater accuracy and using different methods [18] the molar mass distribution of dihydroxylated or other functionalized PDMS. In addition, the miniemulsion process proceeds to the preparation of standards exhibiting narrow dispersities and increasing molar mass [1] that are used to generate an absolute SEC calibration curve. From these measurements, useful insights into the IPE process are gleamed.

2. Experimental section

2.1. High molar mass PDMS syntheses

The procedure used here has been optimized and differs from Ref. [1]. Basically, benzyldodecyldimethylammonium bromide or NBr (Aldrich) (1.46 g) was first introduced in distilled water (56 ml). While sonicating the solution using a sonifier 450 from Branson Ultrasonics Corporation (6 min at power 70 Hz), 30 g of D_4 (Aldrich, purity checked by ^{1}H NMR) was added dropwise in the beaker immersed into an ice bath to prevent local temperature rising. The stable miniemulsion was then poured in a reactor maintained at 57°C using a thermoregulated oil bath. The reaction was initiated by adding 3.8 ml of NaOH 1 M solution (purchased from Fisher) and allowed to proceed with gentle mixing. 5 ml aliquots were withdrawn from the emulsion at about every 15 min, and quickly neutralized using a 1 M HCl solution in order to stop the polymerization reaction. The siloxane phase (PDMS + remaining cycles) was recovered by addition of $AlKO_8S_2{\cdot}12H_2O$ salt and by freezing the sample in liquid nitrogen. The upper organic phase was dried with $MgSO_4$ before filtration.

2.2. Low molar mass PDMS syntheses

For the preparation of trimethyl and vinyl α,ω-functionalized PDMS the miniemulsion procedure was again applied to the polymerization of D_4 (18 g) in the presence of hexamethyldisiloxane (M_2, 12 g, ABCR purity 99%) and 1,3-divinyltetramethyldisiloxane (M_2^v, 9.2 g, Aldrich, purity 97%), respectively. The chain-blocker quantities were chosen so as to reach a final number average molar mass of about 400 g mol^{-1}.

As low molar mass α,ω-dihydroxy PDMS oligomers could not be obtained by the miniemulsion process, a mixture of oligomers HO–D_n–H where $n = 5$–18 and kindly provided by Rhodia Silicones was used. Distillation under vacuum (150°C, 10^{-3} Torr) [19] was carried out to isolate a mixture of low oligomers ($n = 5$–9). This fraction was subjected to trimethyl derivatization according to the procedure described in Ref. [20] prior to GC analysis. Basically, 2.42 mmol of hydroxyl oligomeric PDMS in 22 ml of methylene chloride (analytical grade from SDS) was placed in the 50 ml round-bottomed reactor thoroughly purged with nitrogen. 12.9 mmol of imidazole (ACROS), 3.1 mmol of triethylamine (ACROS) and 12.9 mmol of trimethylchlorosilane (ABCR) were successively added to the solution. The reaction was let to proceed for 24 h before washing several times the solution with water. The solvent was let to evaporate and the final product dried with $MgSO_4$ before filtration.

2.3. Determination of small cycle concentrations by gas chromatography

The GC technique is used here to independently quantify linear oligomers from small cyclic species [21,22]. The analyses were performed using a Carlo Erba (Italy) GC 6000 Vega Series equipped with a capillary column (HP-5, cross-linked 5% PH ME siloxane, 15 m × 0.53 m × 1.5 μm film thickness), an injector 'on column' and a FID detector. The column temperature was programmed as 40°C for 3 min, from 40 to 180°C at 12°C min^{-1}, from 180 to 250°C at 25°C min^{-1}, and at 250°C for 10 min. The detector temperature was 280°C and helium was used as the vector gas. Correction factors have been applied in order to obtain truly quantitative results from detector response [23].

The concentration of cyclic species D_x created while polymerizing a cyclic dimethylsiloxane (D_3 or D_4) in the presence of a chain-transfer agent (typically M_2) either in bulk or in solution can be estimated from established models [24]. The concentration of cyclic species $[r_x]$ of ring size x at equilibrium is given by

$$[r_x] = K_x p^x, \tag{1}$$

where K_x is a constant experimentally determined. p is calculated from the concentration of end-groups and dimethylsiloxy repeating units given by initial conditions [24]. The concentration of cycles of different sizes is thus deduced from Eq. (1) (see Table 4).

2.4. Triple detection size exclusion chromatography

The device is composed of a 515 HPLC pump (Waters), an autosampler S5200 (Viscotek), a differential refractomer/viscometer S200 (Viscotek) and a light scattering mini-DAWN (Wyatt) detectors. Three columns (KF 802.5L, KF 804L, KF 805L from Shodex) thermostated at 30°C were eluted with toluene containing

2 wt% *N*,*N*-diisopropylethylamine at a flow rate of 1 ml min^{-1}. A calibration curve was constructed from polystyrene standards provided by Viscotek (between 300 and 1.8×10^6 g mol^{-1}). The exact PDMS concentration was derived from the refractometer signal, using a differential refractive index d*n*/d*c* of -0.093 ml g^{-1} [25]. When not specified, reported SEC traces are derived from the refractometer detector response. It has previously been reported that the triple detection SEC analyses could be very sensitive to the interdetector delay [10]. To ensure that our device is well calibrated, MHS parameters were recalculated for polystyrene standards giving $K = 12 \times 10^{-5}$ dl g^{-1} and $a = 0.717$ at 30°C (molar masses between 3.46×10^3 and 5.98×10^6 g mol^{-1}), within acceptable error of literature values (average values of $K = 11 \times 10^{-5}$ dl g^{-1} and $a = 0.72$) [26].

2.5. MALDI-TOF mass spectrometry

Samples were analyzed on a PerSeptive Biosystems Voyager Elite (Framingham, MA) time of flight mass spectrometer, equipped with a nitrogen laser (337 nm), a delayed extraction and a reflector. Both linear and reflector modes were operated at an accelerating potential of 20 kV. The MALDI-TOF mass spectra were the averages of 256 shots at 3 Hz repetition. 5–10 μl of the sample (0.5–2 g l^{-1}) was mixed with 50 μl of matrix (2,5-dihydroxybenzoic acid) dissolved in THF (15 g l^{-1}). Sodium iodide (NaI) salt (5 g l^{-1}) was systematically added to favor Na$^+$ cationization during the desorption/ionization process [27]. A 1 μl portion of the final solution was deposited onto the sample target and allowed to dry in air at room temperature prior to analysis.

2.6. Determination of surface tensions from contact angle measurements

The device is similar to the one in Ref. [28] using a CCD camera and in-house image processing software. Films of the various PDMS oligomers synthesized in this study were prepared by simply casting these oils onto aluminum pans. Contact angles in air of water drops deposited onto these films were then measured at equilibrium [29]. Each contact angle data was the average of at least 3 drops analyses.

The surface tension of a polymer film (i.e. of low surface energy) can be divided in two components [29]

$$\gamma = \gamma^{\mathrm{d}} + \gamma^{\mathrm{p}} \tag{2}$$

where γ^{d} and γ^{p} represent the surface tensions induced from dispersive and polar forces, respectively. The contact angle θ of a liquid (index *l*) onto a polymer film (index *s*) is generally expressed as a function of the dispersive and polar components of both constituents using the mean geometric model

$$\gamma_l(1 + \cos\theta) = 2\sqrt{\gamma_l^{\mathrm{d}}\gamma_s^{\mathrm{d}}} + 2\sqrt{\gamma_l^{\mathrm{p}}\gamma_s^{\mathrm{p}}} \tag{3}$$

Table 1
Surface tensions of functionalized PDMS chains using contact angle measurements

End-groups	$\bar{M}_n$ (g mol^{-1})	θ (deg.)	γ_s^{d}[a] (mJ m^{-2})	γ_s^{p} (mJ m^{-2})
Hydroxyl	480	71	20.6	14.3
	930	74	20.5	12.5
	1750	81	20.5	8.6
	4200	90	20.4	4.6
	15000	89	20.4	5.0
Methyl	610	83	18.5	8.4
	1750	89	19.5	5.3
	15000	90	20.4	4.6

[a] From Ref. [30].

Bulk surface tensions of various functionalized PDMS oligomers were quoted using the pendant-drop method [30] and shown elsewhere to be mainly ascribed to non-polar forces (the polar component held only for 5% of the overall value and could be neglected) [31]. The polar surface tension component of dihydroxylated or methylated PDMS oligomers *in water solution* is deduced from Eq. (2) and (3) where $\gamma_l^{\mathrm{d}} = 21.8$ mJ m^{-2}, $\gamma_l^{\mathrm{p}} = 51.0$ mJ m^{-2}. Table 1 reports the contact angle of a water droplet on various PDMS samples, as well as the dispersive (from Ref. [30]) and the polar (calculated in this study) components of the surface tension. Important variations are observed as a function of both oligomer functionality and length.

3. Results and discussion

3.1. Molar mass analyses

3.1.1. Molar mass distribution from SEC^3 analyses and comparison with MALDI-TOF-MS

Fig. 1 shows the typical SEC traces of the samples intermittently withdrawn up to 70% conversion. The molar mass

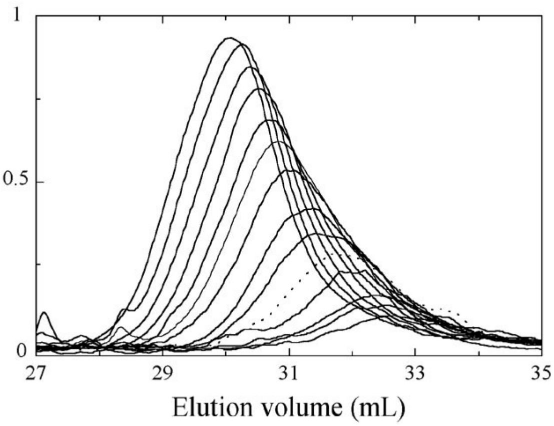


Fig. 1. Normalized SEC traces × fractional conversion of α,ω-dihydroxy functionalized PDMS prepared by the miniemulsion process (below 70 wt% conversion). (- - -) sample MB67-11.

Table 2
Comparison between SEC^3 and MALDI-TOF molar mass measurements

Sample	Triple detection SEC		MALDI-TOF-MS	
	$\bar{M}_n$(g mol^{-1})	*PI*	$\bar{M}_n$ (g mol^{-1})	*PI*
MB67-8	2640	1.11	2270	1.08
MB67-11	3100	1.10	3110	1.10
MB67-14	4010	1.11	4130	1.14
MB67-18	5590	1.24	4950	1.18

distribution regularly increases with conversion although still exhibiting a narrow dispersity throughout the polymerization course. Thus, these samples can be used as standards for SEC calibration.

Table 2 summarizes the properties of different samples ($\bar{M}_n$ and *PI*) extracted from MALDI-TOF and SEC^3 methods. A very good agreement is shown between the two methods, a result anticipated from both the narrow dispersity and relatively low molar mass of the samples [13]. Fig. 2 shows a comparison of SEC and MALDI-TOF distributions for sample MB67-11 (MALDI-TOF distribution was reprocessed by multiplying the response by M^2 so as to give a $w(\log M)$ distribution) [17]. Molar masses obtained from both methods overlap quite well on the whole distribution range.

Fig. 2 also shows that the molar mass distributions obtained by SEC^3 are particularly noisy because of low d*n*/d*c* ($= -0.093$) [25] for PDMS in toluene (to be compared with the dotted distribution in Fig. 1). It shows the necessity of building up a universal calibration [18] rather than determining an absolute molar mass from direct multi-detection measurements. This step calls for the determination of the correct Mark-Houwink parameters for the conditions of analysis [11].

3.1.2. Determination of the Mark-Houwink parameters by SEC^3

The Mark–Houwink–Sakurada equation is

$$[\eta] = KM^a \tag{4}$$

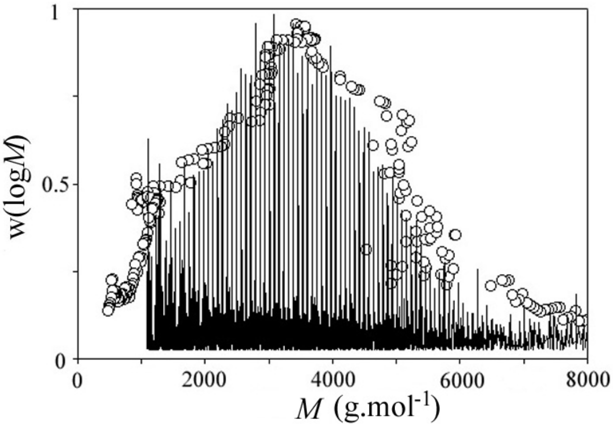


Fig. 2. Triple-detection SEC (○) and MALDI-TOF mass spectrum (|) for the sample MB67-11.

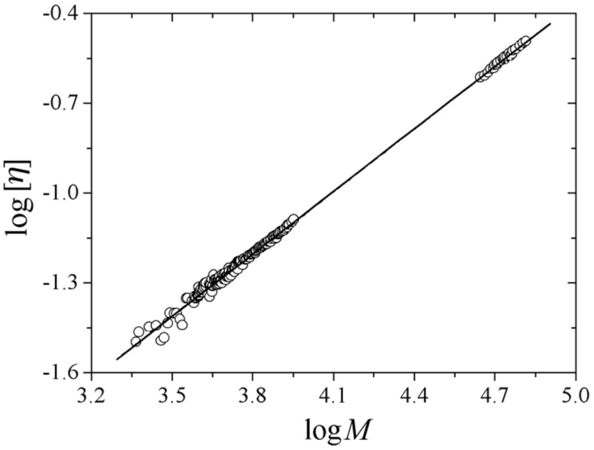


Fig. 3. log [η] vs. log M plot for various PDMS standards obtained from the miniemulsion process. (○) experimental data; (—) best least-squared linear fit.

where [η] and M are the intrinsic viscosity and molar average molar mass of a given polymer chain, respectively. The advantage of using a SEC^3 device is that both [η] and M are measured on each point of a whole polymer distribution. In theory, injecting one broad polymer sample in a SEC^3 apparatus would be enough to derive MHS parameters; in practice, multiple injections are carried out so as to minimize the errors [10]. Fig. 3 shows the log[η] vs. log M plot for PDMS standards of various sizes and K and a found in this work and in the literature are compiled in Table 3. These latter were selected from studies where molar masses were determined using different techniques than SEC or viscometer methods. By doing so, discrepancies observed in a previous paper [25] comparing data from various studies do not appear in Table 3. The influence of temperature that both affects K and a can also be seen in Table 3.

3.1.3. Calibration curve construction

Fig. 4 shows a calibration curve constructed from different molar mass measurements.

The dotted line corresponds to the polystyrene standards calibration. Applying the universal calibration relationship

$$[\eta]M = KM^{\alpha+1} = \text{cte} \tag{6}$$

and using the MHS parameters determined in this study for PS and PDMS in toluene at 30°C (Table 4), it was possible to derive an absolute calibration curve for PDMS between 3.5×10^3 and 3.2×10^6 g mol^{-1} (dashed line). The close values in the parameter pairs resulted in similar polystyrene and PDMS calibration curves. The absolute molar mass distributions given by SEC^3 are likewise reported and overlap nicely with the universal calibration curve.

However, universal calibration is not applicable for low molar masses and calibration using PDMS standards is required. Trimethyl and vinyl terminated oligomers were specifically obtained by adding sufficient amount of a transfer

Table 3
Mark–Houwink parameters for PDMS and PS (in italics) in toluene

K (10^5 dl g^{-1})	a	Temperature (°C)	MW determination method	MW range (10^3 g mol^{-1})	Reference
18.7	0.658	25	Light scattering	3–300	[40]
16.5	0.67	30	Light scattering	75–800	[9]
14.2	0.696	30	Triple detection SEC	2.3–71	This work
12.5	0.703	35	Calculated from living anionic polymerization	24.4–700	[41]
9.8	0.725	60	Osmometry	34–175	[42]
12.0	*0.717*	*30*	*Triple detection SEC*	*3.4–350*	*This work*

agent in the miniemulsion recipe, whereas hydroxyl ones were obtained as outlined in the experimental part. Table 4 reports the oligomer concentrations in the vinyl, trimethyl and hydroxyl samples; SEC peaks were attributed to the actual oligomer sizes from their corresponding abundance found in GC. Oligomer functionality exerts a striking influence on SEC retention time, as clearly exemplified in Fig. 4. Trimethyl and vinyl-terminated oligomers show retention times almost similar to PS standards. On the contrary, dihydroxylated oligomers are definitively retained on the columns, due to reversible adsorption of the oligomer hydroxyl groups on the columns at least up to molar masses of about 10^3 g mol^{-1}. A small amount of *N*,*N*-diisopropylethylamine was added in the eluent to prevent any column interactions. However, this addition was not effective for samples with high silanol group content. While a usual polystyrene calibration curve is suitable for measuring trimethyl-PDMS molar masses, a specific calibration curve needs to be built for hydroxyl-functionalized PDMS oligomers.

3.2. Mechanism scheme

The anionic polymerization in emulsion process applied to other monomers than siloxane was previously published for phenyl glycidyl ether (PGE) [32] and *n*-butyl cyanoacrylate (BCA) [33]. PGE polymerizes very slowly in miniemulsion and irreversible termination limits the size of oligomer chains. Molecular weight can be increased by modifying the interface polarity with the addition for instance of a cosurfactant. On the contrary, BCA polymerizes spontaneously in water. A suspension process at very low pH is generally required to 'control' the polymerization.

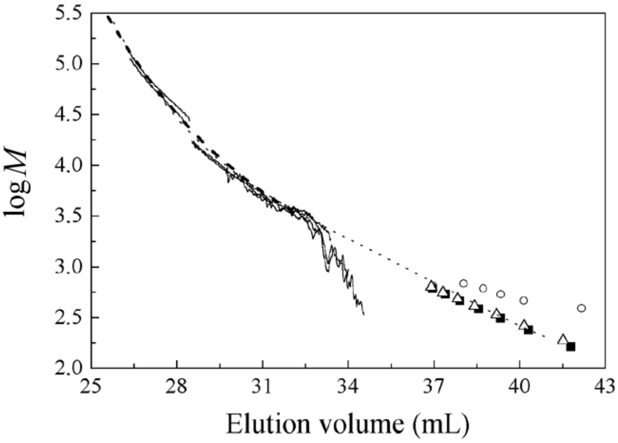


Fig. 4. Calibration curve for functional PDMS. (- -) polystyrene calibration curve; (– –) universal calibration curve; (—) triple detection molar masses of samples from Fig. 1; (○) dihydroxylated oligomers; (■) trimethyl-terminated oligomers; (△) vinyl-terminated oligomers.

Though these two systems are very different in nature, common features also prevail. Only interfacial reactions are involved in the process (initiation, propagation and termination). In addition, this process leads to short oligomers even for a very fast propagating system like BCA [33]. It was previously proposed [32] that chains entered the particles after reaching a critical DP of about 8 where they do not propagate anymore. This value obtained in both systems corresponds to the maximum chain-length obtained so far, which confirms the dramatic effect of chain entry in the polymerization process.

On the basis of these previous published data and from new results presented here, a similar mechanism scheme for siloxane polymerization is proposed in Scheme 1. The main point is that reactions involving small active chains (propagation, backbiting) take place at the interface and control the process, whereas those involving long chains (condensation and redistribution) are retarded due to restrained catalysis.

3.2.1. Initiation, propagation and termination

Chains are only initiated by the hydroxide anion borne by the ammonium surfactant [1]. The active center is associated to the surfactant head through ion-pairing and further propagates. Propagation at the interface is a very fast reaction, as no small oligomers could be seen even at very low conversions (see Fig. 1). Due to the relatively moderate polymerization rate observed here, the previous approximation [1] that very few active centers were generated at the same time seems valid. Termination occurs through protonation by water to give silanol end-groups. The reversibility of the termination reaction is undoubtedly a key factor for long-chain generation. A close examination of the absolute mass from the MALDI-TOF spectrum confirms the perfect dihydroxylation of the PDMS chains (Fig. 5). These results are in agreement with the ^{29}Si NMR chain-ends analyses reported in the first part of this series [1].

Table 4
Concentration (in wt%) of linear and cyclic species obtained in the anionic polymerization of D_4 in miniemulsion in the presence of M_2 and M_2^{v}. Hydroxylated oligomers were from standards mixture

End-groups	Oligomer content (wt%)								
	E_2	E_2D	E_2D_2	E_2D_3	E_2D_4	E_2D_5	E_2D_6	E_2D_7	E_2D_8
Methyl[a]	2.18	13.57	18.04	17.15	14.83	11.31	7.16	4.56	3.64
Vinyl[b]	13.25	16.65	16.78	15.00	12.04	9.02	6.46	4.84	0
Hydroxyl[c]	0.42	2.77	7.67	16.30	31.53	26.03	10.85	3.52	0.92
	Cycle content (wt%)								
	D_4	D_5	D_6	D_7	D_8	D_9			
Methyl (exp.)	3.48	2.63	0.39	0.07	0.01	0			
(calc.)	3.77	1.77	0.76	0.31	0.12	0.05			
Vinyl (exp.)	3.68	1.95	0.29	0.04	0.01	0			
(calc.)	3.90	1.82	0.79	0.32	0.12	0.05			

[a] $E = M$.
[b] $E = M^{v}$.
[c] $E = M^{OH}$.

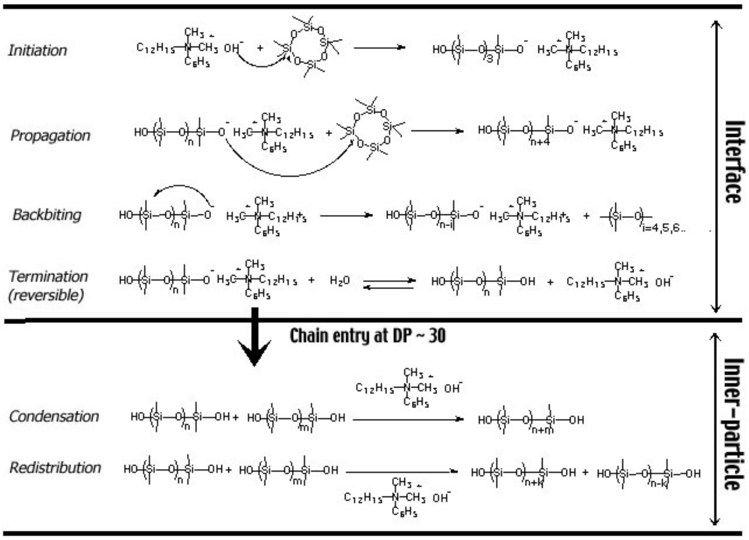
3.2.2. Backbiting

Backbiting reactions can be quantified using the miniemulsion process in the presence of transfer agents (chain-enders M_2 or M_2^{v}) similarly to what has been done in bulk and solution reaction [24]. The measured and calculated cycle amounts from the miniemulsion recipe are given in Table 4. Basically, backbiting reactions produce small cycles (D_4, D_5) in similar concentrations that were observed in bulk, whereas those of higher ones (D_6, D_7…) drastically decrease with size. It was previously quoted that the miniemulsion polymerization of D_4 resulted in a reduction of cycle amounts compared to bulk reactions, especially those bigger than D_7 [1]. In addition, there was no evidence of macrocycle synthesis in the miniemulsion process, as confirmed here by MALDI-TOF (Fig. 5). Cycle production thus takes place at the interface, where the steric constraints imposed by the ion-pairing limits the size of the obtained rings.

3.2.3. Chain entry at a critical DP

Fig. 6 shows the corresponding $\bar{M}_n$ and polydispersity index of the samples in Fig. 1 calculated from the universal calibration curve. For a given critical chain-length estimated at 2400 g mol^{-1} from the molar mass extrapolation in Fig. 6, the chains 'enter' the particle. The extrapolated polydispersity index is found to be close to 1 (1.06 exactly), which indicates that chain entry toward the particle core is complete for oligomer sizes of 30 D units or more.

This critical DP is dictated by the surface activity of the chains. Though straightforward, studies reporting the surface affinity of small dihydroxylated PDMS chains towards water were not found in the literature. Contact angle measurements of water drops on silicone films were carried out from which polar surface tension components were extracted (Table 1). The dispersive component of the interfacial tension was given from bulk data where polar



Scheme 1.

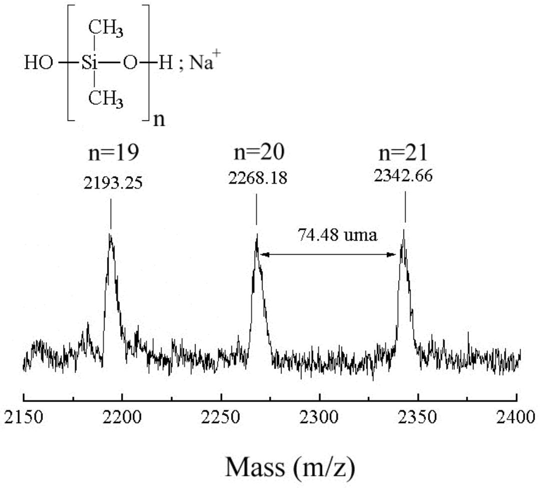


Fig. 5. Enlarged section of the MALDI-TOF spectrum from Fig. 2.

forces are negligible (Table 1) [30]. A sharp decrease in the polar surface tension of dihydroxylated oligomers is observed while increasing the PDMS chain-length with an intercept estimated at 2500 g mol^{-1} very close from the critical DP. It should be noted that chain entry in this system occurs for longer chain-length than for the other monomers reported before (DP$_{\text{crit}}$ ≈ 30 D units for siloxane to be compared to DP$_{\text{crit}}$ ≈ 8 units for PGE and BCA) which confirms the high surface activity of PDMS chains.

Because chain propagation is a fast process at the interface, small dihydroxylated oligomers could not be obtained by this technique. Comparatively, methyl-terminated chains exhibit somehow low but not nil polar surface tensions whatever their length (minimal plateau value around 5 mJ m^{-2}). Trimethyl (and vinyl)-terminated oligomers are thus easily prepared using the miniemulsion process.

Once the chains have penetrated the particles, they cannot undergo further propagation steps as showed for PGE and BCA. This point has been checked for a very fast propagating fluorinated tricyclosiloxane where $\bar{M}_n$ remains constant with conversion [34]. In the D$_4$ system however, the average molar mass and polydispersity index gradually increase with conversion (Fig. 6) indicating that side reactions also occur.

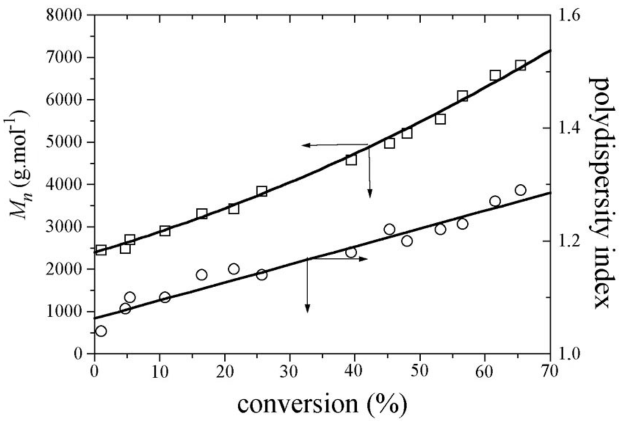


Fig. 6. Absolute molar average molar mass (□) and polydispersity index (○) vs. monomer conversion deduced from SEC using universal calibration.

3.2.4. Condensation

Fig. 1 shows that the molar mass distribution shifts as a function of conversion without overlapping on the low molar range. Small chains (albeit with DP > DP$_{\text{crit}}$) are disappearing in the course of polymerization due to condensation reactions. Because propagating oligomer chains saturate the interface, very few catalysts are available for condensation reactions to occur which in turns allows for molecular weight control. Above 70% conversion, a deep increase in the average molar mass together with a wide broadening of the polydispersity index [1] indicates faster condensations from growing silanol concentration and better activation from the interface.

It is striking that condensation takes place after chains have penetrated the particles whereas propagation does not. The former reaction could thus be suspected to proceed deeper in the particle rather than strictly at the interface, for instance through phase transfer catalysis as suggested in Scheme 1. The condensation of PDMS oligomers ($\bar{M}_n \approx 3000$ g mol^{-1}) in miniemulsion has been studied in a cationic [35] and anionic [36] polymerization systems with outstanding similarities. Polyaddition reactions in miniemulsion have also been reported [37,38]. Different arguments held for a bulk condensation reaction: (i) in the siloxane system, the activation energy found for condensation in emulsion is very close from values in solution where water is eliminated from the medium; (ii) polyaddition of various molecules (diol/diacid, diol/dialdehyde) has shown to occur only when both monomers were insoluble in water [37,38].

3.2.5. Redistribution

Redistribution reactions remain difficult to study as they do not involve specific variations in the system (the numbers of chains, the polymer conversion or cycle productions are not affected). They however show up in MALDI-TOF spectra (Fig. 5), where peaks are separated by one D unit (74 g mol^{-1}) instead of one *monomer* unit (i.e. D$_4$). MALDI distributions of samples withdrawn at various conversions also showed that redistribution reactions occur during the entire polymerization course. As for condensation, these reactions involving long-chains are believed to occur inside the particles.

4. Conclusion

The anionic polymerization in miniemulsion process has been applied to the synthesis of functional PDMS chains. These latter were further characterized by analytical techniques such as triple detection SEC or MALDI-TOF-MS. SEC^3 enabled measurements of absolute PDMS molar masses together with calculations of MHS parameters from which a universal calibration curve was plotted. MALDI-TOF-MS both confirmed the structure of the polymer chain (main-chain units, end-groups) and showed evidence of redistribution reactions from the commencement of polymerization.

The SEC analysis of small oligomers confirmed that in the low molar mass range universal calibration curve is not applicable. It also appeared that dihydroxy end-groups would cause the oligomers to skew on the columns through non-specific interactions, even in the presence of a hindered amine in the eluent.

Close examination of the results of molar mass analyzes together with previous results, showed that the main polymerization reactions (initiation, propagation, termination and backbiting) take place at the interface. In addition, contact angle measurements showed that chains of DP of 30 D units or more were long enough to lose their surface affinity, penetrate the particle and stop propagating. Still, slow molar mass evolution showed that side-reactions (condensation and redistribution) do occur inside the particles presumably through phase transfer catalysis. At high conversion better interface access enhance both reactions.

Another alternative mechanism was proposed long ago for the D_4 anionic polymerization in *emulsion* by Weyenberg et al. [39]. They stated that initiation and immediate termination produced disiloxanol oligomers that condense together in the water phase before reaching a critical size and re-entering the particles to further grow. Though it is now established that water is not a locus of reaction, [6] still short chains could condense at the interface. Kinetic studies on the condensation reactions of PDMS chains in miniemulsion catalyzed by OH^- are now in progress in our laboratory to establish whether short oligomers are likely to condense below DP_{crit}.

Acknowledgements

FG is grateful to Dr L. Bouteiller for fruitful conversations and Dr R. Balic for his critical reading of both original and subsequent manuscripts.

References

[1] De Gunzbourg A, Favier J-C, Hémery P. Polym Int 1994;35:179–88.
[2] Klimisch HM. In: Lee Smith A, editor. The analytical chemistry of silicones. New York: Wiley, 1991. p. 117–32.
[3] Kan C-Y, Zhu X-L, Yuan Q, Kong X-Z. Polym Adv Tech 1997;8:631–3.
[4] He W-D, Cao C-T, Pan C-Y. Polym Int 1996;39:31–6.
[5] Kong XZ, Ruckenstein E. J Appl Polym Sci 1999;73:2235–45.
[6] de Gunzbourg A, Maisonier S, Favier J-C, Maitre C, Masure M, Hemery P. Macromol Symp 1998;132:359.
[7] Gilbert RG. Emulsion polymerization: a mechanistic approach. London: Academic Press, 1995.
[8] Trathnigg B, Feichtenhofer S, Kollroser M. J Chromatogr, Part A 1997;786:75–84.
[9] Büyüktanir EA, Küçükyavuz Z. J Polym Sci, Part B 2000;38:2678–86.
[10] Zammit MD, Davis TP. Polymer 1997;38:4455–68.
[11] Hutchinson RA, Paquet DA, McMinn JH, Beuermann S, Fuller RE, Jackson C. DECHEMA Monographs 1995;131:467.
[12] Hunt SH, George GA. Polym Int 2000;49:633–5.
[13] Montaudo G, Montaudo MS, Puglisi C, Samperi F. Rapid Commun Mass Spectrom 1995;9:453.
[14] Servaty S, Köhler W, Meyer WH, Rosenauer C, Spickermann J, Räder HJ, Wegner G, Weier A. Macromolecules 1998;31:2468–74.
[15] Hill DJT, Preston CML, Whittaker AK, Hunt SM. Macromol Symp 2000;156:95–102.
[16] Dong X, Proctor A, Hercules DM. Macromolecules 1997;30:63–70.
[17] Lloyd PM, Suddaby KG, Varney JE, Scrivener E, Derrick PJ, Haddleton DM. Eur Mass Spectrom 1995;1:293–300.
[18] Götz H, Maschke U, Wagner T, Rosenauer C, Martin K, Ritz S, Ewen B. Macromol Chem Phys 2000;201:1311–6.
[19] Cypryk M, Sigwalt P. Macromolecules 1994;27:6245–53.
[20] Rubinsztajn S, Cypryk M, Chojnowski J. J Organometallic Chem 1989;367:27–37.
[21] Kala SV, Lykissa ED, Lebovitz RM. Anal Chem 1997;69:1267–72.
[22] Bischoff R, Sigwalt P. Polym Int 1995;36:57–71.
[23] Steinmeyer RD, Becker MA. In: Lee Smith A, editor. The analytical chemistry of silicones. New York: Wiley, 1991. p. 255–303.
[24] Buese MA. Macromolecules 1987;20:694–6.
[25] Lapp A, Herz J, Strazielle C. Makromol Chem 1985;186:1919–34.
[26] Kurata M, Tsunashima Y. Polymer handbook. 4th ed. New York: Wiley, 1999.
[27] Dourges M-A, Charleux B, Vairon J-P, Blais J-C, Bolbach G, Tabet J-C. Macromolecules 1999;32:2495–502.
[28] Cunanan CM, Ghazizadeh M, Buchen SY, Knight PM. J Cataract Refract Surg 1998;24:341–51.
[29] Bouali B, Ganachaud F, Chapel J-P, Pichot C, Lanteri P. J Colloid Interface Sci 1998;208:81–9.
[30] Jalbert C, Koberstein JT, Yilgor I, Gallagher P, Krukonis V. Macromolecules 1993;26:3069–74.
[31] Wagner R, Richter L, Wu Y, Weissmüller J, Reiners J, Hengge E, Kleewein A, Hassler K. Appl Organometallic Chem 1997;11:645–57.
[32] Maitre C, Ganachaud F, Ferreira O, Lutz J-F, Paintoux Y, Hémery P. Macromolecules 2000;33:7730–6.
[33] Behan N, Birkinshaw C. Macromol Rapid Comm 2000;21:884–6.
[34] Barrère M, Maitre C, Hemery P. To be published.
[35] Saam JC, Huebner DJ. J Polym Sci, Part A 1982;20:3351–68.
[36] Barrere M, Maitre C, Ganachaud F, Hemery P. Macromol Symp 2000;150:359–64.
[37] Baile M, Chou YJ, Saam JC. Polym Bull 1990;23:251–7.
[38] Landfester K, Tiarks F, Hentze H-P, Antonietti M. Macromol Chem Phys. 2000;201:1–5.
[39] Bey AE, Weyenberg DR, Seibles L. Polym Prepr 1970;11:995–6.
[40] Brzezinski J, Czlonkowska-Kohutnicka Z, Czarnecka B, Kornas-Calka A. Eur Polym J 1973;9:733–8.
[41] Zilliox JG, Roovers JEL, Bywater S. Macromolecules 1975;8:573–8.
[42] Mandik L, Foksova A, Foltyn J. J Appl Polym Sci 1979;24:395–404.