Looking over Liquid Silicone Rubbers: (1) Network Topology vs Chemical Formulations

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Ⓢ *Supporting Information*

ABSTRACT: This study proposes a comprehensive study on liquid silicone rubber (LSR) formulations to unravel which components (among functional polydimethylsiloxane polymers and modified silica fillers) improve the mechanical properties of the final materials. In this first part, various industrial products have been deformulated using conventional chemical analyses. The silica content and their surface chemistry were assessed by TGA. Architecture and molar mass of polymers were deduced from ^{29}Si NMR and SEC in toluene, respectively. Relative concentrations of hydride and vinyl reactive groups and stoichiometric imbalance ($r = n_{\text{SiH}}/n_{\text{SiVi}}$) were quantified by proton NMR. Stoichiometric imbalance is slightly higher than 1.5 for cross-linker with hydride functions well redistributed along the chain, whereas for some formulations, r's as high as 3.7 were implemented. These variations has strong implications on the cross-linking density of the final material, since the remaining hydride groups react together and decrease the molar mass between cross-links. From the comparison between formulations, it was shown that hardness adjustment is mainly performed by playing on two parameters: filler content and molar mass between cross-linking points for hardness ranging from 20 to 30 Shore A. Above this limit, it is necessary to modify the silica surface with reactive groups, such as vinyl functions. Surprisingly, two formulations were shown to use a dual cross-linking catalysis systems, peroxide and platinum, leading to efficient and full cure even at lower temperature (typically 140 °C). Network topologies were estimated from the predicted chemistry of the materials in a final discussion part.
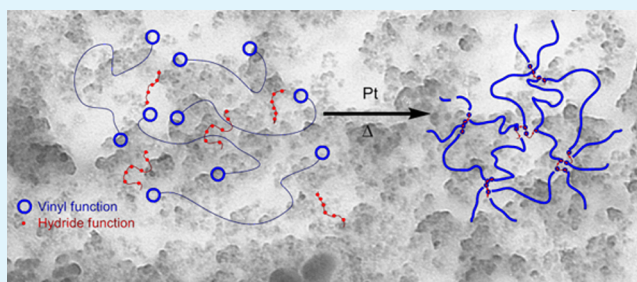
KEYWORDS: liquid silicone rubber, platinum cured silicones, peroxide cured silicones, cross-linker structure, molar mass between cross-links, silicone hardness

1. INTRODUCTION

Polydimethylsiloxane (PDMS) or other silicone-based polymers are well-known for their excellent mechanical and thermal properties. In particular, the class of silicone grades called liquid silicone rubber (LSR) enables fast-cured, high-precision injection molding for high performance parts, such as seals or medical devices. Because they are cured by addition reaction of hydride on vinyl groups, these formulations enable high degree of control on the network topology and thus, on the mechanical properties of the final material. This study aims at understanding how each components of a LSR affect the final network and, consequently, the ultimate properties. In this first part, several formulations are characterized in their noncross-linked state to determine the prepolymers chemical structures and to show how small variations in these formulations influence the reactivity and the network configuration (molar mass between cross-links, for instance). In the second part of this series,[1] the mechanical properties (especially hardness, tear resistance, tensile strength, compression set) will be correlated

to the previously asserted network configuration. The final purpose of this work is to propose the most favorable architecture of the prepolymers to reach reinforced materials with optimal properties in tensile and tear tests, as well as in compression set experiments.

liquid silicone rubbers are provided as two parts formulations by major silicone suppliers. After mixing in a 1/1 ratio, these two components called part **A** and part **B** are cured through hydrosilylation, which refers to the addition of Si–H bonds to carbon double bonds borne by poly(dimethylsiloxane) chains. Hydrosilylation reaction is catalyzed by platinum compound, preferably platinum(0) complexes such as Karstedt's catalyst,[2] for its stability and compatibility with silicone.[3,4] Inhibitors are widely used in hydrosilylation systems to prevent premature cross-linking of polymers at ambient temperature, whereas

rapid platinum-mediated cross-linking reactions take place at higher temperatures.[5] Commonly used inhibitors include electron-deficient alkenyl molecules, such as maleates, fumarates, and β-alkynol.[2] By calculating the binding energy between inhibitor or vinyl and platinum, Faglioni et al.[6] concluded that all inhibitors coordinate the catalyst more weakly than the vinyl substrate. Hence, the catalyst is not inhibited by a chemical process but rather by segregation in a phase in which the catalyst is solvated by the inhibitor. Reaction is initiated when the temperature exceeds the boiling point of the inhibitor phase; once the inhibitor is volatilized, an architectured controlled network of polymer is formed (see a pictural scheme of the network formation in the TOC graphic). Because the hydrosilylation reaction takes place at room temperature even in the presence of inhibitor, the partition of LSR formulation into two parts allows either the separation of one functional group from the other or the catalyst isolation from the functionalized polymer chains.

Cross-linked silicones are inherently weak material.[7] Filler incorporation enhances the mechanical properties by first, a hydrodynamic effect arising from the inclusion of rigid particles,[8] filler agglomeration or network formation and second, by an increase in the cross-linking density created by polymer−filler bonding. Silica is generally preferred because of its outstanding reinforcing capability, which results from the numerous interactions between silanol from silica surface and siloxane backbone. In LSR, fumed silica is often preferred for its reasonable cost, its high compatibility and high surface area ($150-380$ m^2/g,). However, crepe-hardening of formulation, caused by strong hydrogen bonds between silica and PDMS, is likely to occur.[9] To decrease the silanol content on the silica surface, the filler is either (both) physically modified by adding α,ω-bis-silanol PDMS oligomers[10] or (and) chemically modified with hexamethyldisilazane,[11−13] ethoxysilane or chlorosilane[14,15] and cyclosiloxane.[16−18] The blends prepared with modified filler exhibit softening instead of crepe hardening typically reported for unmodified silica filled systems.[19] In addition to decreasing the surface silanol concentration, the coupling agent, for instance vinylethoxysilane,[20] brings additional improved properties by connecting the polymer matrix and the filler.[21−23] To the best of our knowledge, silica in LSR formulations is mainly modified by in situ reaction of surface silanol groups with hexamethylsilazane or 1,3-divinyltetramethyldisilazane when a coupling agent is required.[24,25]

In this paper, we extended the range of common techniques used for characterizing silicone formulations[26] (FTIR, ^{1}H and ^{29}Si NMR) in order to determine the filler content, the architecture of the main polymers (molar mass, position of reactive functions), and to calculate the relative concentration and reactive functions' ratio. These techniques were estimated to be sufficiently accurate to characterize all the formulation additives in concentration higher than 1000 ppm. In a first part, silicone formulation analyses are done on a model un-cross-linked formulation. Then, chemical analyses are generalized to eight materials ranging from 20 to 50 Shore A to establish the polymers and fillers architectures. Besides, reactivity of these materials is considered from kinetics measurements at various curing temperature. Materials prepared by injection-molding are treated by various solvent swelling techniques to extract data such as, the molar mass between cross-links M_c, the content of extractible species and/or the presence of network defects. In a final discussion, we compare these different parameters to tentatively deliver a picture of the network

configuration in agreement with the chemical structures described previously.

At this point, we shall note that because we deformulated LSR formulation devoted to specific automotive sealing applications, materials present self-lubricating properties. After formulation curing, a specific silicone oil exudes, driven by its partial incompatibility with the polymer network. Since it complicates the plot of deformulation, the characterization of these unreactive components was necessary and is also reported here.

2. EXPERIMENTAL SECTION

Materials. Eight silicone formulations were provided by different suppliers. All the studied products are self-lubricating LSR grades for automotive applications (Table 1).

Table 1. Properties of Analyzed LSR Formulations (data given by the suppliers)

name	theoretical hardness (Shore A)	density	oil content (wt %)	viscosity in part **A** (Pa s)	viscosity in part **B** (Pa s)
1	29	1.11	3	400[a]	400[a]
2	30	1.11	7	650[a]	650[a]
3	20		5		
4	31	1.107	5	395[a]	280[a]
5	50	1.12	4	400[a]	400[a]
6	33	1.136	4	150−190[b]	150−190[b]
7	50	1.14	2	250[b]	270[b]
8	32	1.12	4	210[a]	190[a]

[a]Measured at 20 °C and 10 s^{-1}; [b]Measurement conditions not reported.

Toluene (CHROMASOLV Plus, for HPLC, ≥99.9%), Tetrahydrofuran (inhibitor-free, CHROMASOLV Plus, for HPLC, ≥99.9%), methylcyclohexane (ReagentPlus, 99% Sigma-Aldrich) Cr(acac)3 (97% Aldrich) and ammonia (puriss., anhydrous, ≥99.9%) were purchased from Sigma Aldrich and used as received. Deuterated chloroform (≥99.9%) is provided by Eurisotop.

Methods. Thermogravimetry (TG) analyses were performed on a Q50 from TA Instrument. Twenty mg of sample in a platinum pan was heated from room temperature to 900 °C under a nitrogen flow (60 mL/min). The experiments were carried out at a heating rate of 50 °C/min.

Size exclusion chromatography (SEC) in toluene equipped with a refractive index detector (RI) enables the determination of the polymer molar masses present in each component, especially the longest ones. More interestingly, it is possible to differentiate polymers absorbing in UV (i.e., typically bearing aromatic groups) by SEC in THF, equipped with both RI and UV detectors (set at 254 nm). SEC analyses in toluene were carried out using a Spectra-Physics apparatus, equipped with a set of PLgel (5 μm, 300 mm) MIXED-D columns from Polymer Laboratories and a RI detector. The solvent was eluted at a flow rate of 0.8 mL min^{-1}. SEC analyses in THF were performed using a Spectra-Physics apparatus, equipped with a set of PLgel (5 μm, 300 mm) MIXED-C columns from Polymer Laboratories. Low molar mass polymers were analyzed with a set of PLgel (3 μm, 300 mm) MIXED-E columns from Polymer Laboratories. Measurements were performed through two detectors, refractive index and UV absorption (λ=254 nm). The eluent was tetrahydrofuran at a flow rate of 1 mL/ min^{-1}. The samples were prepared by dissolving materials in the SEC eluent (60 mg in 5 mL) and by filtrating the solution using decreasing pore size filters (from 5 to 0.2 μm). This simple operation removes silica filler prior to injection. For all SEC measurements, universal calibrations were performed using polystyrene standards.[27] For cross-linker molar mass determination, we assumed that both parts contain the same amount of long polymer and the signals intensities were then

normalized by setting the maximum intensity of this polymer at 1.[28] Then, trace of part **B** was subtracted from the trace of part **A**. All SEC calibration curves were established using polystyrene standards from Polymer Laboratories.

The chemical structure of the products was determined by ^{1}H NMR, and ^{13}C NMR (Bruker AC 400 MHz) at room temperature in $CDCl_3$ solutions. ^{29}Si NMR experiments were performed on a 250 MHz spectrometer in 10 mm tubes with Chromium(III) acetylacetonate $Cr(acac)_3$ to decrease relaxation time and thus, to get quantitative signals.

In an attempt to measure the silica particle size, both un-cross-linked formulations and cured materials were characterized by transmission electron microscopy (TEM). Cutting silicone material with a cryomicrotome in liquid nitrogen, produced slices too thick to transmit electrons, because of the extreme silicone softness (low T_g). Un-cross-linked formulations were spread to an adequate thickness, from which the diameter of elementary particles were estimated at 30 nm (see Figure S1 in the Supporting Information).

Kinetics and Curing. The kinetics of curing were recorded by a Moving Die Rheometer, a heated biconical oscillating chamber, at various temperatures (120, 140, 160, and 180 ± 0.5 °C). The lower part applies an oscillation strain (strain, 0.5°; frequency, 1.7 Hz), whereas the upper part records the complex torque $S*$ as a function of time. For elastic materials, the most important parameter is the elastic (or storage) torque S', the real component of $S*$ ($S* = S' + iS''$). The curves obtained by curing 5 g of materials were discussed on the maximum torque reached (S'_{max}) and on reaction rate ν taken between 10 and 90% of S'_{max} (see an example in Figure 1 and eq 1).
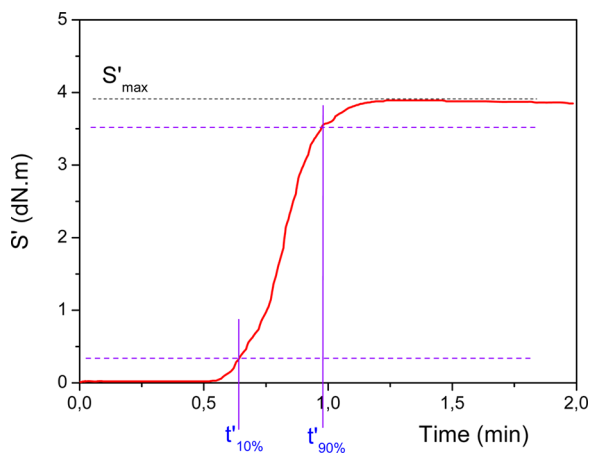

Figure 1. Example of values extracted from kinetics curve (formulation **1** cured at 120 °C).

$$\nu = \frac{0.9S'_{max} - 0.1S'_{max}}{t_{90\%} - t_{10\%}} \tag{1}$$

Thanks to these kinetics data, the curing of 30 Shore A formulations were adapted. Both sheets of 2 and 6 mm thick were injection molded at a pressure set at 165 MPa, at three temperatures (180, 200, and 220 °C) and different times (55, 47, and 36 s, respectively). Durometer hardness (Shore A) values were obtained on 6 mm thick sheets using a standard durometer hardness tester from Bareiss, with three hardness values collected per system.

Extraction and Swelling Measurements on Final Materials. Exudation oil was easily extracted by submerging 10 g of cured material in THF (CHROMASOLV Plus for HPLC, ≥99.9%, inhibitor-free, Sigma-Aldrich). After 5 days of extraction, the solvent was evaporated to obtain a transparent oil which was then analyzed by SEC and ^{29}Si NMR.

Sample immersion in a good solvent of the polymer produces material swelling, extent of which is a reciprocal function of the cross-linking density. Such cross-linking knots are brought both by the chemical links between PDMS chains and by physical interactions between a PDMS chain and the filler network.

In swelling measurements, a typical sample (#0.6 g, cylindrical disk of 13 mm diameter and 6 mm thickness) was first wiped to remove oil bled from material, then weighted for evaluating the initial dry weight (W_i) and plunged in 100 mL of methylcyclohexane in a sealed bottle. After 5 days, the equilibrium weight was considered to be reached; the sample was extracted, gently wiped to remove the liquid solvent present on the sample surface and immediately weighted (W_s). The sample was then dried overnight at 70 °C under vacuum and reweighted (W_f). Extractable material (E) and volume fraction of polymer in the swollen sample (V_r^T) are calculated as follows

$$E(\%) = \frac{W_i - W_f}{W_i(1 - c)} 100 \tag{2}$$

$$V_r^T = \frac{W_f - (W_i c)}{W_f - (W_i c) + (W_s - W_f)\frac{\rho_p}{\rho_s}} \tag{3}$$

where c represents the silica weight fraction; ρ_s and ρ_p the solvent and polymer densities, respectively.

NH_3 modified swelling method was used to provide an estimation of the polymer−filler interaction in the system. As ammonia fumes break the hydrogen bonds between silica surface and polymer backbone,[29,30] swelling measurements in methylcyclohexane in presence of ammonia saturated atmosphere (during 7 days) give the sole chemical contribution to cross-link density, V_r^{Ch} (eq 4, where subscript a refers to ammonia).

$$V_r^{Ch} = \frac{W_f^a - (W_i^a c)}{W_f^a - (W_i^a c) + (W_s^a - W_f^a)\frac{\rho_p}{\rho_s}} \tag{4}$$

Then, the molar mass between the chemical cross-links (M_c^{Ch}) is estimated using the Flory−Rehner equation relative to an ideal network[31]

$$M_c^{Ch} = \frac{-M_s \frac{\rho_p}{\rho_s}\left(V_r^{Ch1/3} - \frac{V_r^{Ch}}{2}\right)}{\ln(1 - V_r^{Ch}) + V_r^{Ch} + \chi(V_r^{Ch})^2} \tag{5}$$

with M_s the solvent molar mass and χ the Flory−Huggins interaction parameter (taken at a value of 0.45 as a fair approximation). The hydrogen bonding contribution to cross-linking density, V_r^{Ph},[32] which investigates the specific surface area as well as the surface modification of the filler, is calculated as

$$V_r^{Ph} = V_r^T - V_r^{Ch} \tag{6}$$

As few samples were available in each curing conditions, only the swelling measurements in methylcyclohexane (in absence of ammonia) could be reproduced twice. In these conditions, the reproducibility on V_r^T was as low as 0.5×10^{-3}. The experiments performed in presence of ammonia (V_r^{Ch}) were estimated to give similar experimental errors, though maybe slightly higher because of the NH_3 volatility during the weighting. This hypothesis was confirmed, during a different study on high temperature vulcanization (HTV) rubbers owing the same hardness and about the same range of V_r^{Ch} (not shown). Indeed, the difference between two measurements was found to be about 2×10^{-3} ($\Delta V_r^{Ch} = 1 \times 10^{-3}$).

3. RESULTS

3.1. Typical Deformulation Procedure Applied to Material 1. All chemical analyses were carried out on the un-cross-linked material, i.e., on each component (**A** and **B**) separately. We propose here to develop the systematic procedure used to characterize the different formulations as

applied specifically to the simplest system (formulation **1**). First, the nature and content of filler were deduced from thermogravimetric analyses; the polymer fraction was then extracted and analyzed by size exclusion chromatography in toluene and THF. ^{29}Si NMR provided information about the functional groups as well as the prepolymers architecture, data otherwise confirmed and completed by ^{1}H NMR.

Thermogravimetric Analyses. Thermogravimetric analysis under nitrogen of each part enables to determine the filler content. Our group[33] recently carried out an exhaustive TGA study on silica-PDMS model samples, mimicking HTV or LSR formulations. Without platinum in the recipe, thermal post-cross-linking does not occur and all the PDMS chains are depolymerized into volatile cyclosiloxanes, leading to no residue. Thus, the residue at 900 °C corresponds to the initial filler content. With platinum, the residue content depends on the silica surface modification: PDMS blended with hexamethyldisilazane-modified silica presents a residue of 10−15% above the filler content while residue improvement increases up to 40% for vinyl-modified silica.[33]

Figure 2 presents the degradation curves under N_2 of each part of formulation **1**. Part **B** degradation produces 30 wt % of a

Figure 3. SEC traces in THF; upper graph: part **A** recorded by RI (red) and UV detector (orange); lower graph: part **B** by RI (dark blue) and UV (light blue).
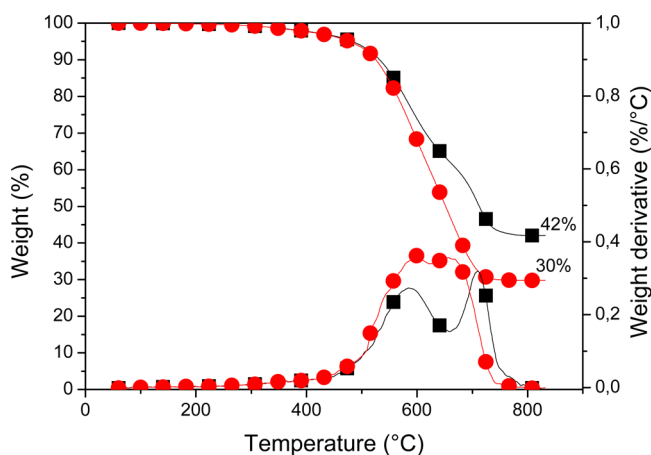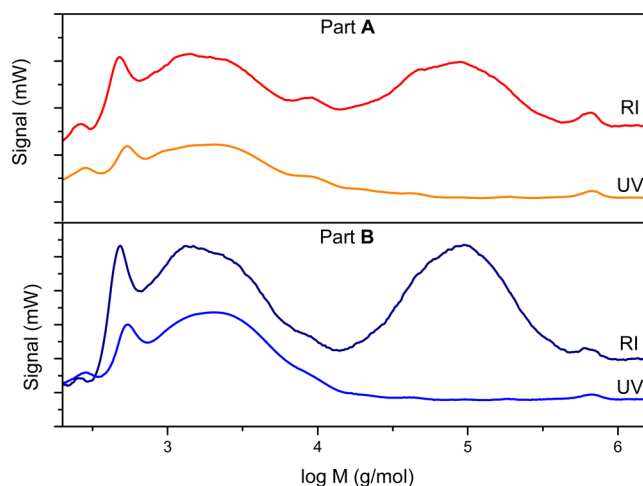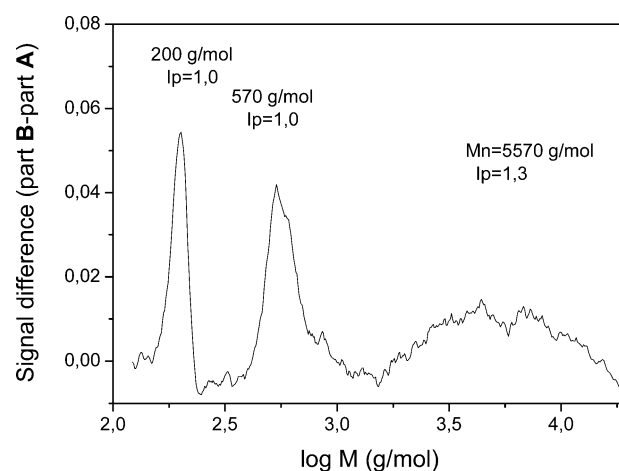

Figure 2. Effect of platinum on the degradation curve of part **A** (black squares) and part **B** (red circles) of formulation **1**.

white powdered residue, whereas part **A** gives a hard and shiny black solid residue of 42 wt % of the initial weight. It can be concluded that the formulation contains 30% of filler, and part **A** contains the platinum catalyst for hydrosilylation.

Size Exclusion Chromatography. UV SEC traces proved the presence of aromatic groups in both components A and B, for a polymer of number average molar mass of 1700 g·mol^{-1} (PI = 1.5) ascribed to the exuding oil (Figure 3). RI detectors revealed the presence of an additional long polymer of M_n = 40 000 g mol^{-1} (PI = 2.5) present in both parts **A** and **B**.

Attempts to isolate the cross-linker from the formulation by reprecipitation failed because of its strong compatibility with the long vinyl terminated PDMS. To study more accurately the cross-linker polymer (<10 000 g mol^{-1}), we used the signals recorded with a set of columns specifically designed for separation of low molar mass polymers. First, we set the maximum intensity of large polymer peak at 1 and subtracted the normalized chromatogram of part **A** from the part **B** one. Figure 4 shows that three additional peaks are observed in part **B** (compared to part **A**) at 200, 550, and 5570 g mol^{-1}. The latter would correspond to the cross-linker, whereas the peaks

Figure 4. Subtraction of normalized SEC RI traces of part **A** and part **B** of formulation **1**.

at 200 and 570 g mol^{-1} arise a priori from the inhibitor and either an additive or a silicone synthesis residue, respectively (vide infra).

[29]*Si NMR.* Identification of functional groups present at low concentrations in the formulation requires long acquisition time using the ^{29}Si NMR technique (>24 h). Parts **A** and **B** have close though single spectrograms (Figure 5a). The important peak set at −22.4 ppm corresponds to the D unit of PDMS that shrinks all others signals (for correspondence between chemical shifts and structures, see Table S1 in the Supporting Information). Chain building units are also present at −48 ppm, revealing the presence of D^{Ph2} units otherwise observed by SEC UV. The broadness of this signal unveils that these units are copolymerized with D units. Trimethyl and vinyldimethyl chain end units are observed around 6.8 and 9 ppm, and −4 ppm, respectively. Specific analyses of the silicone oil extracted from cured material by solvent swelling were carried out; the ^{29}Si NMR spectrum (Figure 5b) only shows trimethyl chain end signals at 6.8 and 9 ppm, depending on the adjacent units (D and D^{Ph2} units) also present on the spectrogram.[26] Thus, vinyldimethyl end units are assigned to the long PDMS polymer. The fact that the exudation oil is a poly(dimethyl-*co*-diphenyl)siloxane owes to its incompatibility
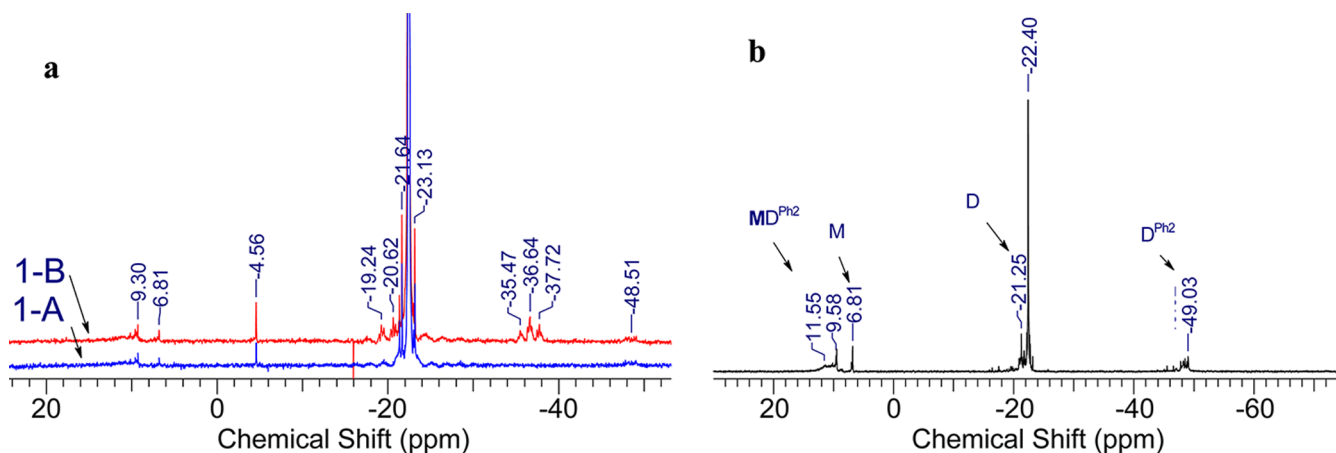
Figure 5. ^{29}Si NMR spectra of formulation **1** (a) parts A and B; (b) exudation oil after extraction (see experimental part for details).

with PDMS: in the literature, polydiphenylsiloxane-polydime-thylsiloxane-polydiphenylsiloxane triblock copolymers were shown to separate into two phases.[34] Note that both parts **A** and **B** contain the vinyl functionalized PDMS chains and the exudation oil.

^{29}Si NMR also confirmed that part **B** contains the cross-linker and part **A** the platinum catalyst. The three environments for methylhydro groups, triads observed between −35 and −37.5 ppm, highlight the cross-linker architecture, basically a trimethylsilyl terminated-poly(methylhydrido-co-dimethyl siloxane). It is worth noting that in this particular formulation **1**, as high as 23% of the $D^H D^H D^H$ sequence is quantified, meaning that the active functions are not perfectly redistributed inside the polymer chain (vide infra).

^{1}H NMR. By proton NMR, aromatic (7−7.5 ppm), vinyl (5.7−6 ppm), and methylsilyl (0 ppm) groups give strong signals (Figure 6). Signals at 0.85 ppm and 1.27 ppm have been
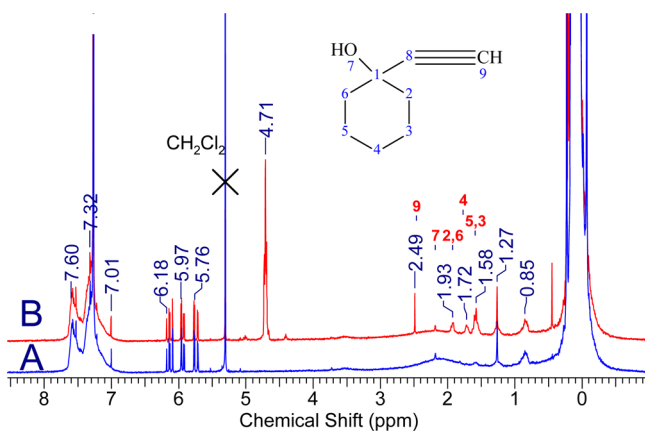

Figure 6. ^{1}H NMR spectrum of components **A** and **B** (formulation **1**).

assigned to hydrogen-bonded geminate silanol and isolated silanol[35] whereas broad signals at 2 and 3.5 ppm are dued to H-bonded silanol and physisorbed water on the silica surface, respectively.[36] These assignations were confirmed by analyzing unmodified and modified silica (see Figure S2 in the Supporting Information). Figure 6 otherwise shows little differences between parts **A** and **B**. As expected, part **B** presents a strong signal at 4.7 ppm ascribed to hydride functions. While some patents claim addition of inhibitor in the same part as platinum catalyst,[37,38] the platinum inhibitor, 1-

ethynyl-1-cyclohexanol, was also located in the part **B** as proved by the precisely assigned signals between 1.26 and 2.49 ppm. The SEC peak observed at 200 g mol^{-1} in part **B** is then logically credited to the inhibitor.[39] The methylsilyl peak integration was set to 1000 to normalize both spectra (part **A** and part **B**). By assuming that methyl silyl content is equivalent in both parts, signal integrations of vinyl and hydride groups enable to quantify the ratio between functional groups, here

$$r = \frac{(n_{SiH})_B}{(n_{SiVi})_A + (n_{SiVi})_B} = 3.7$$

In conclusion from this primary analysis procedure, both parts **A** and **B** of the LSR analyzed here include similar silica content with a long α,ω-divinyl polydimethylsiloxane and a poly-(dimethylsiloxane-co-diphenylsiloxane) as an exudation oil.[40] Part **A** includes the catalyst, the cross-linker bearing methylhydride siloxane group and the platinum inhibitor are located in part **B**.

3.2. Deformulation of All Systems. The eight LSR formulations with various hardnesses and obtained from different suppliers, were studied using the previously described procedure (Table 2 sums up the main results and raw data are given on the Supporting Information in Table S2). Basically, few differences are observed between the formulations which all contain vinyl-terminated PDMS, short cross-linker bearing numerous hydride groups, exudation oil based on phenylated PDMS and filler, which content ranges between 20 and 30 wt %. However, slight discrepancies exist that allows the suppliers to adjust material mechanical properties (presented in the following part of this series).[1] For instance, adjustments of the solubility parameter of the exudation oil was done from one formulation to another by varying the phenylated units fraction in the copolymer (see contents in Table S3 in the Supporting Information).[41]

Reactive Function Concentrations and Imbalanced Stoichiometry. An interesting point concerns the reactive function concentrations which are among the most important parameters for unraveling the network structure. The vinyl concentration roughly controls the hardness, since all 30 Shore A formulations display a relative vinyl concentration close to 1.0 (Table 2). The formulation **3** (20 Shore A) is logically less concentrated in vinyl group. Several formulations, namely **5**, **6**, **7**, and **8**, display D^{Vi} units (vinyl groups located inside the PDMS chain, Figure 7). Both 50 Shore A materials contain between 1.4 and 1.9 methylvinylsiloxane units per chains,

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dx.doi.org/10.1021/am300502r | *ACS Appl. Mater. Interfaces* 2012, 4, 3340−3352

Table 2. Chemical Compositions of LSR Formulations Used in This Study[a]

| formulation | hardness (Shore A)[e] | vinyl-terminated polymer | | | silica | | cross-linker | | | | functional groups | | |
		avg structure	M_n (g mol^{-1})	$n_{D^{Vi}}$[d]	silica content (%)	silica surface modifier[g]	structure HHH (%)	HHD (%)	DHD (%)	M_n (g mol^{-1})	n_{SiVi}[c]	n_{SiH}[c]	r
1	32.9	$M^{Vi}D_nM^{Vi}$	45 000	0	29	methyl	23	49	29	5600	1.01	3.7	3.7
2	30.8	$M^{Vi}D_nD^{Vi}_mM^{Vi}$	47 000	0.16	28	vinyl	0	44	56	7900 and 2000	1.00	1.9	1.8
3	f	$M^{Vi}D_nM^{Vi}$	65 000	0	20	methyl	0	28	72	f	0.56	1.8	3.1
4	30.0	$M^{Vi}D_nM^{Vi}$	51 000	0	31	methyl	0	72	28	5000	0.95	2.2	2.3
5	f	$M^{Vi}D_nD^{Vi}_mM^{Vi}$	47 000	1.92	30	vinyl	b	b	b	f	1.75	3.7	2.1
6	31.7	$M^{Vi}D_nD^{Vi}_mM^{Vi}$	41 000	0.18	28	methyl	b	b	b	2400 (in **B**) 700 (in **A**)	1.12	1.6	1.4
7	45.5	$M^{Vi}D_nD^{Vi}_mM^{Vi}$	31 000	1.36	31	vinyl	0	50	50	2400	1.27	2.3	1.8
8	33.0	$M^{Vi}D_nD^{Vi}_mM^{Vi}$	47 000	0.85	28	methyl	b	b	b	1300	1.00	2.1	2.1

[a]Structures are determined by ^{29}Si NMR, molar masses by SEC in toluene, silica surface modifier and silica content through TGA measurements, relative concentration of functional groups by ^{1}H NMR (see text for details). [b]Spectra resolution did not permit to discriminate between the different hydride group environments. [c]Relative integration with normalized spectra according to the SiCH$_3$ unit, $I_{0\,ppm} = 1000$. [d]Calculated from ^{1}H NMR. [e]Hardness measured on 200 °C cured materials. [f]Not measured. [g]Deduced from TGA analysis (see text for details).

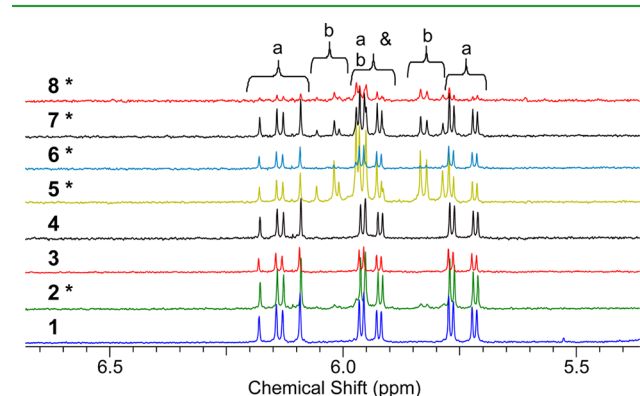whereas softer materials contain between 0.2 and 0.8 of D^{Vi} units.

Figure 7. ^{1}H NMR of part **A** zoomed on the vinyl signals region (5.5 to 6.3 ppm); (a) signals ascribed to vinyldimethylsilyl end-units (M^{Vi}) and (b) signals ascribed to vinylmethylsiloxane units (D^{Vi}). Formulations marked with an asterisk encompass D^{Vi} units.

SiH functions are always present in excess of stoichiometry, between 1.4 and 2.3 of the total amount of vinyl groups, with a noticeable excess of 3.7 for Formulation **1** (Table 2). Unbalancing the stoichiometry guarantees that all long polymer chains will be attached by both ends into the network, a crucial point while considering the mechanical properties of elastomer materials.[1] Moreover, possible hydride degradation through slow premature hydrolysis (Scheme 1) as reported in the literature[42,43] should not affect the overall grafting yield and in turns, the curing behavior. Finally, hydrid excess has been shown to accelerate the reaction compared to the reaction having equimolar or excess of vinyl.[3]

Cross-Linker Structure and Molar Mass. The content of SiH in the various formulations can also be correlated with the cross-linker structure as revealed by ^{29}Si NMR spectra of parts B (see Figure S3 in the Supporting Information). For most formulations, the cross-linker contains only DD^{H}D and DD^{H}D^H environments. Formulation **1** also discloses the pattern D^H**D**^{H}D^H, meaning that the active functions are less redistributed inside this polymer chain.[44] Steric control is extremely important in the hydrosilylation reaction:[45] vicinal SiH functions are less reactive than isolated ones (Table 2).

To determine the cross-linker molar masses, we plotted the subtraction of the parts **B** to **A** SEC signals recorded using low molar mass columns (Figure 8). Deconvolution using Origin-Pro permitted us to calculate the polymer characteristics (see Table S4 in the Supporting Information). All the formulations include the inhibitor, ethynyl cyclohexanol, in the part **B**. The largest peak is ascribed to the cross-linker, which molar mass ranges from 1900 to 7700 g mol^{-1}. For some formulations, an intermediate peak is observed that may correspond to a synthesis residue or other formulation compound (such as an antioxidizer) in the case of very low Mn products (formulations **1**, **7**, and **8**) or to a second type of cross-linker (in formulation **2**). Formulation **7** includes an extra peak of 700 g mol^{-1} in part **A** (vide infra).

Molar Masses between Cross-Links. In the various formulations, the α,ω-vinyl PDMS molar masses cover a broad range from 30 000 to 65 000 g mol^{-1}. When a material is cross-linked by end-linking reaction with a multifunctional

Scheme 1. Hydride Functions Degradation Pathways: (A) Hydrolysis and Silanol Formation; (B) Silanol Condensation; (C) Direct Hydride Addition on Silanol[42]
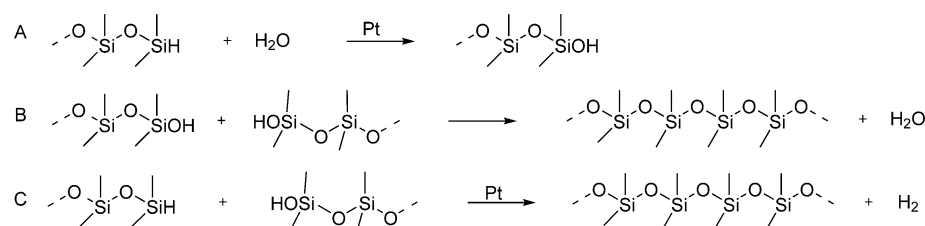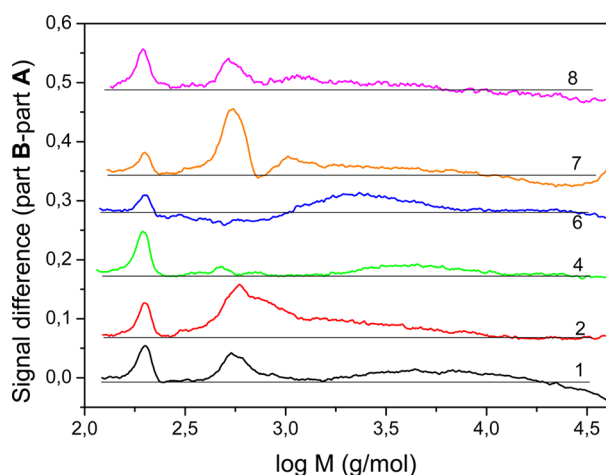
Figure 8. Subtraction between part **A** and part **B** SEC signals (**1** = black; **2** = red; **4** = green; **6** = blue; **7** = orange, **8** = purple).

Figure 10. Influence of the molar mass between cross-linking points (black circles) and filler content (red squares), deduced from part **B** residue at 900 °C, as a function of measured hardness (except for formulations **3** and **5** where the supplier values are given). Black line represents the linear fit of theoretical M_c as a function of measured hardness ($r^2 = 0.84$).

cross-linker, the molar mass between cross-links M_c theoretically corresponds to the number-average molar mass of the vinyl terminated PDMS chains. The average molar mass between cross-links is in the range of 35 000−45 000 g mol^{-1} for 30 Shore A materials while α,ω-divinylpolydimethylsiloxane is two times longer for 20 Shore A material (see Table 2). For all other (harder) formulations, D^{Vi} units inside the chain form extra cross-linking points (Figure 9).
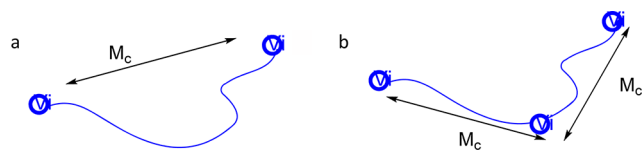

Figure 9. Molecular between cross-linking points for (a) telechelic divinyl polydimethylsiloxane; (b) poly(dimethyl-*co*-vinylmethyl)-siloxane (case of $n_{D^{vi}} = 1$).

The theoretical molar mass between cross-linking points is recalculated from eq 7, including the number of D^{Vi} unit per chain, $n_{D^{vi}}$, estimated from proton NMR by comparing integration of D^{Vi} signals (6.03 and 5.83 ppm) to M^{Vi} ones (6.15, 5.95, and 5.75 ppm) (Figure 7 and Table 2).

$$M_c^{\text{theoretical}} = \frac{M_n^{\text{sec toluene}}}{1 + n_{D^{Vi}}} \qquad (7)$$

Harder materials indeed present shorter molar masses between the vinyl functions (see Table S5 in the Supporting Information). Figure 10 shows a strong correlation between material hardness and theoretical M_c (the molar mass between cross-linking points deduced from chemical analysis).

The case of formulation **8** is not trivial. On one hand, the total relative vinyl concentration (Table 2) is similar to other formulations; but on the other hand, the vinyl bearing polymer is shorter and includes D^{Vi} units (0.8 per chain), bringing additional end-and inside-chains vinyl groups, respectively. As both ^{1}H and ^{29}Si NMR spectra confirmed the presence of D^{Vi} units, we exclude the possibility of NMR artifact. A possible explanation would be that some neutral PDMS chains are added to the recipe to act as a long molar mass plasticizing agent, as is often done in silicone gel formulations.
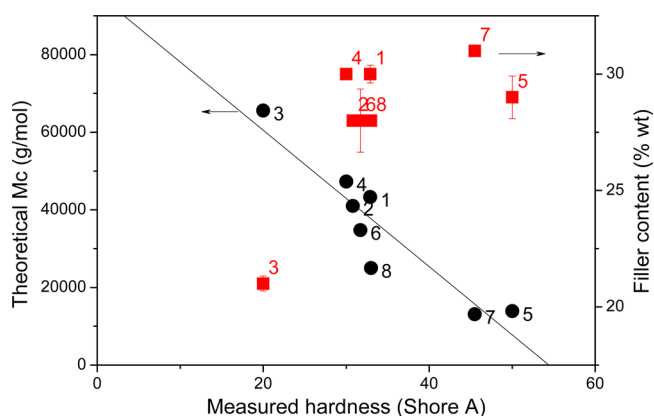
Silica Content and Surface Modification. Industrially, hardness, measured on Shore A scale for silicones, is one of the major physical parameter for material choice. Plotting the filler content, deduced from TGA measurements for all formulations, shows no significant differences between the 30 Shore A grades (Figure 10). Decreasing hardness to 20 Shore A is obtained by likely decreasing the silica content to 20%.[46,47] The hardest 50 Shore A materials do not include extra filler compared to 30 Shore ones. Indeed, it is well know that silicone formulations containing more than 40% filler are difficult to prepare even in the presence of processing aids.[48] To overcome the 30 Shore A limit, other tricks include to decrease the M_c and/or to functionalize the silica surface.

When embedded in a formulation, exploring the silica surface is, from our experience, an impossible task to achieve. The equivalent chemical nature of silicone and silica induces (i) a strong compatibility between products, precluding easy separation and (ii) complex analyses of the blends, since analytical techniques are not sensible enough to discriminate silica from PDMS (see representative pictures of the silica particles and aggregates observed in the final elastomer material, given in Figure S1 in the Supporting Information). Nevertheless, information can be deduced from indirect evidence. As discussed in our previous study,[24] the residue difference between parts **A** and **B** varies accordingly to the silica surface modification and the platinum concentration. Figure 11a shows three formulations' groups (values given in the Supporting Information, Table S6). In the first group (**1**, **3**, **4**, and **8**), incorporation of platinum catalyst (in part **A**) increases the residue of 12−15% compared to the part **B**, which is commonly observed for typical LSR formulations[49,50] (blends of silicone, standard modified silica and 10−15 ppm of platinum catalyst). The second group of formulations (**2** and **5**) presents strong residue differences between both formulation parts (higher than 30%). We could attribute the residue increase to chain immobilization via chemcial reaction with vinyl groups grafted on the silica surface.[51] In the third group (formulations **6** and **7**), the extremely low residue difference, 5 and 9 wt % respectively, indicates low platinum content. This fact was confirmed by degrading cured materials under nitrogen (Figure 11b), the degradation residue reached
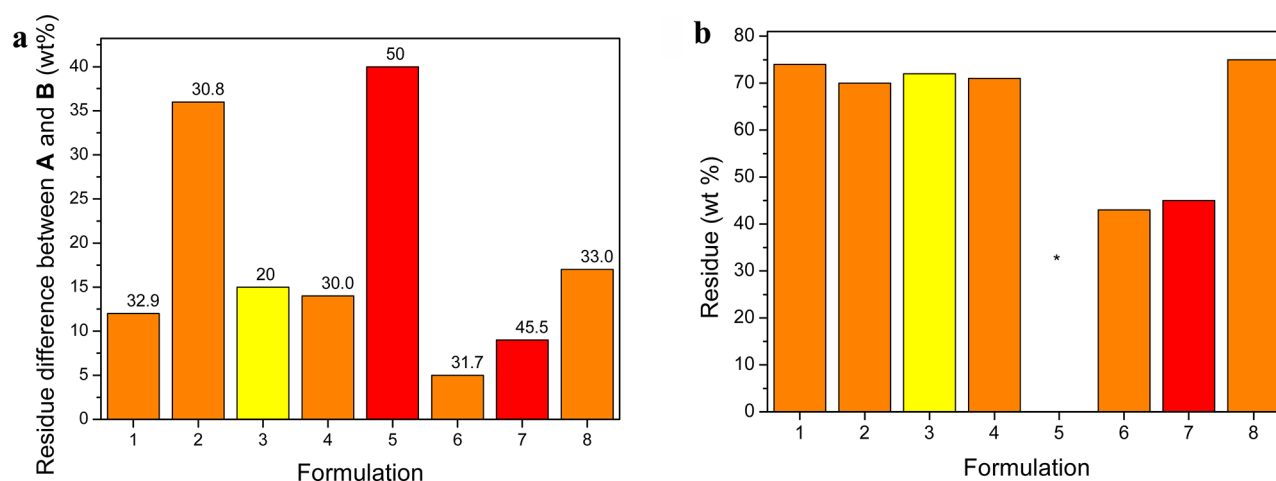
Figure 11. (a) Difference of remaining residue at 900 °C between **A** and **B**; labels indicate the measured hardness; (b) degradation residue at 900 °C of cured materials (* not measured).
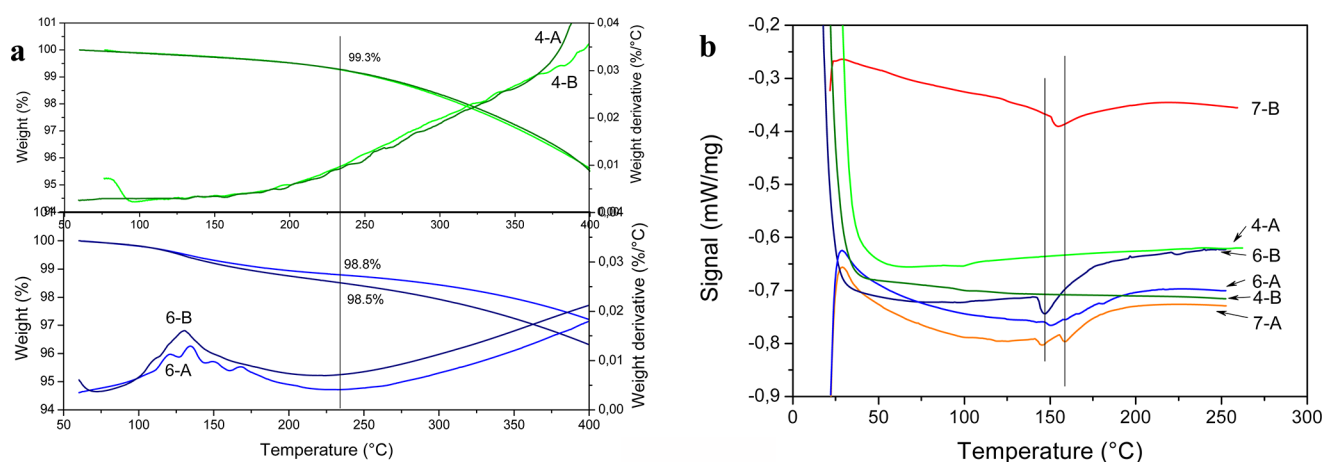

Figure 12. (a) Zoom (below 400 °C) on the TGA thermograms under nitrogen of formulations **4** and **6** and (b) DSC traces of parts **A** and **B** taken separately, formulations **6** and **7** and formulation **4**, for comparison.
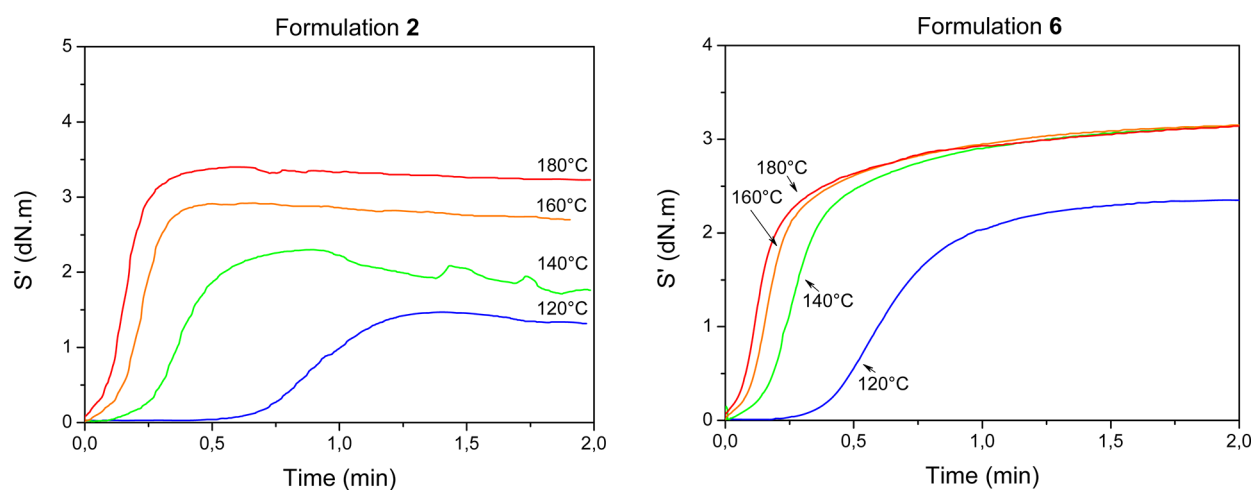

Figure 13. Elastic torque evolution of formulation **2** and **6** during the curing at 120 °C (blue curve), 140 °C (green curve), 160 °C (orange curve), and 180 °C (red curve). (Other formulations' curing curves are given in Figure S4 in the Supporting Information).

around 73 wt % for most of the materials against only 45% residue for formulations **6** and **7** (vide infra).

Dual Catalysis. As seen before, the formulations **6** and **7** are special cases that deserved finer analysis. By heating both parts

under nitrogen, visual observation of the part **A** residue at 900 °C exhibit a hard black and shiny surface, as expected when platinum catalyzes the degradation. The heart of the residue is composed of a brownish, matte, friable solid, as does the entire

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dx.doi.org/10.1021/am300502r | *ACS Appl. Mater. Interfaces* 2012, 4, 3340–3352

part **B** residue. We observed residues with similar microstructure and color in a previous study while degrading peroxide-silica-PDMS blends.[33] On the derivative weight loss curves of the thermograms, a primary product degradation of about 1.2 wt % is observed between 120 and 150 °C (Figure 12a). By DSC (Figure 12b), a broad endotherm is seen from 140 to 170 °C for parts **B** and double endothermic peaks for parts **A**. Other formulations do not show any thermal phenomena (e.g., **4-B**, Figure 12b). All these results suggest that a peroxide, which decomposing temperature would be set at about 130 °C, is included in both parts; the peroxide mostly used in EVC silicone formulation is 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, degrading at 156 °C (216 g·mol^{-1}). Another possible candidate is 2,4-dichlorobenzoyle, which is not vinyl specific and does not require pressure. The formulations **6** and **7** are likely cross-linked by hydride addition on vinyl groups through radical mechanism. Nevertheless, several clues also indicate the presence of platinum catalyst, though in lesser quantities: (i) peak characteristic of inhibitor at 2.47 ppm is observed by ^{1}H NMR in part **B**; (ii) shiny black ceramized residue surface is obtained after part **A** degradation; (iii) the residue of part **A** is slightly higher than the part **B** residue, which would not be the case if only peroxides were added as curing agents.

3.3. Curing and Physical Chemistry of Final Materials.

3. 3. 1. Kinetics of Curing and Injection Molding. For formulations **1**, **2**, **6**, **7**, and **8**, the curing behavior at 120, 140, 160, and 180 °C was followed by recording the elastic torque evolution. Three stages were observed in a less than 90 s range: (i) inhibition step corresponding to the degradation of the ethynyl cyclohexanol molecule and the induction period during which the active catalytic species are generated;[3] (ii) cross-linking and (iii) stabilization (Figure 13). For all formulations, similar behavior was observed: as the temperature increased, the inhibition time turned out to be shorter and the reaction rate increased. It should also be noted that the final torque rised from 120 to 180 °C. At the end of the cross-linking step, formulations **1**, **2**, **8** presented constant torque, whereas the final torque of **6** and **7** continued to evolve, confirming that cross-linking system(s) for these two formulations is (are) more complex than a simple platinum-catalyzed hydrosilylation. Moreover, increasing the curing temperature for formulations **6** and **7**, respectively above 140 and 160 °C, did not show any torque improvement, whereas formulations **1** and **8** exhibited higher final torque with curing temperature (Figure 14). From 160 to 180 °C, torque increased only slightly, the worst case being observed for formulation **2** for which each curing temperature increase corresponded to a constant torque increase.

The study of the average reaction rate gave similar trends (see Figure S5 in the Supporting Information). To summarize, the formulations **6** and **7** are highly reactive at low temperature compared to the others. High curing temperature is required to fully cross-link formulation containing two cross-linkers (formulation **2**, see Figure S6 in the Supporting Information). Formulations **1** and **8** stand between these two limiting cases.

Thanks to these kinetics measurements, conditions for curing the final formulations were set; an industrial injection molding machine was used at three temperatures, 180, 200, and 220 °C during 55, 47, and 36 s, respectively. Investigations were focused on the 30 Shore A material to get pertinent comparison. Cured materials were then swelled in deuterated chloroform and analyzed by liquid ^{1}H NMR. It is worth to
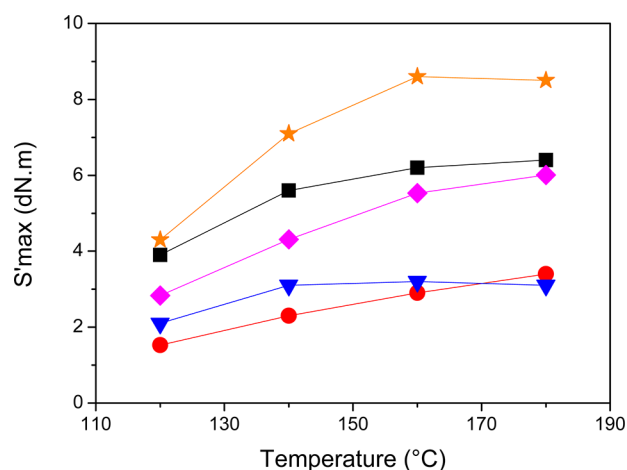

Figure 14. Final elastic torque attained by formulations **1** (black squares), **2** (red circles), **6** (blue down triangles), **7** (orange stars), and **8** (purple diamonds).

mention that whatever the used conditions, all spectra showed that no functional groups remained in the materials, albeit according to the precision of the technique (see Figure S6 in the Supporting Information).

Swelling Measurements. The extractable materials amount is obviously correlated to the oil content (see Figure S7 in the Supporting Information). As the cross-linking temperature increased, little differences were observed, suggesting that temperature of 180 °C is high enough to obtain fully cross-linked materials (Figure 15). A slight improvement was observed when temperature increased for formulation **2**, as already suggested by the reactivity study (vide supra, Figure 14).
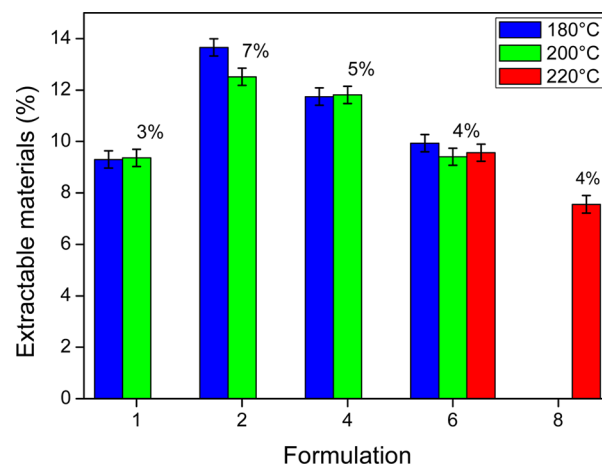

Figure 15. Extractable materials as a function of temperature molding for 30 Shore A materials (labels indicate the oil content).

In addition to quantifying the content of extractable materials, swelling measurements in methylcyclohexane also give useful information on the topology of the network. When performed in presence of ammonia fumes, swelling measurements only provide the chemical cross-link density, i.e. cross-linking points generated by hydrosilylation (Figure 16a). For materials cured at 180 °C, the molar mass between chemical cross-links M_c^{Ch} increased in the following order: **1** < **2** # **6** < **4**. On the other hand, as the curing temperature increased, molar

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dx.doi.org/10.1021/am300502r | *ACS Appl. Mater. Interfaces* 2012, 4, 3340–3352
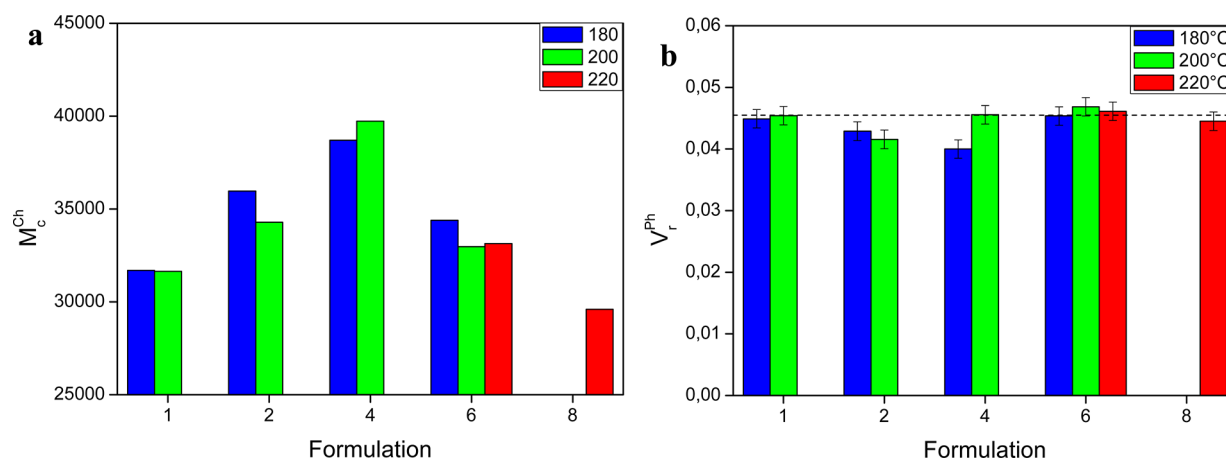
Figure 16. (a) Molar mass between chemical cross-links measured by swelling in presence of ammonia fumes; (b) extent of hydrogen bonds in the materials depending on the curing temperature (dashed line is only a guide for the eye).

mass between chemical cross-links remained constant, which confirms that complete cross-linking is fully achieved at 180 °C for most materials. Only formulations **2** and **6** presented a small improvement as the molar mass between cross-links slightly decreased (4%).

Swelling measurements in absence of ammonia fumes probe both the chemical and the physical contribution to cross-linking. Concerning the latter, the following conclusions can be drawn from formulation comparison: (i) whatever the curing temperature, similar silica surface are observed for materials **1**, **6**, and **8**; (ii) cured at 180 °C, material **2** and particularly material **4**, possess much less physical cross-linking points than others (Figure 16b). However, increasing curing temperature led to a slight increase of the immobilization of PDMS chains on silica surface. Finally, all materials cured at 200 °C are close to each others in terms of physical cross-links. Slightly lower hydrogen bonds were observed for formulation **2**, possibly because of the vinyl modified silica surface. Depending on the curing temperature, two cases are distinguished, as shown in Figure 16b. On the one hand, hydrogen bonding remains constant as curing temperature increases for formulations **1**, **2**, and **6** (−3 to +3%). On the other hand, formulation **4** shows an enhancement of physical cross-link as T_c increased, +14%.

4. DISCUSSION

The comparison of the chemical recipes of eight different LSR formulations highlights fundamental trends between the chemical structures in the formulation and the network topology of cured material. Cross-link density, modulus and hardness are often correlated using rubber elasticity and the classic Flory-Rehner approach, assuming an ideal, filler-free network and Gaussian chain statistics.[52] Mark et al.[47] reported that the molar mass between cross-links M_c impacts the hardness. Recent work has demonstrated that the theory of Boussinesq potentially relate Shore A durometer hardness and elastic modulus.[53] In a first, rough approximation, we showed that the filler content sets the hardness. Silica concentrations ranging between 20 and 35 wt % approximately lead to materials in the range of 20 to 35 Shore A. Second, modifying the silica surface with coupling agent strengthens the materials. By decreasing the molar mass between cross-linking points, finer hardness adjustment can finally be done.

Even in the case of unfilled elastomers, the optimal yield of hydrosilylation reaction is not reached under stoichiometric

ratio but rather by introducing an excess of the high functional cross-linker. The imbalance giving the highest modulus (r_{opt}) increases according to the molar mass of vinyl terminated PDMS: for low molar mass polymer, the maximum modulus is obtained for a stoichiometric ratio around 1.3[54,55] and reaches 1.8 for 54 000 g mol^{-1} telechelic polymer.[56] Two explanations were proposed to explain such imbalance: (i) the viscosity increase limits the active species diffusion;[54] (ii) side reactions consume Si−H functions.[57−59] Obviously, lower r would favor the formation of dangling chains, i.e., chains linked only by one end to the network, not to say extractible species, i.e., un-cross-linked chains, in the worst case (Scheme 2).[59] By decreasing

Scheme 2. Schematic Representation of a (non-perfect) Polymer Network Formed by End-Linking Reactions
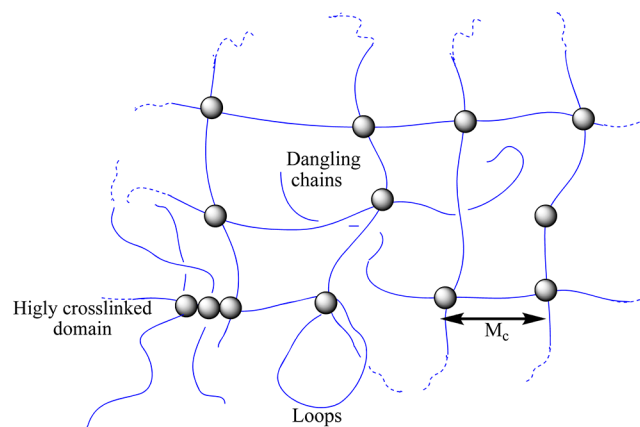
the effective cross-linker functionality, and increasing the number of defects, the material properties would be degraded since the number of elastic chains decreases and dangling chains relax stress. The loss modulus (G'') of these networks depends on the concentration and the molar mass of the dangling chains.[60,61]

To anticipate potential hydride degradation or nonreactivity, all the formulations accordingly contain hydride excess. Proton NMR spectra of the cured materials proved that all the functional groups have reacted when formulation is cured as low as 180 °C, supporting the hypothesis that the hydride groups in excess react together during the curing, probably by hydrolysis and condensation reactions (Scheme 2). M_c, the

average molar mass between cross-linking points, is greatly affected by these reactions that connect two cross-linkers through a very short bridge. Although not clearly explained, the bimodal behavior of materials obtained by hydrosilylation of vinyl terminated PDMS with poly(methylhydrido-*co*-dimethyl siloxane) has been already observed.[62] As shown in Figure 17,
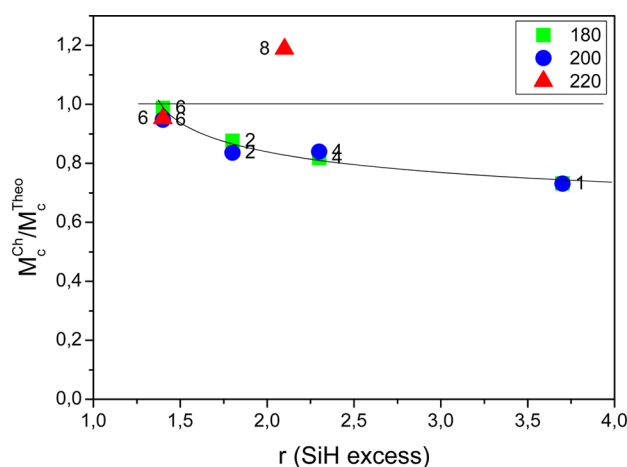

Figure 17. Cross-linking reaction efficiency measured by the ratio M_c^{Ch}/M_c^{Theo} as a function of hydride excess. Labels indicate the formulation numbers. Lines are only guides for the eyes.

the ratio between theoretically and experimentally determined molar masses between cross-linking points decreases as the ratio SiH/SiVi increases from 1.4 to 3.7. Higher hydride concentration leads to a depressed control of the network architecture by creating extra cross-linking points randomly distributed, decreasing M_c^T compared to the theoretical values measured as the length of the chains between two vinyl groups.

Surprisingly, two liquid silicone rubber formulations were proved to be cured by a combination of platinum and peroxide catalysts. Although the hydride excess r is smaller than for the other formulations, the apparent efficiency of the cross-linking reaction approaches 100% (Figure 17). Moreover, the sensibility to curing temperature of the final torque is less pronounced than the final torque of platinum-cured formulations (Figure 13). However, this double-catalyzed cross-linking system suffers from other drawbacks, such as higher degradation at high temperature and lower reaction rate during the final stage of curing. Furthermore, vinyl/vinyl and vinyl/methyl groups couplings by radical means obviously decrease the control on the network architecture.

According to these results, material **4** is defined as the most regular network composed of elastic chains with narrow polydispersity index contrary to material **1** in which the high cross-linked domains due to reaction of hydride in excess, disrupt the regularity. In materials **2** and **8**, introduction of few ramdomly distributed D^{Vi} units induces broadening of the network chains polydispersity index. Most likely, neutral chains have been incorporated into the formulation **8** to act as a plasticizer. As nearly stoichiometrically balanced formulation containing short cross-linker, the network strands in material **6** should be highly unimodal. However, radical mechanism probably cause vinyl-methyl coupling that may strongly increase the polydispersity index of the elastic chains.

Network structures of softer (formulation **3**) and harder (formulations **5** and **7**) materials were not analyzed by swelling measurements. However, according to the chemical analyses,

they should follow similar features: (i) molar mass between vinyl groups correlating with the hardness., (ii) hydride excess inducing extra-cross-linking points.

■ CONCLUSION

Different LSR formulations from various providers have been investigated through conventional chemical analyses. TGA revealed to be a powerful tool to probe the silica content and to give information about surface modification. This technique also permitted to rank formulations according to their platinum catalyst concentration. The architecture and molar mass of polymers were established by ^{29}Si NMR and SEC in toluene, respectively. Although hydride and vinyl reactive groups are in concentration as low as 1×10^{-5} mol/g, relative concentrations and stoichiometric imbalance could be quantified by proton NMR. Basically, all 30 Shore A formulations contained about 30% by weight of silica filler, a long vinyl terminated poly(dimethylsiloxane) and poly(diphenyl-*co*-dimethylsiloxane) as a bleeding agent. Part **A** contains the platinum catalyst, whereas the cross-linker, a short poly(methylhydro-*co*-dimethyl siloxane), is included in part **B** with the catalyst inhibitor.

By comparing the different formulations, it has been shown that hardness adjustment is mainly performed by playing on two parameters: for hardness ranging from 20 to 30 Shore A, the filler content and molar mass between cross-linking points were adjusted; above this limit, it is necessary to modify the silica surface with reactive groups, such as vinyl functions. With hydride functions well redistributed along the cross-linker chain, stoichiometric imbalance is slightly higher than 1.5, whereas for some formulations, r as high as 3.7 were implemented. This showed strong implications on the cross-link density. Since no functional groups were observed by NMR spectroscopy in the cured (swollen) material, we concluded that the hydride groups in excess react together decreasing the molar mass between cross-linking points, i.e. lowering the control on the network architecture. Finally, as the curing temperature increased from 180 to 200 °C, cross-linking due to hydrosilylation reactions exhibited no significant variation while physical contribution to cross-linking, related to the amount of hydrogen bonding between silica surface and poly-(dimethylsiloxane) backbone, was slightly increased. Two formulations have been proved to use a combination of two cross-linking systems, hydrosilylation and radical coupling leading to better cure at lower temperature.

The first part of this series allowed us to identify the influence of LSR chemical compositions on the material network topologies. We now have in our hands a large variety of materials ranging from tightened to lose networks (i.e., small to large molar mass between cross-linking points), with gradual number of defects and more or less polydisperse knots. In the next part of this series, we will look specifically at the influence of these network structures on the final material mechanical properties.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Nomenclature and chemical shifts for various siloxane units as well as raw data used in this study; additional kinetics curves, ^{1}H and [29]SI NMR spectra of cured materials. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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