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Cationic polymerization of 2,4,6,8-tetramethylcyclotetrasiloxane processed by tuning the pH of the miniemulsion

Guillaume Palaprat [a], François Ganachaud [b], Monique Mauzac [a,*], Patrick Hémery [c]

[a] Laboratoire Interactions Moléculaires et Réactivité Chimique et Photochimique, UMR CNRS 5623, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse cedex 9, France
[b] Laboratoire de Chimie Macromoléculaire, UMR 5076 CNRS/ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier cedex 5, France
[c] Laboratoire de Chimie des Polymères, UMR CNRS 7610, Université Pierre et Marie Curie, tour 44-4 Place Jussieu, 75252 Paris cedex 5, France

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Abstract

The preparation of 2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) miniemulsions stabilized by commercial surfactants, i.e. sodium dodecylbenzenesulfonate (NaDBSA) and sodium laurate/lauric acid mixture, was studied and is first reported. Then, the pH was tuned in order to process polymerization through interfacial protonic initiation. With lauric acid, no polymerization was observed, even at high temperature or large acid contents. Such effect is ascribed to the poor dissociation and reactivity of high pKa's carboxylic acids. With NaDBSA, acidification by HCl was enough to initiate the polymerization, but the pH of the continuous phase was shown to have a strong effect on the polymerization process. Optimal conditions (at pH 5) gave chains with average number molar masses around 16,000 g mol^{-1} and polydispersity index close to 1.6, for a total conversion in polymer of about 60% after 2 h reaction. Lower pH (4.2) quickly led to a cross-linked network whereas at higher pH (6.1), conversions were too slow (around 10% after 350 min).

Keywords: Cationic polymerization; Emulsion; Poly(methylhydrogenosiloxane)

1. Introduction

Linear polymethylhydrogenosiloxanes or poly(methylhydrogenosiloxanes-*co*-dimethyl-siloxanes) are useful intermediate polymers for preparation of high value silicone materials, due to their easy derivation by hydrosilylation reactions with vinyl molecules. We are particularly interested in using these polymers to prepare some liquid crystalline materials. The mesomorphous polysiloxanes that we have previously synthesized have shown unusual mechanical behavior [1]. Besides, we recently proved that they can also lead to molecular imprinted networks with high capacity and enantioselectivity [2]. For these two domains we are looking for polymers with higher molar masses and lower polydispersity than those of commercial products.

Homo and copolymers containing hydrogenosilane bonds are, however, quite difficult to prepare and store, due to their sensitivity towards nucleophilic agents. Once Si–H groups hydrolyze into Si–OH, these condense each other to raise an insoluble gel, together with a release of (harmful) hydrogen gas. The difficulty is then to favor the formation of linear poly(methylhydrogenosiloxane)s (PMHS) while avoiding the hydrolysis of the silane bonds.

The preparation of PMHS is recorded in the academic literature since 1978. Lasocki and Graczyk [3,4] were the first to perform cationic ring-opening homopolymerization of 2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) and its copolymerization with octamethylcyclo–tetrasiloxane (D_4). The reactions were performed in CH_2Cl_2, CCl_4 or CH_3NO_2 using methanesulfonic or benzenesulfonic acids as initiators. The molar masses of the polysiloxane were set to a maximum of about 12,000 g mol^{-1}, due to side reactions with sulfonate groups or residual water, leading, respectively, to termination or transfer reactions. Sigwalt and co-workers [5] also performed the cationic polymerization of D_4^H in dichloromethane solution, this time using a super-acid (trifluoromethanesulfonic acid) as initiator. Even if molar masses reached as high as 100,000 g mol^{-1}, the polymer conversion never exceeded 60% and a notable amount of insoluble cross-linked material was observed, despite thorough drying of glassware and reactants.

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* Corresponding author. Tel.: +33 5 61 55 86 96; fax: +33 5 61 55 81 55.
E-mail address: mauzac@chimie.ups-tlse.fr (M. Mauzac).

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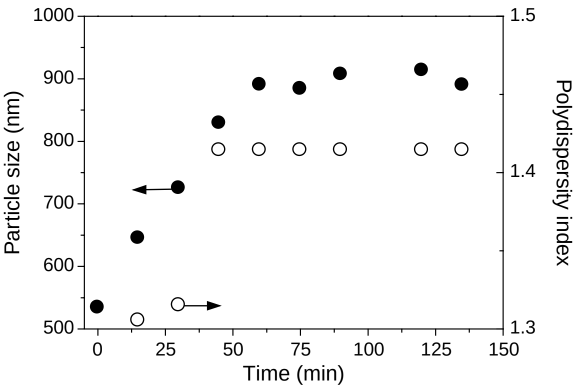


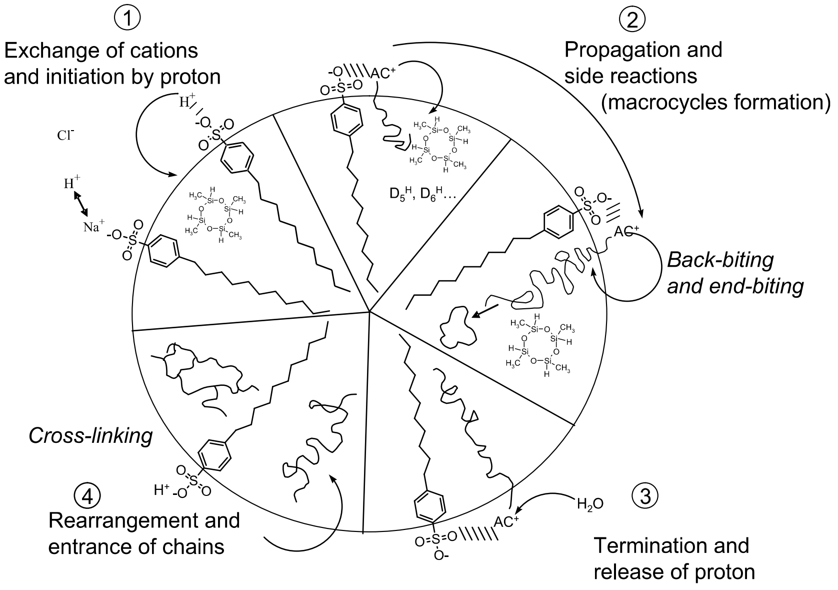
Fig. 1. Average diameter (plain symbol) and corresponding polydispersity index (open symbol) of droplets as a function of time. Data obtained for a miniemulsion of D_4^H performed at 35 °C with 10/90 sodium laurate/lauric acid mixture (Table 1, run 9).

More recently it was shown [6] that cationic polymerization of D_4^H could be performed under simpler experimental conditions, in aqueous emulsion, using dodecylbenzenesulfonic acid (DBSA) as surfactant/initiator (INISURF) and a nonionic surfactant (Brij35) as coemulsifier. The role of this latter was to slow down the polymerization rate, compared to runs carried out with the strong acid alone, and thus to avoid cross-linking reactions. Ninety percent of linear chains (the rest of low molecular weight cycles) were obtained with molar masses going from 5000 to 70,000 g mol^{-1}, a priori without formation of networks. Yactine et al. [7] recently proposed new conditions to produce high molar masses with high conversions and no formation of gel, using a surfactant bearing mono- and diphosphonic acid groups. The obtained chains present molar masses close to 23,000 g mol^{-1} and a polydispersity index lower than 2, but with a large amount of macrocycles generated after 5 h reaction.

The mechanism of ring opening polymerization (ROP) of cyclosiloxanes proposed previously [6,8] is quite complex (Fig. 1). Initiation reaction is induced by protons provided via the initiator/surfactant to open a cycle. This initiation step is slow and limits the overall rate. Various kinds of active centers (siloxonium, cationic silicenium…) could a priori be generated, [9] but no clear answer are available so far; the multiplicity of growing species may, however, explained the higher polydispersity observed compared to anionic initiations [10,11]. Polymerization proceeds also at the particle surface, whereas intramolecular and intermolecular redistribution reactions produce small and large cycles, respectively.

Some authors recently suggested [7] that the intraparticular condensation reactions occurring with PDMS cannot exist in the particular case of PMHS synthesis. Indeed, transfer reaction by water molecule produces a silanol chain-end that rapidly rearrange in an irreversible one [6,7] [either $(CH_3)_3Si$ or $(CH_3)_2SiH$] unable to undergo condensation. Another drawback in PMHS synthesis is the hydrolysis reaction of the silane groups, catalyzed by protons, that is likely to convert the polymer chains into an irreversible network (Scheme 1).

The present article tends to stress the line on the effect of the pH and acidity constant of the surfactant/initiator in the synthesis of poly(methylhydrogenosiloxane)s by cationic polymerization of D_4^H. Surfactants with extreme pKa values (sulfonate and carboxylate fatty acids) were tested, mainly by tuning the pH value of the continuous phase. These surfactants are commercially available (unlike fatty phosphonic acids [7]) and sufficiently hydrophilic to recover PMHS with no surfactant residues (contrary to experiments done with Brij [6]).



Scheme 1. Polymerization mechanism as proposed from previous studies, and exemplified with DBSA surfactant (numbers 1–4 symbolize the various steps; AC, active center).

2. Experimental part

2.1. Materials

2,4,6,8-Tetramethylcyclotetrasiloxane (D_4^H), from ABCR, was used without further purification. Its purity ($>99\%$) was checked by gas chromatography before polymer synthesis. All other products were of analytical grade (purity $>98\%$) and used as supplied. Sodium dodecylbenzenesulfonate (NaDBSA) was purchased from Acros Organics, lauric acid and sodium laurate from Fluka, and Alun salt ($AlKS_2O_8 \cdot H_2O$) from Acros Organics. Diluted hydrochloric acid and sodium hydroxide solutions were prepared from products commercialized by Prolabo. All solvents, i.e. toluene (SDS), dichloromethane (SDS), $CDCl_3$ (Euriso Top) were of HPLC analytical grade.

2.2. Methods

Miniemulsions were prepared using a Bioblock Scientific Vibra Cell sonicator with a CV17 probe. The pH of the emulsions were measured with a Thermo Orion 420A + pH-meter. Centrifugation was realized at 4000 rpm on a BHG-Hermle Z230 bench apparatus. Gas chromatography (GC) was carried out on a Varian Chrompack CP-3800 equipped with a capillary Restek Rtx-1 column with helium as vector gas, an 'on-column' injector and a FID detector. Column temperatures were programmed as follow: 40 °C for 1 min then from 40 to 280 °C at 15 °C min^{-1}. The temperature of the detector was fixed at 300 °C. Size exclusion chromatography (SEC) was conducted on a Waters Associates equipment with three Styragel® HR(7 μm) 7.8 mm × 300 mm columns (10^4, 10^3, 100 Å pore size) thermostated at 35 °C. Toluene was used as eluent with a flow rate of 1.2 mL min^{-1}. A differential refractometer (Waters associates) was associated as detector with a light-scattering diffusion mini Dawn® apparatus purchased from Wyatt Technology Corporation. The d*n*/d*c* refractive index increment values taken into account for D_4^H monomer and linear polymethylhydrogenosiloxane were, respectively, -0.081 and -0.078 (the small and macrocycle species were not specifically analyzed). ^{29}Si NMR spectra were recorded using a Brüker AC 300 spectrometer equipped with a 5 mm diameter BBO BB-1H ^{29}Si probe. $CDCl_3$ was used as solvent and iron III acetylacetonate ($Fe(acac)_3$) was added as relaxation agent [6] (15 mg/mL). Particle size measurements were determined on a Malvern instruments, Zetasizer model 3000 HSa. The PDI (polydispersity index) was calculated from the mean deviation Poly given by the device using the following relation: $PDI = (1 + poly^2)^{1/2}$.

2.3. Synthesis of PMHS

The procedures of emulsification, polymerization and emulsion breaking are similar to those previously applied [6,7,10,11]. Typically, 200 mL of an 2.6×10^{-3} M aqueous solution of surfactant (NaDBSA or various mixtures of lauric acid/sodium laurate) were emulsified in a beaker by the sonicator (power 7–55 W) during 2 min 20 mL of monomer were added drop by drop at the beginning of the emulsification. The recipe was kept in an ice bath to limit overheating of the mixture. In case of NaDBSA, the medium was acidified at various pH by addition of drops of hydrochloric acid (10^{-2} M) to initiate the polymerization. The emulsion was then transferred into a reactor maintained at different temperatures and continuously stirred at 100 rpm. At regular time intervals, 2 mL aliquots were withdrawn and neutralized (pH is fixed to around 7 to limit cross-linking reactions) with few drops of sodium hydroxide (10^{-1} M solution) to stop the polymerization. The emulsion was broken by addition of Alun salt and an equivalent volume of CH_2Cl_2, then phase separation was achieved by centrifugation. The organic phase was dried on $MgSO_4$ before filtration and solvent evaporation. A fraction of each sample was dissolved in toluene and immediately analyzed by SEC in order to determine the molar masses and the conversion ratio.

3. Results and discussion

All the formulations tested in this study are summarized in Table 1. Two conventional anionic surfactants (sodium laurate

Table 1
Formulations used in this study with NaDBSA (runs 1–6) and lauric acid/sodium laurate mixtures (runs 7–13)

Run	Monomer concentration (mol/L)	Surfactant concentration ($\times 10^3$ mol/L)	Temperature (°C)	Lauric acid/laurate (molar ratio)	pH
1	0.41	3.2	35	–	5.0[a]
2	0.37	2.6	35	–	5.0[a]
3	0.37	2.6	35	–	5.0[a]
4	0.37	2.6	35	–	4.1[a]
5	0.37	2.6	35	–	4.2[a]
6	0.37	2.6	35	–	6.1[a]
7[b]	0.37	2.6	35	10/90	–
8[b]	0.37	2.6	35	50/50	–
9[b]	0.37	2.6	35	90/10	6.75
10[b]	0.37	2.6	60	90/10	
11[b]	0.37	2.6	85	90/10	
12[b]	0.37	3.2	35	90/10	6.35
13[b]	0.37	2.6	35	90/10	4.2[a]

[a] Addition of hydrochloric acid solution.

[b] Lauric acid/sodium laurate mixtures.

and sodium dodecylbenzenesulfonate, NaDBSA) were chosen. The interfacial acidity was tuned by adding hydrochloric acid or the conjugated acid (lauric acid) in the case of sodium laurate surfactant.

3.1. Miniemulsions prepared with different surfactants

Lauric acid (pKa = 5.02) alone, cannot emulsify the monomer into stable droplets. This acid is weakly soluble in water whereas it is perfectly soluble in D_4^H; it hardly dissociates in water and does not locate at the interface. Lauric acid/sodium laurate mixtures were then tested, and produced stable miniemulsions, even at low laurate salt content. One example of the evolutions of the particle size and polydispersity with time is reported in Fig. 1. Ostwald ripening induces an increase of the average particle size and polydispersity index with time. Each parameter then reach a plateau, the former due to a very slow ripening process once the volume of the various droplets are not significantly different, the latter corresponding to the limit of the apparatus.

Whatever the surfactant ratios (from 10/90 to 90/10 in lauric acid/sodium laurate) or the temperature (from 35 up to 85 °C), no formulations were able to initiate the ROP of D_4^H. The continuous evolution of particle size with time is indeed an indication that no polymer is formed inside the droplets, since Ostwald ripening ceases for a conversion in polymer in the order of 10% [12]. Even after lowering the pH to 4.2, by addition of hydrochloric acid (Table 1; run 13) no polymerization was observed, although the emulsion remained stable.

On the other hand, miniemulsions prepared with sodium dodecylbenzene sulfonate, whether they were acidified or not, exhibit a strong difference in particle size evolution. Fig. 2 reports two examples of particle size and size distribution evolution with time where NaDBSA concentration was varied and pH set at 5 (Table 1, runs 1 and 2).

If the surfactant content is large enough (here 3.2 mmol L^{-1}), both size and polydispersity of the droplets/particles remain almost constants. This is the main criteria of a true miniemulsion system, i.e. each droplet is converted into a particle. Final latexes show an average particle diameter around 345 nm, with a good homogeneity, and stability for months. When the NaDBSA content is lower (2.6 mmol L^{-1}), Ostwald ripening occurs alike in the lauric acid system. However, once polymerization proceeds, the tendency is inverted: particle size decreases to a final average value lower than the system with large contents of surfactant (215 against 345 nm), whereas polydispersity ends up to a similar value (set at about 1.005), indicating a very good latex homogeneity. Such 'inverse ripening' has been justified by looking at the thermodynamics of droplets containing low contents of insoluble species, here the polymer [13]. According to the low particle size reached by the final latex dispersion, nucleation of new particles is likely to occur in the present systems. This behavior may partly be explained by the hydrophobicity of the cyclosiloxanes, thus entering and converting micelles. Such micellar nucleation hypothesis is in agreement with recent reports on D_4 emulsion polymerization [12–13].

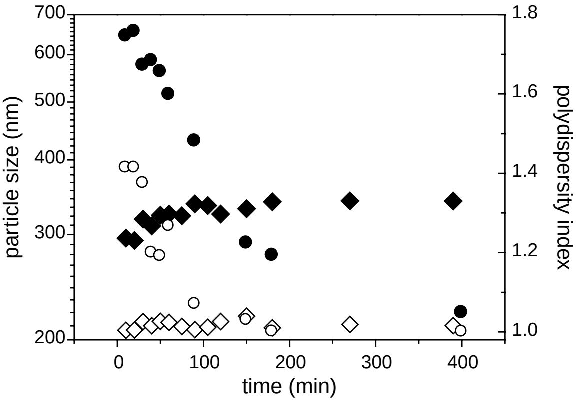


Fig. 2. Average diameter (plain symbols) and corresponding polydispersity index (open symbols) of particles as a function of time. Data obtained for the emulsion of D_4^H performed at 35 °C with NaDBSA (Table 1, ◇: [surfactant] = 3.2×10^{-3} mol/L; run 1 and ○: [surfactant] = 2.6×10^{-3} mol/L run 2).

3.2. Polymerization of D_4^H catalyzed by NaDBSA

In the following, the polymerization of D_4^H performed only with NaDBSA as a surfactant and at different pHs (from 4.1 to 6.1) are described. All informations, including the polymer conversion, the molar masses and the polydispersity index values, reported in Table 2, were obtained from the exploitation of SEC chromatograms as a function of time, an example of which is given in Fig. 3.

3.2.1. Kinetics and molar mass evolutions

The kinetics of polymerization was studied by integrating the monomer and polymer peaks in the SEC chromatograms, and correcting by the respective refractive indexes (Section 2). In the example given Fig. 3, one sees that the proportion of monomer decreases, but new cycles of larger units formed, as well as polymer chains of quite complex distribution appear (vide infra). Fig. 4, reporting the polymer conversion versus time, clearly shows that for the lowest acidity, the reaction rate is very low (only 14% of monomer had disappeared after 6 h). On the other hand, there are no striking variations in polymerization rate between the two experiments performed at pH = 5 and 4.2 (around 50% in conversion after 100 min of reaction).

Table 2
Main results for polymerization of D_4^H in miniemulsion with NaDBSA

Run	Time for max conversion (min)	Max conversion (%)	M_n ($\times10^{-3}$)	M_w/M_n
1	60	93	161	1.4
2	120	55	16	1.6
3	120	62	16	1.9
4	100	96	163	1.4
5	140	87	274	2
6	360	14	13	1.7

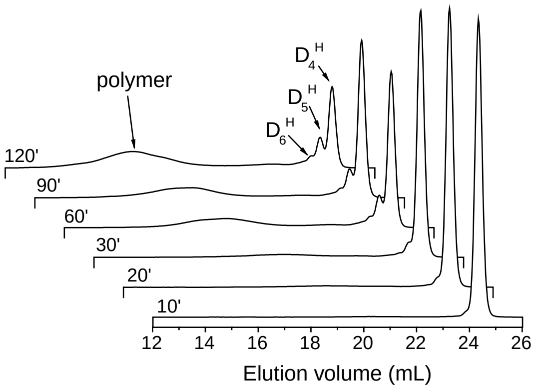


Fig. 3. SEC traces of samples extracted at different times from a miniemulsion prepared with [NaDBSA] = 2.6×10^{-3} mol/L and pH = 5 (Tables 1 and 2, run 3).

In Fig. 5 are plotted the average number molar mass and polydispersity index as a function of time for the three experiments. In all cases, the molar masses rise quickly up to 12,000 g mol^{-1} and then gradually to a plateau at about 16,000 g mol^{-1} whereas the polydispersity index decreases from 2 to about 1.6 in best conditions. A good reproducibility was observed between the two experiments (runs 2 and 3) realized in these conditions (Table 2).

3.2.2. *Cross-linking and redistribution reactions*

In experiments where polymerization proceeded readily, the reaction was stopped after 2 h due to some cross-linking phenomena appearing. Before that, no loss of materials by gelling was evidenced (the sample mass calculated by the SEC chromatograph using the values of the refractive index increment corresponds to the introduced mass). Besides, the polydispersity index rised sharply from 1.6 to about 2 after roughly 40% of conversion, which let us believe that before gelling, a 'sol' state may exist (i.e. only few condensations give a branched polymer still soluble in toluene) (Fig. 5).

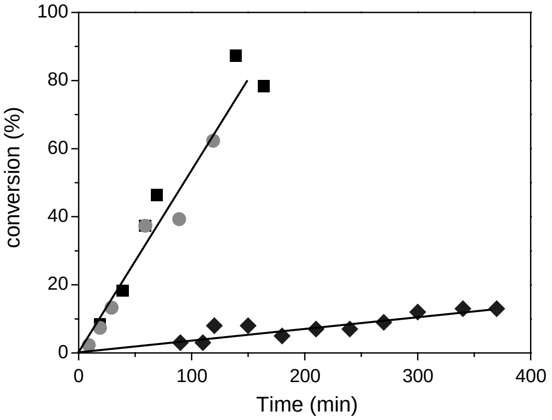


Fig. 4. Polymer conversion as a function of time for pH 4.2 (■ run 5), pH 5 (● run 3), pH 6.1 (◆ run 6) with NaDBSA-HCl ([NaDBSA] = 2.6×10^{-3} mol L^{-1}, $D_4^H = 0.37$ mol L^{-1}). Lignes are only guides for eyes.

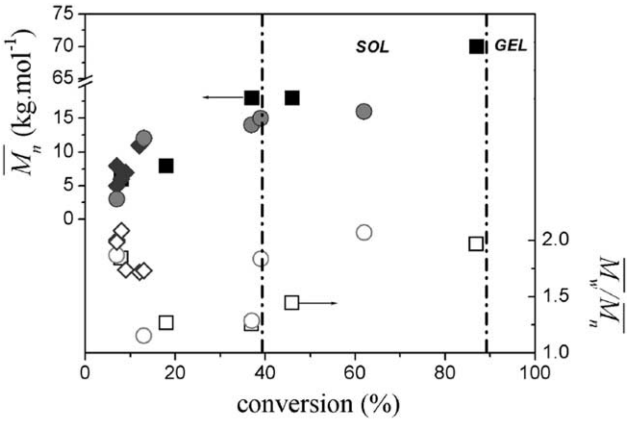


Fig. 5. Evolutions of average number molar masses (plain symbols) and polydispersity index (open symbols) as a function of conversion for different pH (similar symbols as in Fig. 4).

To examine this point, we took a closer look at the polymer distributions given by SEC in Fig. 3. Three molar mass distributions in the experiment carried out at pH 5, where the polydispersity index shows the sharpest rise with conversion (Fig. 5, circles), are given in Fig. 6. A clear bimodal distribution is observed for the two first samples (taken at 60 and 90'), centred at 6000 and 13,000 g mol^{-1} approximately. The SEC traces do not allow to conclude whether this bimodal distribution is the result of one or few condensation reactions between two chains, or end-biting: both branched chains and macrocycles have hydrodynamic volumes that differ from linear chains. One key point anyway is that, at 120 min, a shoulder appears on the large molar mass edge, thus reflecting some condensations to occur. Such cross-linking reactions are quite slow with time, thus reflecting the slow transition from a sol state to a gel one with time (or conversion) depicted in Fig. 5.

^{29}Si NMR analyses were also performed with one sample extracted from run 3 after 120' (Fig. 7). Although a long accumulation time was taken, only the signal of the repeating unit is visible with a small shoulder on the left (−34 ppm) corresponding to a weak proportion of small cycles. No peak of

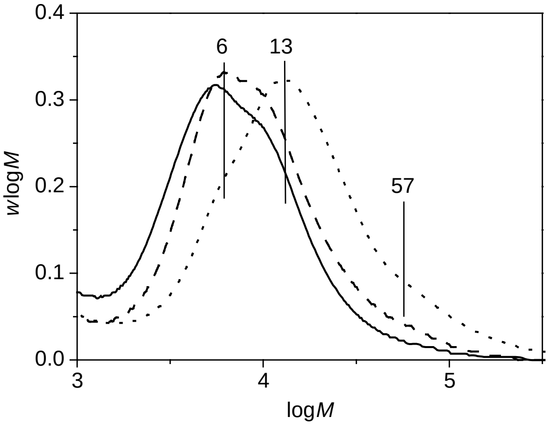


Fig. 6. Molar mass distributions of polymers in samples extracted from run 3. (—) 60′ (37% conv.). (– –) 90′ (39% conv.); (···) 120′ (62% conv). Values given in the graph are expressed in kg mol^{-1}.

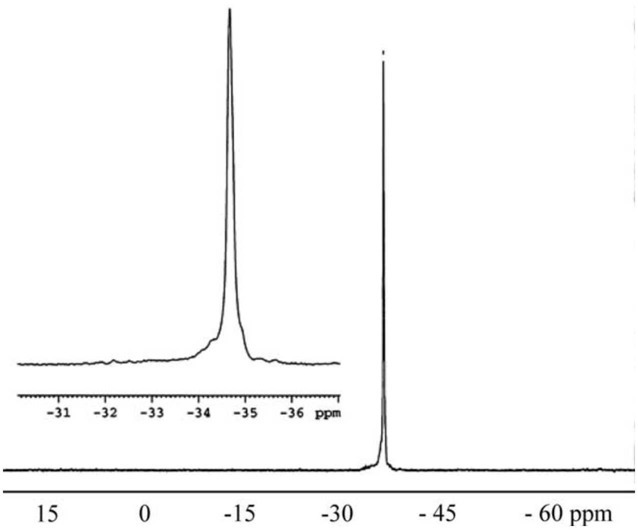


Fig. 7. ^{29}Si NMR spectrum of sample from run 3, 120′ using Fe(acac)$_3$ as relaxation agent. Accumulation conditions: 300 MHz, CDCl$_3$, 25 °C, 10,000 scans, delay between pulses = 10 s.

silsesquioxanes ($CH_3SiO_{3/2}$) relating to cross-linking reactions via oxygen bridges are observed at −65 ppm. Likewise, no chain end groups, such as $(CH_3)_3Si$ (10 ppm) or $(CH_3)_2SiH$ (−4 ppm) moieties can be observed. Such absence can be explained by the low quantity of end groups and cross-linking points relative to the repeat units ($M_n = 16{,}000$ g mol^{-1}). Another explanation would again be the large number of macrocycles that may form after polymerization proceeded, as confirmed recently in the cationic polymerization of D_4^H using fatty phosphonic acids [7].

4. Conclusion

The present study showed that D_4^H polymerization process was optimized by using NaDBSA-HCl system and fixing the value of the pH at 5. In these conditions, average number molar masses reached 16,000 g mol^{-1} in 2 h with a polymolecularity of 1.6 and 55–60% conversion. Protons are sufficiently present at the surface to initiate the polymerization without catalyzing side-reactions until 60% conversion. Before reaching this limiting value, linear rise of the molar masses with conversion is believed to arise from few cross-linking reaction between chains, thus creating branched polymers (‘sol’ state). Weak fatty acids alike lauric acid (pKa = 5.02) have been demonstrated to be inefficient to stabilize a miniemulsion. Although an additive little quantity of salt derivative improves the stabilization of the emulsion, protons should be too hardly associated with the surfactant to initiate the ring opening process.

From the viewpoint of the different studies, [6,7] including the present work, performed on the cationic polymerization of D_4^H in miniemulsion, it now appears that the pH is not the main parameter for successful polymerization. Most likely, the strength of the acid born by the surfactant is responsible for interfacial polymerization. For instance, at pH around 6 or even 4, lauric acid did not start a polymerization, whereas NaDBSA did; similarly, polymerization of D_4^H at pH 2 proceeded readily with phosphonic acids, whereas it gave a crosslinked material once using NaDBSA. We will report soon on the copolymerization of D_4^H and D_4 in miniemulsion to generate multiblock copolymers.

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