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Karstedt Catalyst – Catalyzed stepgrowth co-polyaddition of 1,9-decadiene and 1,1,3,3-tetramethyldisiloxane

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Abstract

Low to medium molecular weight H–Si-terminating and alkyl–Si-terminating co-polyadducts of 1,9-decadiene and 1,1,3,3-tetramethyldisiloxane have been synthesized. Molecular weight determination from ^{1}H NMR data is described. Product features indicate that this novel class of siloxane-modified paraffins offers quite interesting properties.

Keywords: 1,9-Decadiene; 1,1,3,3-Tetramethyldisiloxane; Hydrosilylation; Silalkylenesiloxanes; Karstedt Catalyst

1. Introduction

Bonding characteristics and polarities in the backbone of *n*-paraffins generate a significant degree of intermolecular order through London forces [1]. Therefore, *n*-paraffins are able to crystallize and have well defined melting points up to $C_{16}H_{34}$ (m.p. 18 °C).

In contrast, linear polydimethylsiloxanes (PDMS) with their extremely low degree of intra- and intermolecular order remain pourable liquids down to -50 °C even at chainlengths of 1000 and more dimethylsiloxy units [2].

Molecular structures and bonding characteristics determine a wide variety of product properties, e.g., in rheology, surface activity, chemical resistance, ecological behaviour, etc. Both paraffins and PDMS show similarities and differences, advantages and disadvantages in these product properties with respect to practical applications. Therefore, industrial and academic research groups have looked for potential synergistic effects from chemically combining polysiloxane and polyalkylene building blocks in one molecular copolymer backbone.

Patents and papers published during the past 10–15 years were primarily focussed on the generation of long-chained crosslinkeable and non-crosslinkeable products of maximum molecular weights.

Kobayashi [3] synthesized polysilalkylene siloxanes and silalkylene siloxanediorgano-siloxane copolymers of average molecular weights of 7000–10000 by reacting 1,5 hexadiene with nearly equimolar quantities of SiH-terminated polysiloxanes incl. tetramethyldisiloxane **A** in refluxing toluene with a Pt/carbon catalyst. Sargent and Weber [4,5] and independently Domenico et al. [6] described the synthesis of silalkylenesiloxane copolymers by reacting αω-dienes incl. 1,9-decadiene **B** with **A** in equimolar quantities in the presence of a 1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum complex. Domenico et al. used the copolymers as intermediates for the synthesis of cyclosilalkylenesiloxane monomers. The latter were finally subject to ringopening polymerization (ROP).

Noda et al. [7] produced linear polymethylene–polysiloxane alternating block copolymers by reacting alkadiens incl. **B** with SiH terminated dimethylpolysiloxanes in the

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presence of a catalyst, e.g., H_2PtCl_6. Herzig et al. [8] described emulsion–polymerization of organic compounds with at least two C=C per molecule incl. **B** and organopolysiloxanes with in average more than one SiH per molecule in the presence of a catalyst selected from the group of platinum group metals or platinum group metal compounds and an emulsifier.

1.1. Objectives of our study and basic design

Firstly, we wanted to synthesize low to medium molecular weight silalkylenesiloxanes and study key characteristics of such "siloxane-modified paraffins", e.g., in comparison to unmodified paraffins especially when additional alkyl endgroups were attached. More specifically, "siloxane-modification" should be chemically effected by incorporating via SiC-bonds siloxane fragments as few as possible and as short as possible between $-(CH_2)_x-$ building blocks, which should be as long as possible. Thus, the silicone character should be kept at minimum and reduced to expected "flexible joint" functions in the molecule.

Hydrosilylation-type stepgrowth polyaddition between suitable αω-HSi- and αω-H_2C=CH– carriers was the synthesis of choice for our study.

In line with this basic concept, 1,1,3,3-tetramethyldisiloxane **A**, the shortest possible linear siloxane building block, was used exclusively as siloxane linker in our study. The longest-chained αω-diene commercially available was 1,9-decadiene **B** and hence, was also exclusively used as paraffinic building block in our study.

Secondly, the present study focussed on molecular weight determination by routine NMR techniques of the novel oligomeric silalkylenesiloxanes. The question of how ^{1}H NMR based average molecular weight determination would correspond to the expected molecular weights with respect to the stoichiometry of the educts and with respect to GPC data was to be addressed.

Finally, an straightforward and safe laboratory method for the reproducible synthesis of the target co-oligomers from the extremely reactive educt system: **A**/**B**/catalyst was to be established.

If not specifically mentioned otherwise, all co-polyaddition reactions in this study were performed by controlled addition of catalyst/**B** mixture to excess **A**. Thus, in a first step, oligomeric HSi-terminated silalkylenesiloxane intermediates were expected with one –SiOSi– link per every 10 $-CH_2-$ units in the backbone. They were investigated as such or further converted to alkyl-endcapped derivatives, which were entirely stable in air and remained unaffected by moisture or elevated temperatures.

1.2. Key issues

Selection of the catalyst was a key issue for the smooth synthesis of our target products. From the numerous catalysts and catalyst compounds referenced in the literature for hydrosilylation reactions [9] we tested an assortment of Pt-based catalysts typically used in the industry for hydrosilylation namely *cis*-dichloro-platinum(II)-diamine, hexachloroplatinum acid-hexahydrate in *i*-propanol (Speier Catalyst [10]), a Pt/activated carbon catalyst, and a 1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum complex (Karstedt Catalyst [11]). The latter was most reactive even at RT. Thus, the low boiling point of **A** was of no concern and the reactions were complete within few hours or less. The catalyst remained fully active and entirely soluble in the system even after extended interruptions of the synthetic procedure or after the storage of intermediates. There was no inhibition or induction effect observed (safety issue) and the system remained free of contamination by any ionic or acidic components, alcohol or carrier-solids. Therefore, a Karstedt-type catalyst **C** was used exclusively in this study.

Throughout our studies, **C** was predissolved in **B** directly in the dropping funnel prior to the reaction.

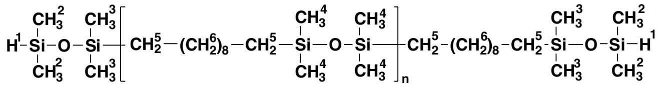
Migration of terminal C=C double bonds to an internal position under the influence of the platinum catalyst complexes and in the presence of SiH is a known feature in hydrosilylations. The process, studied for the first time as early as 1965 [12], is well described and explained in the literature. Sargent and Weber have dealt with the consequences of this C=C isomerization particularly for the maximum achievable chain lengths in equimolar αω-diene/**A** copolymerizations [4,5].

2. Results and discussion

We found that the strongly exothermic stepgrowth co-polyaddition of **A** and **B** proceeds smoothly under the conditions of our study with easily controllable reaction velocity. Several defined average chain lengths up to $\mathbf{A}(\mathbf{BA})_{15}$ have been synthetically tailored simply via the applied molar educt ratio of **A**/**B**. Also, subsequent αω-additions of 1-alkenes to the HSi-terminals of the intermediates could be easily performed at RT or at slightly elevated reaction temperatures.

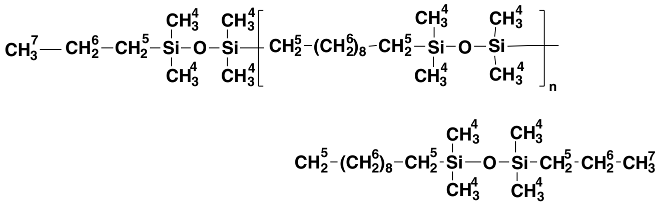
Based on the ^{1}H NMR signal integrals at 5.4 ppm (inner –HC=CH– after migration) in comparison to the signal integrals at 0.5 ppm (methylene groups directly linked to Si after successful addition) it was found that max. 3% of the terminal H_2C=CH– moieties originally present in **B** had been converted to internal C=C double bonds under the applied reaction conditions and formed $C_{10}H_{19}$-endblocker groups. Considering the large stoichiometric excess of **A** over **B** at any time of our experiments based on the reaction design, we ignored the C=C migration in the molecular weight calculations.

According to the ^{1}H-NMR data, the oligomeric HSi-terminating intermediates of the stoichiometric formula $\mathbf{A}(\mathbf{BA})_{\mathbf{n+1}}$ resulting from reacting **B** with **A** under the conditions applied have the following molecular formula (Formula 1)



$$H^1\text{-}Si(CH_3^2)_2\text{-}O\text{-}Si(CH_3^3)_2\text{-}[CH_2^5\text{-}(CH_2^6)_8\text{-}CH_2^5\text{-}Si(CH_3^4)_2\text{-}O\text{-}Si(CH_3^4)_2]_n\text{-}CH_2^5\text{-}(CH_2^6)_8\text{-}CH_2^5\text{-}Si(CH_3^3)_2\text{-}O\text{-}Si(CH_3^2)_2\text{-}H^1$$

The propyl-endcapped derivatives display Formula 2:



$$CH_3^7\text{-}CH_2^6\text{-}CH_2^5\text{-}Si(CH_3^4)_2\text{-}O\text{-}Si(CH_3^4)_2\text{-}[CH_2^5\text{-}(CH_2^6)_8\text{-}CH_2^5\text{-}Si(CH_3^4)_2\text{-}O\text{-}Si(CH_3^4)_2]_n\text{-}CH_2^5\text{-}(CH_2^6)_8\text{-}CH_2^5\text{-}Si(CH_3^4)_2\text{-}O\text{-}Si(CH_3^4)_2\text{-}CH_2^5\text{-}CH_2^6\text{-}CH_3^7$$

Six groups of protons and three different ^{29}Si signals (δ −7.1, 7.2, 9.8 ppm) are present in the NMR spectra of the HSi-terminating intermediates. The propyl-endcapped derivatives show four different groups of protons. Also, three ^{29}Si nuclei with slightly different chemical shifts can be identified (δ 7.0, 7.25, 7.3 ppm). The absence even of trace signals in the −21 ppm area of the ^{29}Si NMR spectra seems noteworthy and is evidence for the absence of any noticeable quantity of D-type siloxane moieties $–O–Si(CH_3)_2–O–$ in the products of Formula 1 or 2. Such moieties would have been formed if moisture would have converted terminating H–Si groups to HO–Si groups under the influence of platinum catalysts with subsequent condensation to $–Si(CH_3)_2–O–Si(CH_3)_2–O–Si(CH_3)_2–$, a common and undesirable side reaction in industrial hydrosilylations. All proton signals were assigned to their positions in the molecules as indicated in the formulae above. Furthermore, the proton signals fall into two catagories in both the intermediates and the propyl-endcapped derivatives: signals with their integrals independent from chain-length *n* and signals with their integrals being a function of *n*. Hence, average chain length and molecular weight can be conveniently calculated and confirmed by various signal references. Tables 1 and 2 list all proton signal positions (against a chloroform standard at δ 7.24 ppm) and the signal integrals.

Charts 1 and 2 present the proton-NMR spectra of the compounds $\mathbf{A}(\mathbf{BA})_{3.03}$ and $C_3H_7–\mathbf{A}(\mathbf{BA})_{3.03}–C_3H_7$, respectively, in the key area of −0.1 to +1.5 ppm.

Table 1
Proton signals and signal integrals of the compound $\mathbf{A}(\mathbf{BA})_{3.03}$

Nucleus	ppm	Signal integral
H^1	4.7	Sept. 2
H^2	0.15	d 12
H^3	0.04	s 12
H^4	0.01	s 12 n
H^5	0.5	m $4n+4$
H^6	1.3	m $16n+16$

Overlapping triplets from the H^5 – signals in the individual $(\mathbf{BA})_n$ homologues.

Table 2
Proton signals and signal integrals of the compound $C_3H_7–\mathbf{A}(\mathbf{BA})_{3.03}–C_3H_7$

Nucleus	ppm	Signal integral
H^7	0.95	t 6
H^4	0.01	s $12n+24$
H^5	0.5	m $4n+8$
H^6	1.3	m $16n+20$

Overlapping triplets from the H^5 – signals in the individual $(\mathbf{BA})_n$ homologues.

The results of the average molecular weight calculations based on the ^1H NMR data and on the stoichiometric educt relationship of **A**/**B** are similar to each other but significantly different from the GPC/Mn results. Three typical examples (Table 3) illustrate this finding. Similar findings were reported by Sargent and Weber [4].

Nevertheless, the GPC plots depict impressively (see Chart 3) the stepgrowth polyaddition process in the lower molecular weight area up to eight or nine multiples of (**BA**), each displaying a distinct individual peak. This is applicable for both products from the reaction of **B** in excess **A** and vice versa. With a calibration system better adapted to the specific chemistry of the products investigated here, GPC might also be well suited for direct molecular weight determination.

Evidently, routine proton NMR-recordings provide a quick and straightforward tool for calculating fairly accurately the average molecular weights of "Karstedt Catalyst" catalyzed stepgrowth co-polyaddition products of **A** and **B** under the conditions applied in our study.

3. Product properties

All silalkylenesiloxanes synthesized in this study are clear, colourless or slightly yellowish liquids. They remain liquid even below 0 °C. The product with the molecular formula $C_3H_7–\mathbf{A}(\mathbf{BA})_{3.03}–C_3H_7$ with in average 34 $–CH_2–$ units in one molecule chain, interrupted by four disiloxy links solidifies only at −21 to −25 °C upon cooling and becomes liquid again at −12 to −10 °C upon heating. Even the product with the average molecular formula $C_8H_{17}–\mathbf{A}(\mathbf{BA})_{6.67}–C_8H_{17}$ with ≈80 $–CH_2–$ and seven disiloxane units in one molecule starts solidifying not before −15 °C and melts at 0 °C. Obviously, already a few short "flexible joints" of disiloxane links integrated into a longchained linear hydrocarbon backbone hinder the formation of intermolecular structures very efficiently. This might be an interesting aspect for tailoring bulk product properties per se or via αω-functionalized silalkylenesiloxane building blocks for synthesis.

One such bulk property of practical relevance is the viscosity index (VI). Compared to a 62.5% paraffin based industrial standard gear oil of VI 102 (DIN ISO 2909), the product octyl-$\mathbf{A}(\mathbf{BA})_{6.67}$-octyl of our study showed a VI of 151 which means significantly less dependance of kinematic viscosity from temperature.

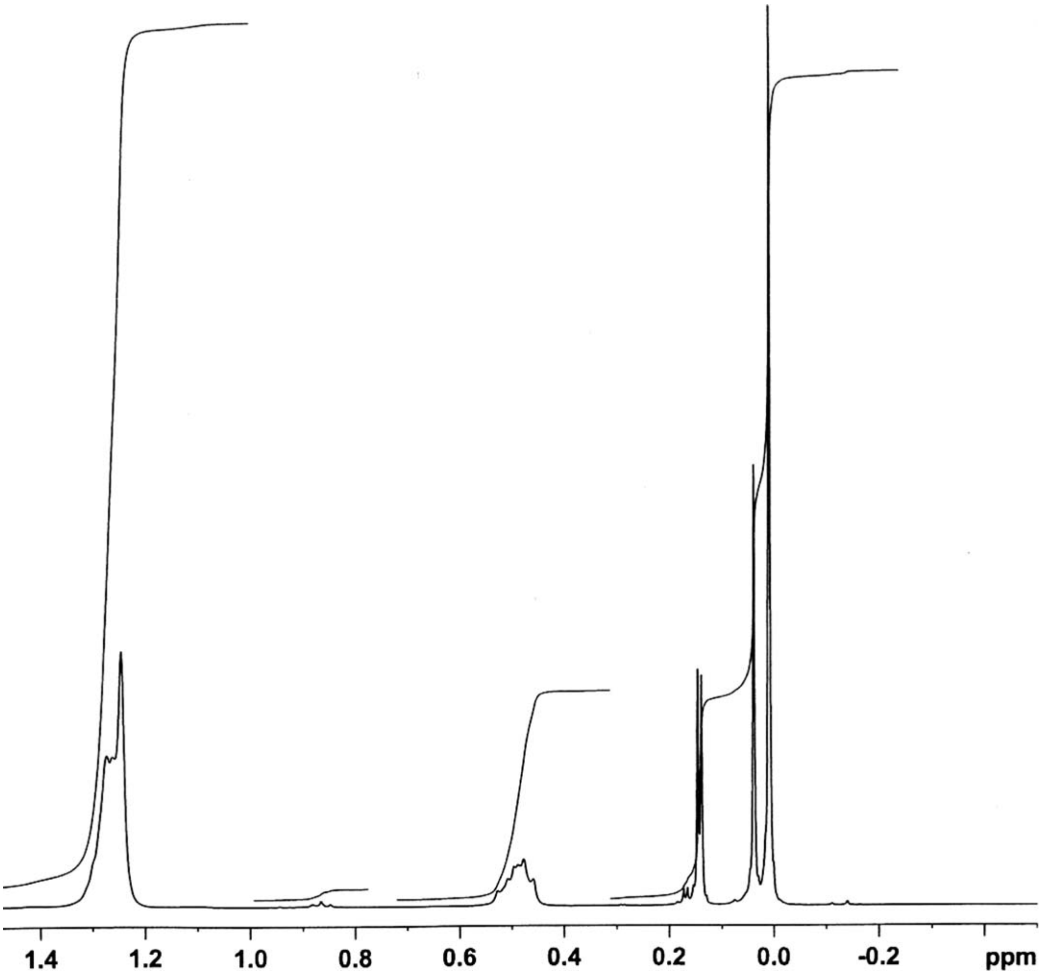


Chart 1. ^{1}H NMR spectrum of the compound $\mathbf{A}(\mathbf{BA})_{3.03}$.

Surface activity of a liquid is another product feature of great importance in many practical applications. With 24.3 mN/m the product C_3H_7–$\mathbf{A}(\mathbf{BA})_{3.03}$–$C_3H_7$ shows significantly lower surface tension than *n*-dodecane or *n*-tridecane (27.12 and 27.73 dyn/cm^2, respectively ([13]) and standard industrial grade paraffin oil (30.9 mN/m). Another indicator of visibly stronger surface activity of the silalkylenesiloxanes of our study compared to paraffins was enhanced spreading capability. One drop (0.015 g) of the propyl-terminated product, placed on a degreased carbon steel surface, spreads over night over a surface of $\approx$24 cm^2 whereas the paraffin oil (0.019 g/drop) covers only $\approx$8 cm^2. On polycarbonate the relation was $\approx$15 vs. 7 cm^2.

Already these few preliminary findings indicate that some interesting product properties could be associated with these novel oligomeric silalkylenesiloxanes and seem worth to be investigated more deeply.

4. Experimental

4.1. Raw materials

All raw materials were industrial grades and were used as received without further purification.

1,9-Decadiene was received from Degussa Fine Chemicals, 1,1,3,3-tetramethyl-disiloxane (>97%) from Wacker Chemie, Karstedt Catalyst (20.71% Pt) from OMG Group, now Umicore. Paraffin Oil was obtained from Brenntag AG, 1-octene from Sigma–Aldrich and propene from Linde Technische Gase.

4.2. Instrumentation

All nuclear magnetic resonance spectra were performed on a Buker DPX 400 instrument. GPC analyses were performed on a HP1100 system with 8.0 mm × 650 mm SDV1000/10000 Å columns; mobile phase: THF.

4.3. Equipment and general procedure

4-Necked rb glass flasks were equipped with sealed mechanical stirrer, thermo sensor, reflux condenser, pressure-equalizing dropping funnel, N_2-inlet and checkvalves attached to the reflux condenser head. For reactions with propene, the propene source was adjusted to max. 0.7 bar supply pressure with downstream flow control valve. The gas was administered directly to the glass flask via an additional gas inlet. Check valves were adjusted to 0.5 bar relief

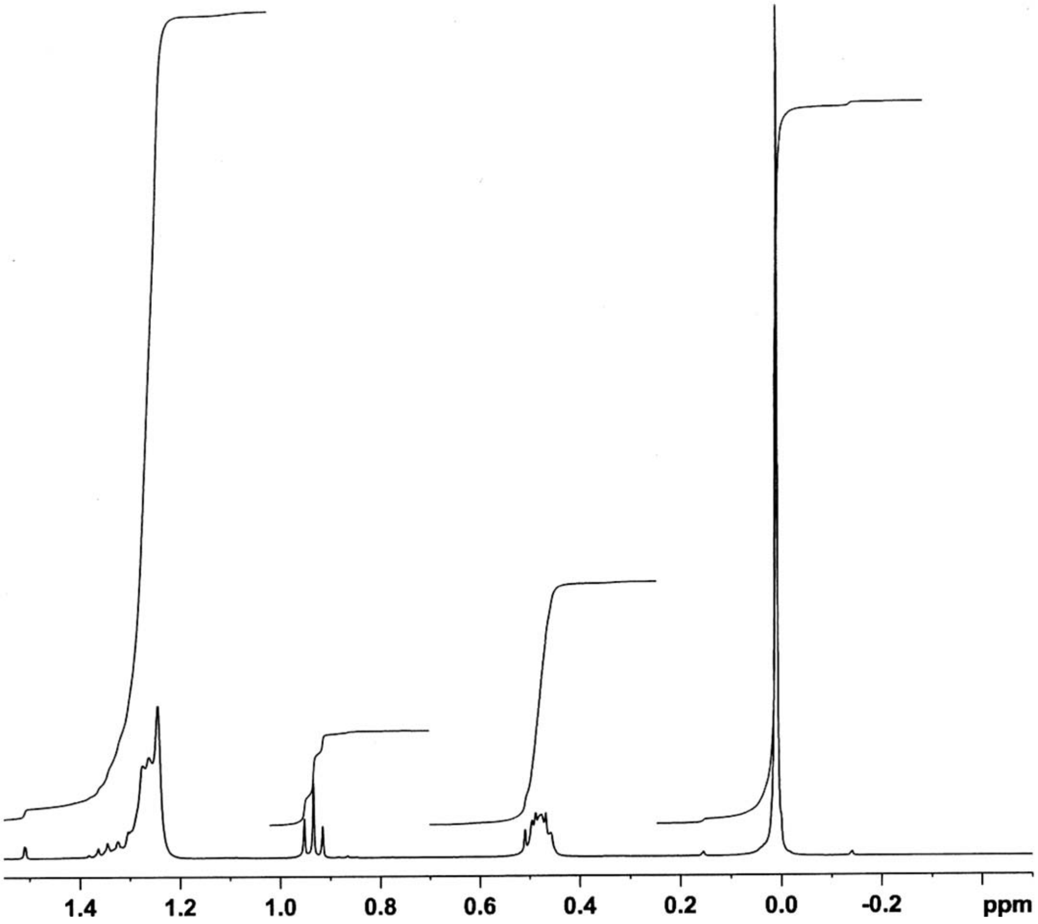


Chart 2. ^1H NMR spectrum of the compound C_3H_7–**A**(**BA**)$_{3.03}$–C_3H_7.

Table 3
Average molecular weights

Molar ratio **A**/**B** by educts; terminals	Calc. from ^1H NMR	By stoichiometry	By GPC (Mn)
133/100; **A**(**BA**)$_{3.03}$	≈950	958	1898
133/100; C_3H_7–**A**(**BA**)$_{3.03}$–C_3H_7	≈1009	1044	1774
115/100; **A**(**BA**)$_{6.67}$	≈1970	1947	2343

pressure. Thus, max. 0.5 bar propene partial pressure could be maintained.

The hazard characteristics of **A** and its high volatility require special attention and safety awareness!

Prior to any operation with **A**, the entire equipment was thoroughly N_2-inerted. To avoid unintended air contamination, slight N_2 purge was maintained whenever parts of the equipment were opened or when educts were filled into the dropping funnel. Negative internal pressure resulting from product temperature drops were immediately equalized with N_2.

For synthesizing the H–Si-terminating intermediates **A**(**BA**)$_{n+1}$, the first step after inertization was filling the weighed (in air) quantity of **A** under constant slight N_2 purge through the open discharge valve of the dropping funnel directly into the flask.

After the discharge valve was safely closed again (important!) the weighed quantity of **B** was filled into the dropping funnel. Finally, **C** (calculated to provide 10 ppm of Pt per total educts) was added to **B** and thoroughly homogenized. It should be emphasized for safety reasons that any uncontrolled contact of **A** with **B** in the presence of **C** must be avoided. The components react vigorously even at RT!

Although we were sure after numerous experiments at various temperatures that the reaction by this design would commence without noticeable induction phase even at RT and the exothermic reaction would heat up the reactants immediately, we chose to pre-heat **A** in the flask to ≈60 °C, just below the b.p. (68 °C) of **A**. Thus, potential energy build-up for whatever still unknown reason would cause **A** to reflux and absorb the energy. As soon as the system had reached the desired starting temperature between 60 and 65 °C the external heat source was removed and efficient stirring was started. Now the product temperature could conveniently and exactly be adjusted by the addition

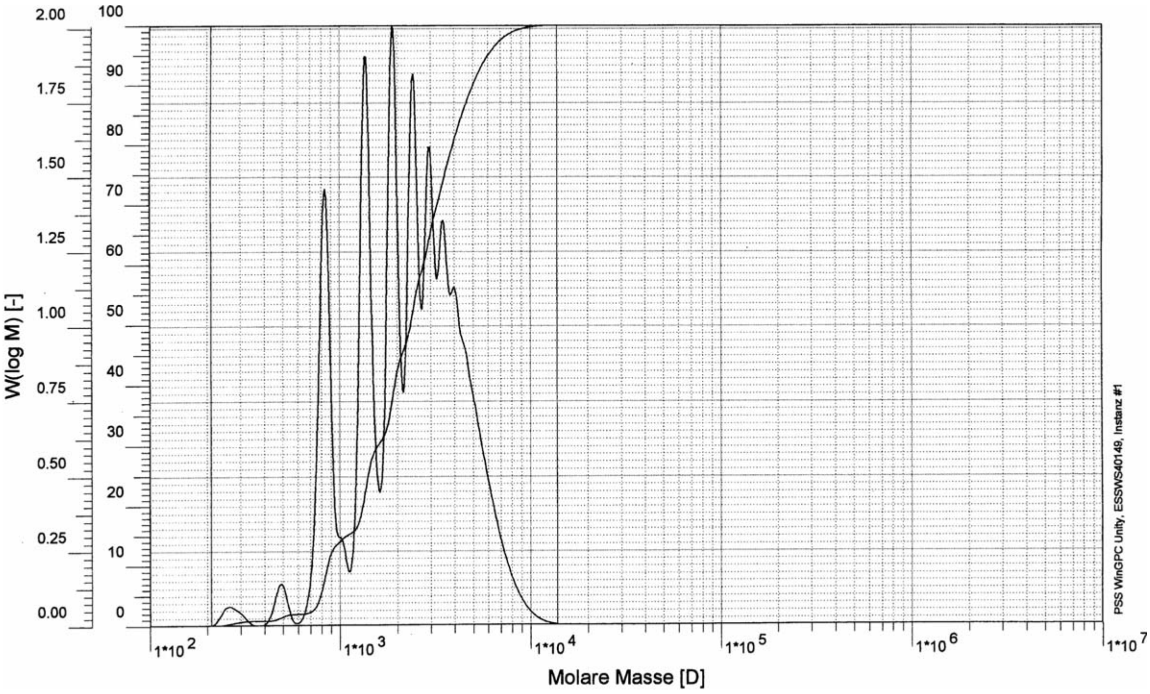


Chart 3. GPC spectrum of the compound C_3H_7–$\mathbf{A}(\mathbf{BA})_{3.03}$–$C_3H_7$.

speed of catalyzed **B** and optionally by additional cooling. We found no product damage or other disadvantage if the exothermity of the reaction was allowed to increase the product temperature to 75 °C towards the end of the reaction. Under the conditions described above, production lots of a total educt weight of 200 g took ≈1.5 h for the addition of all **B** to **A**. Thereafter, the reaction mixture was stirred another 2 h at 70–75 °C.

It has to be mentioned at this point that the HSi-terminating intermediates, thermally treated as described above, remained fully active even after extended storage. We could not find any hint of a catalyst change (color change or appearance of an induction period) or for colloid formation [14].

For subsequent endgroup capping of the HSi-terminated intermediates with α-olefins, additional catalyst was only administered to liquid olefin prior to the reaction if the new material balance was short of 10 ppm Pt: total educts by more than 20%. For the reaction with propene (see above) no additional catalyst was necessary. This olefin reacts spontaneously even at RT and develops considerable heat initially depending on the amount of HSi– available in the intermediate. When the propene absorption slowed down the partial pressure was slowly increased to 0.5 bar. Efficient stirring was a decisive factor for speedy propene absorption especially in the final phase. According to our experience, 2 h postreaction treatment at 0.5 bar propene partial pressure at 50 °C and thorough stirring were sufficient to drive the residual SiH below detection limit (by ^{1}H NMR spectroscopy and chemically with Na-butylate).

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