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Facile Manufacture and Storage of Poly(methylhydrogenosiloxane)s

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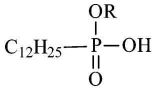
ABSTRACT: This paper describes the ring-opening polymerization of 2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) in miniemulsion, using mono- and diphosphonic acid surfactants. In the simplest formulation conditions, polymerization proceeds in less than 15 min to generate linear poly(methylhydrogenosiloxane) (PMHS) of large molar masses (typical number-average of 25 kg/mol), of low polydispersities (around 2), and in good yields (up to 94%). Molar masses can be tuned at will since for similar conversions but increasing times, $\overline{M_n}$ varies between 10 and 30 kg/mol. After 4 h reaction, some redistribution reactions start to proceed, responsible for PMHS chains switching into macrocycles. It was shown that rising the pH to stop the polymerization and breaking the emulsion with excess of alun salt induced hydrolysis/condensation reactions, which rapidly convert the polymer chains into an unwished macrogel. Rather, extracting the polymer by simple centrifugation and using the diacid surfactant induce a physical gelling that very efficiently suppresses side reactions, as shown by minor evolution of the molar mass distribution for 10 months.

Introduction

Linear silicone chains with reactive groups, e.g., poly(methylhydrogenosiloxane) (PMHS), are sought from many end-users that want to produce comb polymer chains with definite properties, such as pro- or anti-adhesion behaviors, amphiphilicity or hydrophobicity. These are prepared by hydrosilylation reaction between the Si−H groups and olefin-functionalized molecules, whenever these latter are attached to a silicon atom or not.[1] The main drawback of using PMHS as a primary material is its sensitivity to bases; Si−H hydrolyzes into Si−OH[2] which condenses on itself to raise an insoluble gel while releasing hydrogen gas (this property is used to prepare silicone foams). Most references described the synthesis of PDMS-*co*-PMHS by usual cationic copolymerization in solution, i.e., ring-opening polymerization of 4−6 units of cyclodimethyl and cyclomethylhydrogenosiloxane, respectively, using anhydrous triflic acid as a catalyst and hexamethyldisiloxane as an end-capper.[3−6] Homo-PMHS synthesis was hardly reported, and the maximal average molar mass that we could trace was 9000 g/mol in a patent.[7] Only 1000−3000 g/mol PMHS are supplied commercially by ABCR, sometimes with molar mass distributions that show considerable deviations from the attended one.

Clearly, there is a need for a simple, quick, reliable, and reproducible technique to prepare long homo-PMHS chains at will and stock them, if not permanently, at least a few months in a refrigerator. A previous study from the main author's previous team[8] already reported conditions to prepare PMHS from the commercially available cyclic monomer, 2,4,6,8-tetramethyltetracyclosiloxane or D_4^H by cationic ring-opening polymerization (ROP) in (mini)emulsion. Basically, dodecylbenzenesulfonic acid (DBSA) was used as a proton source, whereas a nonionic surfactant (namely Brij35) competed with DBSA adsorption on the surface to slow the kinetics of reactions and to avoid parasite cross-linking. Chains with average molar masses of 5−70 kg/mol were produced, depending on the contents of surfactants and water, with no apparent formation of $SiO_{3/2}$ units ("T" network knots) in the backbone chain. Unfortunately, nonionic surfactants are difficult to remove from the polymer even after repeated methanol precipitations, which in turns induce PMHS gelling. Other unpublished preliminary experiments from the same group using different surfactant systems failed to produce clean PMHS material. Using the sodium salt of DBSA solely and tuning the pH of the continuous phase led to high loads of gels before the polymerization was completed, whereas weak fatty acids such as lauric acid were unable both to stabilize the miniemulsion and to catalyze the polymerization. These unsuccessful experiments nonetheless showed that a surfactant with intermediate acidity between sulfonic and carboxylic acids may catalyze the polymerization without favoring hydrolysis reactions.

Chart 1



$C_{12}H_{25}-P(=O)(OR)-OH$

R = CH_3 **1**

H **2**

The present article proposes new conditions to produce PMHS with high molar masses, at high conversions, and with no formation of gel over a due period of time. We chose to work with surfactants bearing phosphonic (di)acid groups (Chart 1), of primary pK_a's around 2 (the second pK_a of the diacid arises at 7, too high for it to catalyze the polymerization). These surfactants, whose syntheses are well-documented,[9] are known to exhibit complex physicochemical properties.[10,11] In the conditions of the present study, the diluted solution of monophosphonic acid produces vesicles, whereas the diacid surfactant phase separates from water under a lamellar solution. They were also extensively used for their intrinsic surface activities in catanionic systems.[12] This study is part of a larger program on the syntheses and use of phosphonic monomers,[13] "surfmers" (surface-active monomers)[14] and surfactants,[9] in modern emulsion-designed anticorrosive coatings.

Experimental Part

Materials. All products were of analytical grade (>98% in purity) and received from Aldrich unless otherwise stated. D_4^H

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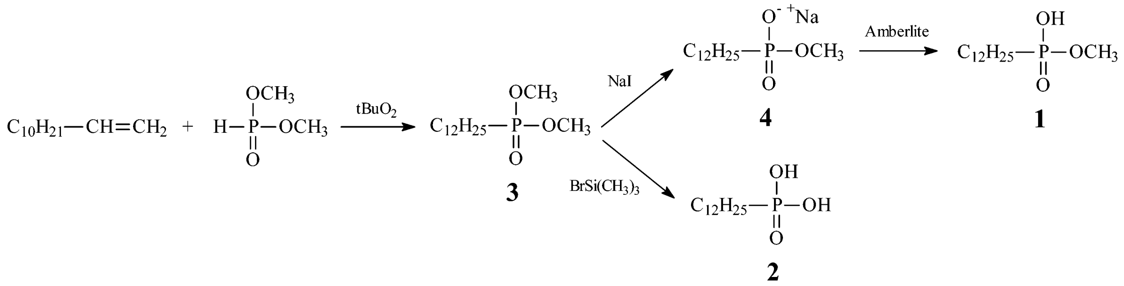
Table 1. Recipes and Main Features of D_4^H Cationic ROP Process Performed in This Study

run	surfactant concn ($\times 10^3$ mol/L)	monomer concn (mol/L)	temp (°C)	time for max conv (h)	max conv (%)	particle size (nm)	SD (nm)	$\overline{M_n}$ (kg/mol)	$\overline{M_w}/\overline{M_n}$
1	18.3	0.69	25	3	94	235	160	23.0	1.8
2	18.3	1.19	25	3	93	340	130	17.8	2.2
3	18.3	1.55	25	2	92	685	240	20.2	2.4
4	13.7	0.69	25	2		300	300	21.2	1.6
5	9.3	0.69	25	1.5	94	470	270	28.3	1.7
6	6.9	0.69	25	2	92	525	790	33.5	2.5
7	4.7	0.69	25	1.5	94	620	140	45.5	3.9
8	9.3	0.69	0	4	92	*b*	*b*	27.7	1.9
9	9.3	0.69	60	0.5	93	*b*	*b*	30.9	2.2
10[a]	9.3	0.69	25	1.5	91	470	120	20.0	2.1

[a] Run carried out with the diacid **2**. [b] Not measured.

Scheme 1



was purchased from ABCR. Dimethylhydrogenophosphonate (DMHP), triethylamine (TEA), di-*tert*-butyl peroxide, 1-dodecene, and the solvents were used as received.

Methods. The ^1H and ^{31}P NMR spectra have been registered at room temperature with a Bruker AC 200 instrument, whereas ^{29}Si NMR was achieved on a Bruker WH250 apparatus. $CDCl_3$ was used as the solvent in all cases. Tetramethylsilane (TMS) was used as a reference in ^1H and ^{29}Si NMR; *o*-phosphoric acid (H_3PO_4) was the reference for ^{31}P NMR. For ^{29}Si NMR, two procedures of accumulation were chosen, whether the signal from H-bearing silicon atoms were enhanced and doubled (decoupling procedure) or irradiated (coupling procedure). The letters s, d, t, and m correspond respectively to singlet, doublet, triplet, and multiplet, and the chemical shifts are given in ppm.

Particle size measurements were performed on a Nanotrac 250 from Microtrac, a particle size analyzer that makes use of backscattered quasi-elastic light scattering. Samples were analyzed without further dilution. Intensity diameters and standard deviations are reported in Table 1 to fit with data given by conventional quasi-elastic light scattering measurements.

Electrospray mass spectrometry measurements were carried out on a Q-Tof Micromass apparatus. PMHS was dissolved in acetonitrile prior to analysis and vectorized by nitrogen at 5 mL/min. The other operating conditions were a capillary voltage of 3000 V, a cone tension of 20 V, and temperatures of 100 °C for the source and 120 °C for desolvation.

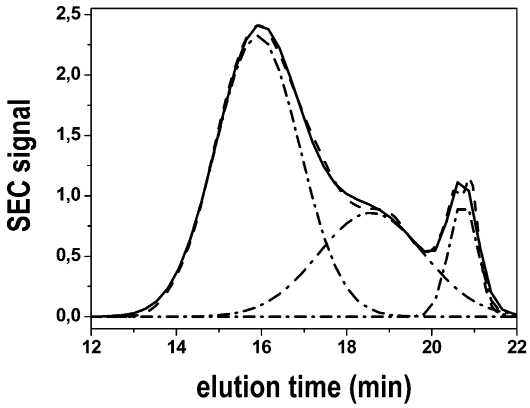


Figure 1. Deconvoluted SEC trace of the sample taken after 24 h in the model experiment (see last SEC trace in Figure 2a): (– –) SEC trace; (– • –) Gaussian peaks for different populations; (—) sum of three deconvoluted spectrum.

Size exclusion analyses (SEC) were conducted on a Spectra Physics equipment using two identical Polymer Labs columns (PL 5 μm Mixed-D) and a precolumn (PL 5 μm Guard). Toluene was used as the eluent with a flow rate of 1 mL/min. Columns were calibrated by polystyrene standards that exhibit similar hydrodynamic volumes as poly(dimethylsiloxane)s (PDMS) with molar masses above 2000 g/mol. SEC traces were deconvoluted by a Gaussian multipeak procedure found in the ORIGIN v7 program, an example of which is shown in Figure 1. Conversions were determined from integration of the three peaks separated by deconvolution, corresponding to the contents to polymer, macrocycles, and small cycles. Cycle/polymer refractive indexes were not corrected here.

Gas chromatography (GC) was carried out on a HP5890 Series II apparatus equipped with a capillary column DB-1, an on-column injector, and a FID detector. A typical temperature cycle was as follows: 1 min at 40 °C, temperature gradient of 15 °C/min up to 240 °C, 5 min at 250 °C.

Differential scanning calorimetry (DSC) traces were taken on a Perkin-Elmer Pyris 1 apparatus. The sample, weighting 15 mg, was placed in an aluminum sample holder and then in a calorimeter where it was heated directly at the rate of 20°/min from −150 up to 100 °C. Two rising scans were taken in the row.

Surfactant Synthesis. These were prepared according to the procedure recently published (ref 9) and summarized in Scheme 1. Final products were stored under nitrogen and in the dark and were pure at greater than 98% after recrystallization.

*Synthesis of Dimethyldodecylphosphonate (**3**).* In a 500 mL three-necked flask fitted with a condenser, nitrogen flux, and pressure-equalizing dropping funnel, 91.7 g (0.834 mol) of dimethylhydrogen phosphonate (DMHP) was introduced under argon bubbling. Then the temperature was increased up to 135 °C. 70 g (0.417 mol) of 1-dodecene containing 3 g (2.1×10^{-2} mol) of di-*tert*-butyl peroxide were added dropwise. The reaction mixture was continuously stirred at 135 °C for 10 h and then distilled under vacuum (6×10^{-1} mmHg, 15 °C) to eliminate the residual DMHP. The telomer **3** was distilled under high vacuum (2×10^{-2} mmHg, 122 °C) at a final yield of ~70%. ^{1}H NMR: $\delta = 0.6$ (t, 3H), 1−1.6 (m, 22H), 3.45 (d, 6H). ^{31}P NMR: $\delta = 35.51$ (RP(O)(OCH$_3$)$_2$).

*Hydrolysis of **3**.* In a 100 mL three-necked flask equipped with a reverse condenser and magnetic stirrer, 30 g (0.108 mol) of dimethyldodecylphosphonate (**3**) with 19.5 g (0.130 mol) of NaI and 100 mL of butan-2-one were introduced. The mixture was kept under reflux (100 °C) for 12 h and then maintained under stirring at room temperature for 6 h. The solid formed was filtered and washed with a large excess of anhydrous acetone. After treatment of the solution under vacuum, 28.4 g of sodium methyldodecylphosphonate (~95% yield) was recovered. ^{1}H NMR: $\delta = 0.9$ (t, 3H), 1.2−1.8 (m, 22H), 3.5 (d, 3H). ^{31}P NMR: $\delta = 29.03$ (RP(O)(OCH$_3$)(ONa).

*Synthesis of Methyldodecylmonophosphonic Acid (**1**).* 7.8 g of sodium methyldodecylphosphonate (**4**) were dissolved in 100 mL of methanol. The solution was filtered through a column filled with a proton-exchange resin (Amberlite IR120). The methyldodecylmonophosphonic acid (**1**) was recovered in quantitative yield after evaporation of solvent. ^{1}H NMR: $\delta = 0.9$ (t, 3H), 1−2 (m, 22H), 3.7 (d, 3H), 11.7 (s, 1H).^{31}P NMR: $\delta = 37.25$ (RP(O)(OCH$_3$)(OH).

*Synthesis of Dodecyldiphosphonic Acid (**2**).* In a 100 mL three-necked flask, equipped with a reverse condenser and a magnetic stirrer, 30 g (0.108 mol) of dimethyldodecylphosphonate (**3**) and 50 mL of dichloromethane were cooled at 0 °C. In a second step, 41.31 g (0.27 mol) of BrSiMe$_3$ was introduced drop by drop. The mixture was kept at 40 °C for 3 h and then maintained under stirring at room temperature for 6 h. Dichloromethane was evaporated, and the recovered solid was dissolved in methanol before precipitation in pentane. The white solid formed was filtered and washed with anhydrous pentane. After drying under vacuum, the white powder was stored in a desiccator. Yield: 90%. ^{1}H NMR: $\delta = 0.85$ (t, 3H), 1.1−1.8 (m, 22H), 5.25 (s, 2H). ^{31}P NMR: $\delta = 31.54$ (RP(O)-(OH)$_2$).

Synthesis and Extraction of PMHS. Polymerizations were carried out by mixing the viscous aqueous solution of surfactant and monomer prior to ultrasonication (2 min on a Heat Systems Sonicator, position 7). From time to time, samples were pipetted from the beaker, from which the emulsion particle size was automatically analyzed. Samples were taken, poured in test tubes, and neutralized by few drops of a diluted hydroxide sodium solution (0.1 M) to be sure to stop the polymerization, even if it eventually led to cross-linking. Miniemulsions were then frozen in liquid nitrogen and let to warm up at room temperature. Alun salt (AlKS$_2$O$_8$) and dichloromethane addition and centrifugation on a bench apparatus (2000 rpm, 10 min, DuPont Instruments Sorvall General Laboratory Centrifuge-2B) were necessary to improve the separation between aqueous and organic phase. After removal of the aqueous phase, the organic phase was dried on a rotavapor and rapidly analyzed by SEC (less than 24 h rest in the test tube, before it gelled).

The procedure for extracting the final emulsion is similar to the one given above, with two noticeable exceptions: the emulsion was neither neutralized nor frozen in liquid nitrogen. Also, only a little content of alun salt was added, since this salt is slightly basic and causes cross-linking upon pouring large excess during the sample treatment. The organic and water phases were likely separated by longer centrifugation (2000 rpm, 30 min), and the polymer phase dried on MgSO$_4$ prior to solvent evaporation.

Results and Discussion

Kinetics. Kinetic studies on a model experiment (Table 1, run 1) were first conducted to analyze the main features of D$_4^H$ polymerization. Polymerization proceeds at room temperature, using moderate concentrations of surfactant **1** (0.5 wt %) and monomer (15 wt %). A stable milky microsuspension of typically 235 nm diameter (in intensity) was prepared by sonication and did not evolve with time (not shown). Sampling was carried out at close reaction times, and the polymer was extracted by conventional means for further SEC analyses (Figure 2a). SEC traces can be deconvoluted according to the procedure described in the experimental part (see Figure 1) to quantify the three different classes of molecules (small cycles, macrocycles, and polymer) in equilibrium in the reaction (Figure 2b). According to Figure 2, D$_4^H$ is very rapidly consumed to produce long polymer chains, since 90% of monomer is converted in less than 15 min, although maximal conversion is reached after 3 h. Molar mass distributions shifts toward large molar masses with time to reach a $\overline{M}_n$ of 23 kg/mol after 5 h and a polymolecularity of less than 2 (not taking into account small cycles and macrocycle species).

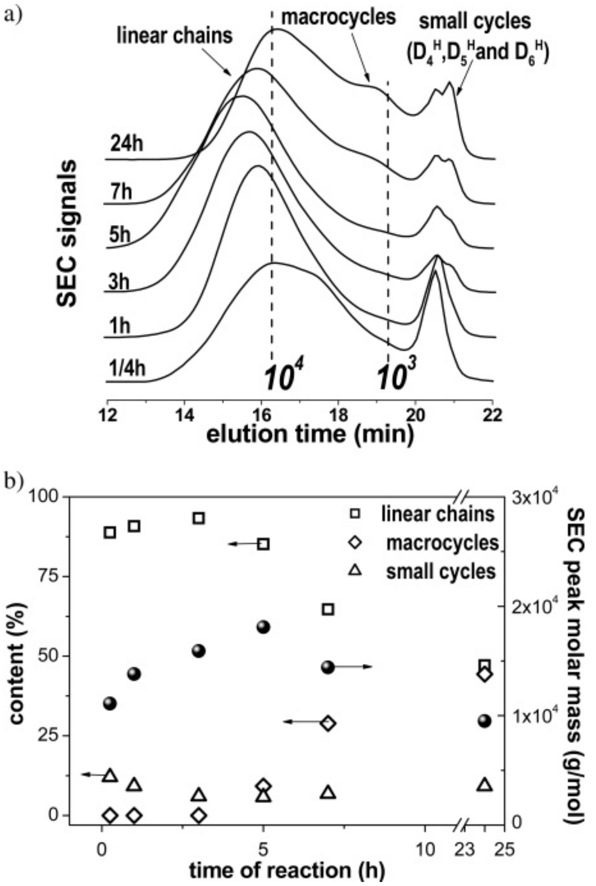


Figure 2. (a) SEC traces of samples extracted at different times from a model miniemulsion (Table 1, run 1). Dashed lines indicate molar mass limits of 1 and 10 kg/mol. (b) Contents in linear chains, macrocycles, and small cycles (open symbols) as well as the SEC peak molar mass for the linear chains (plain circle), as a function of time. Note that in the calculations from SEC traces (see an example Figure 1) differences in refractive indexes were neglected.

Formation of macrocycles is usually observed in cyclosiloxane cationic polymerization processes[15] but needed to be confirmed here in a ROP miniemulsion system. ^{29}Si NMR (Figure 3a) first evidenced that the linear chains are terminated by (CH$_3$)$_3$Si and (CH$_3$)$_2$-SiH moieties, as observed in the previous study.[8] Since the final polymer extract contains a large variety of macrocycles, integrating the main polymer peak compared to chain-end peaks in the ^{29}Si NMR spectrum would give erroneous molar mass estimations and was thus not done.

The four distributions observed in electrospray mass spectrometry (Figure 3b) are easily resolved once the polymer chain ends have been identified. Each series

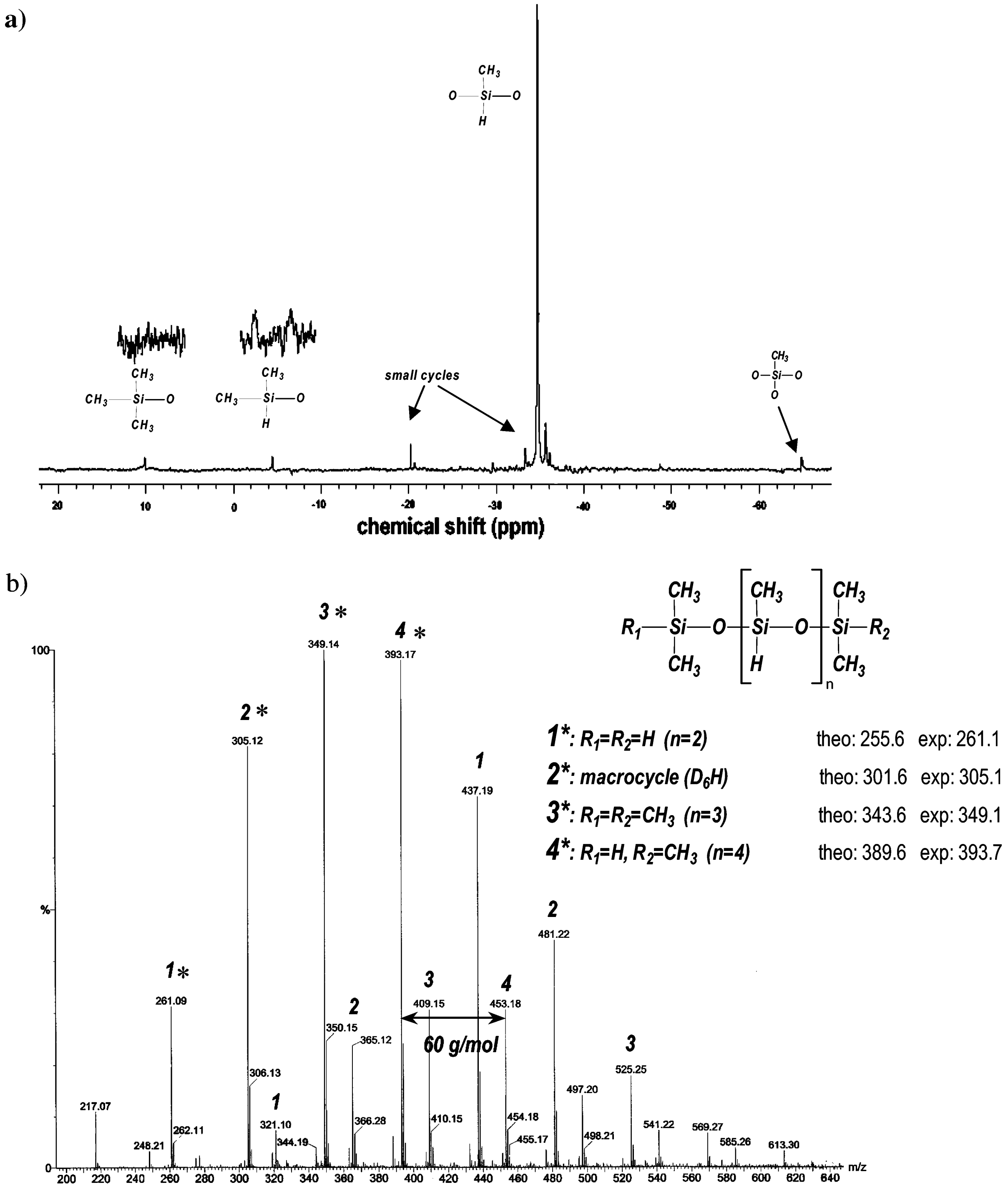
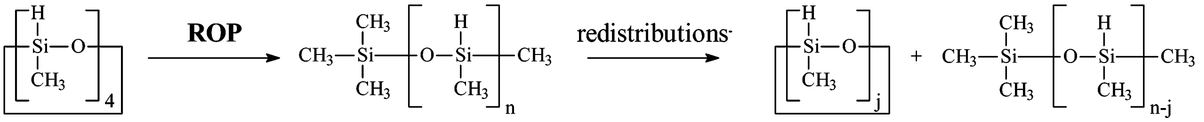


Figure 3. (a) ^{29}Si NMR of a sample from the model reaction let to evolve toward the formation of macrocycles. Both chain ends are visible, whether the hydrogen atoms are irradiated (below) or not (insert). (b) Typical electrospray mass spectrogram for similar sample. All distributions are composed of PMHS (double arrow indicates the increment of one D^H unit) whereas their absolute molar mass differ according to their chain ends ($M + H^+$ assignments given on the spectrum for peaks marked by *). The discrepancy of 4 g/mol observed between theoretical and experimental data is ascribed to a noncorrected calibration curve.

is clearly composed of D^H units (separation of 60 g/mol between peaks), whereas linear polymer chains are differentiated from each other and from macrocycles by their chain ends (see peak assignments in Figure 3b). The fact that PMHS chain ends cannot bear silanol groups is well-known from silicone manufacturers. However, the reaction pathway to generate the groups mentioned above remains unexplained, although it is supposed that each end groups are the results of initiation and termination reactions, respectively. This statement implies that in the present study the variety of chain-end structures observed by electrospray mass spectrometry is the result of extensive redistribution reactions.

Mechanism of Polymerization. The polymerization proceeds according to Scheme 2. First, the surfactant catalyst provides protons to open a cycle: this initiation step is slow and limits the overall rate of reaction. Every new created chain grows very rapidly before a water molecule quickly transfers to produce a dead chain and to regenerate the catalyst. This polymerization scheme truly resembles what is observed commonly in free

Scheme 2



radical polymerization in emulsion and is far from conventional "living/controlled" cationic systems. The rising on molar masses with time, also observed in previous kinetics data for miniemulsion D_4^H polymerization,[8] is not due to chain polycondensation since silanol end groups promptly (if not instantaneously) rearrange. It may rather be due to a decrease of transfer reactions with conversion because of water repellency from increasingly hydrophobic monomer + polymer droplets.

Above 5 h of reaction, redistribution reactions, either intramolecular ("backbiting") or intermolecular, come into play to produce small and large cycles, respectively (Scheme 2). The content of small cycles is not increasing significantly with time, but a substantial scrambling between cycles of 4, 5, and 6 units is observed (see Figure 2a). On the contrary, macrocycles are produced in fair and increasing quantities, to finally exceed the polymer content. Since their hydrodynamic volume is smaller than for linear chains, the degree of polymerization of such species is undervalued by SEC and could not be accurately measured. Neither was it possible to trace these by GC due to the complexity of the chromatograms. (An example for the final mixture of linear/macrocyclic chains is given in Figure 4.)

Both reactions of redistribution chop the polymer chains, as shown by the significant decrease of average molar masses above 5 h of reaction and confirmed by low molar mass linear chains observed by electrospray mass spectrometry analyses (Figure 3b). Such intensive redistributions were not observed before for the DBSA/Brij 35 system,[8] although SEC distributions exhibited similar shoulders between linear chains and small cycles' peaks.[16] This discrepancy emphasizes the need for thorough kinetics study anytime a new species (here the surfactant) is introduced in a ROP miniemulsion process. A final point of interest is that no cross-linking reactions could be traced here, even after long time reactions in emulsion: all samples were sol, i.e., soluble in toluene or dichloromethane, and showed an insignificant $SiO_{3/2}$ peak by ^{29}Si NMR (see Figure 3b; less than 1 Si−H per chain has condensed).

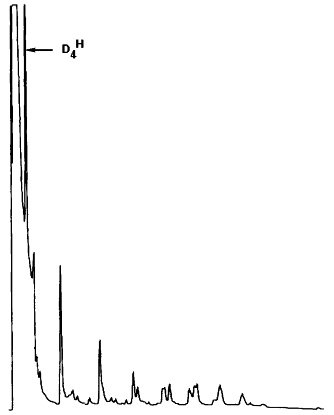


Figure 4. Typical GC chromatogram of a sample let to evolve into macrocycles. D_4^H peak is shown by the arrow.

Optimization of the Polymerization Process. This model experiment thus shows that it is possible to prepare linear PMHS of about 25 kg/mol, with a conversion as high as 94 wt %, with relatively low macrocycle contents (provided that the reaction is stopped on due time) and no gel formation. The question that now arises is whether it is possible to modulate the molar mass distribution of PMHS as observed in previous experiments with various water contents.[8] We studied the influence of different parameters, e.g., nature and content of the surfactant, temperature, monomer over water ratio. Two to three samples were analyzed for each run, the main features of which are summarized in Table 1. General comments that arise from Table 1 are that all experiments were successful in reaching linear PMHS chains, except for the run at 60 °C which started to cross-link after 6 h (not shown). Also, kinetics, maximal conversion, molar masses, and polymolecularity are almost similar among the different runs. All in all, average molar masses could not be drastically varied, in these conditions anyway. **1** and **2** produced similar emulsions and kinetics (only one of the various runs carried out with the diacid is reported in Table 1, run 10). Optimized formulation, e.g., minimum level of surfactants and maximum monomer contents that produce a fluid and stable miniemulsion over the polymerization reaction, can be found for run 5.

The few specific points that differ from one run to another reveal complementary information on the polymerization mechanism. For instance, runs 1 and 4−7 see a particle size exactly inversely proportional (on a semilog scale) to the content of surfactant introduced in the recipe (Figure 5), as found before for other miniemulsion syntheses.[17] The average molar mass seems to increase with decreasing surfactant content, but the increase in polymolecularity may be a good indicator that the material actually slightly cross-links when leveling down the surfactant content. The interfacial polymerization rate should be proportional to the specific surface of the droplets, which could not be observed here because of too fast a kinetics.

PMHS Storage. A last but tricky point concerns the extraction of the polymer from the dispersed medium.

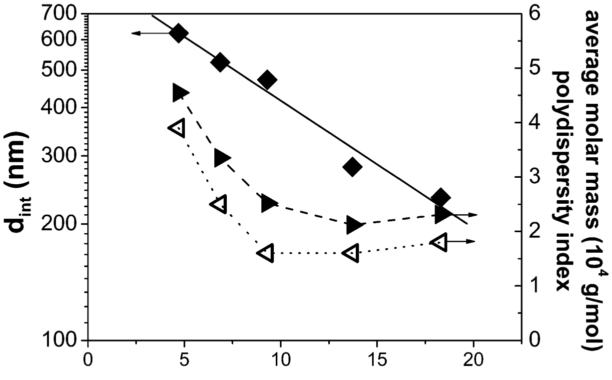


Figure 5. Influence of surfactant concentration on the intensity average particle size (◆, semilog scale), number-average molar mass (▼), and polymolecularity (△).

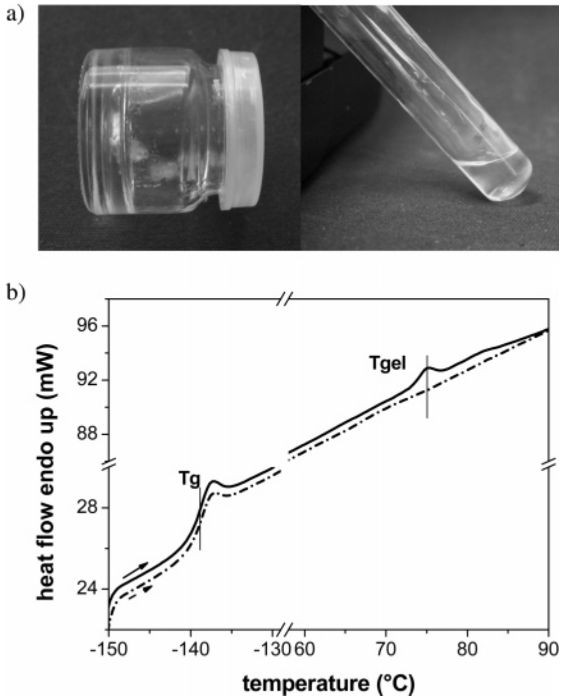


Figure 6. Physical gelling of PMHS in the presence of **2** (run 10, Table 1). (a) (left) Elastomeric gel obtained after emulsion breaking; (right) liquid oil after solvent treatment (see text for detail). (b) DSC chromatograms of the gel during the first temperature rise (solid curve) and second temperature rise (dashed line). The glass transition ($T_g = -139$ °C) is observed in both scans, whereas the gel transition ($T_{gel} = 75$ °C) shows up only on the first scan.

Low volume samples were easily extracted after neutralization and rapidly injected in SEC for characterization, but the liquid oil eventually evolves to a transparent insoluble gel only after 1−2 days. On the other hand, the neutralization of the full volume of the miniemulsion is less straightforward, and the polymer material was often found cross-linked, even before being extracted from water.

An easy way to store linear PMHS after emulsion breaking is depicted now. First, any trace of bases has to be avoided during the sample treatment to prevent cross-linking reaction. Breaking the emulsion without neutralization nor addition of alun salt (which is slightly basic) allows one to isolate the polymer and still to avoid parasite hydrolysis/condensation. Second, the polymerization reaction has to be carried out using the surfactant **2**. The small content of this solid (thus nonvolatile)[18] diacid trapped in the PMHS indeed acts as an organogelator; in other words, it considerably depresses the rates of side reactions by implementing a high viscosity in the oil. A photograph of the elastomeric gel observed after emulsion extraction is given in Figure 6a (left-hand side). Evidences for physical, rather than chemical, gelling are given by two indubitable facts: (1) The clear gel transition (T_{gel}) observed by DSC (Figure 6b), only on the first temperature rise. Passing above the T_{gel}, the network is broken and has no time to form again before the second scan (5 min between the two 10 min analyses). (2) The gel readily dissolves in dichloromethane or toluene, and after evaporation (quick enough to avoid any redistribution reactions by the still active acid catalyst), the sample goes through an oily stage (Figure 6a, right-hand side) before it gradually “freezes back”.[19]

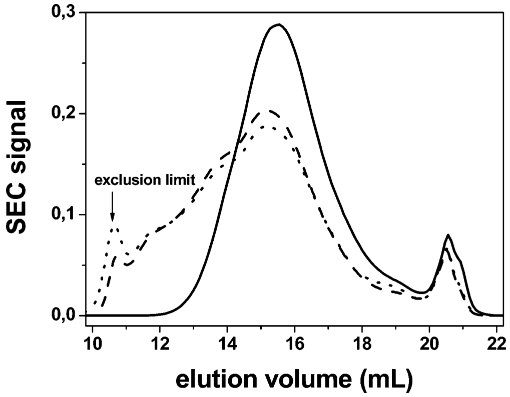


Figure 7. Raw SEC traces of PMHS extracted from a model experiment without neutralization and as a function of time: (—) 1 day, (- -) 5 months, (- - -) 10 months.

The PMHS stored in gel conditions exhibits a molar mass distribution that spreads with time because of very few condensation reactions (Figures 7 and 3a). However, the PMHS oil remains a sol, i.e., keeps entirely soluble in toluene for more than 10 months. The surfactant is easily removed by several washings with water prior to (immediate) polymer use.

In conclusion, this article shows a reliable, fast, and cheap way to prepare and store PMHS homopolymers in a range of molar masses between 10 and 30 kg/mol, with a small content of small cycles and macrocycles, and no significant gel content. These polymers may be used to prepare all kinds of side chain modified polysiloxanes.[1] Particularly in our group, they are about to be used in the generation of highly grafted silicones.

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(16) In the previous reference from Maisonnier et al.,[8] it is difficult to ascertain whether the high molar masses (70 kg/mol) obtained at low water contents are the result of early cross-linking reactions or not. The fact that for two runs of Figure 3 in ref 8 molar masses increase with conversion is in favor of hydrolysis/condensation reactions, although the low polymolecularities observed (Table 2 of the same reference) rather refutes it.

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(19) Investigations on the structure of the network formed by surfactant **2** are under way. Preliminary observations seem to indicate that atmospheric water helps at implementing the organogel network, presumably made of giant micelles. Besides, this particular organization could explain why, by adding these surfactants into bulk D_4^H, polymerization proceeds and produces larger molar masses than for conventional catalysts (triflic acid, for instance), although at a much slower rate (typically 1 night against 10 min, respectively).

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