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Degradation studies on polydimethylsiloxane

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ABBREVIATIONS

$CHCl_3$	Chloroform
cSt	Centi-stokes
CTO	Crude tall oil
EtOH	Ethanol
FT-IR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GC-MS	Gas chromatograph coupled with a mass spectrometer
H_2SO_4	Sulfuric acid
HP-SEC	High pressure size exclusion chromatography
HRMS	High Resolution Mass Spectrometry
KOH	Potassium hydroxide
MW	Molecular weight
NaOH	Sodium hydroxide
NMR	Nuclear Magnetic Resonance
PDMS	Polydimethylsiloxane
SFC	Supercritical fluid chromatography
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TOP	Tall oil pitch

ABSTRACT

Degradation of Polydimethylsiloxane (PDMS) was studied in alkaline and acidic environment. The effect of crude tall oil (CTO) and tall oil pitch (TOP) on the rate of hydrolysis was also investigated. PDMS was heated to 70 °C and hydrolyzed with KOH or H_2SO_4 as catalysts. Solvents used were either water or water and ethanol. The hydrolysis was faster in ethanol with >60 % degradation in 72 h. Separate experiments were also conducted were CTO and TOP was added in a 1:1 ratio with PDMS. The results indicate that the rate of hydrolysis is higher with either CTO or TOP in the mixture. With CTO being more effective. The mechanism of hydrolysis is suggested to be splitting of siloxane units from the ends of the polymer chains in the form of dimethylsilanediol (DMSD).

POPULÄRVETENSKAPLIG SAMMANFATTNING

Silikon är ett samlingsnamn på olika polymerer som består av kisel, syre och organiska föreningar. De används bl.a. i oljor, elaster, och lim. De kan användas även till att förhindra skummande vid framställning av tallolja.

Eftersom silikon används i stora mängder har det studerats hur det bryts ner i naturen där det oundvikligen hamnar. Nedbrytningen sker genom att enheter av polymerkedjan spjälkas av från ändorna av kedjan. Nedbrytningen har studerats i det här arbetet genom att se hur olika miljöer och lösningsmedel påverkar nedbrytningshastigheten. Silikonolja lades i sur och basisk miljö och även i närvaro av tallolja och återstoden från destillering av talloljan. Det visades att oljan bröts ner snabbare i närvaro av en bas och mycket snabbare med tillsatt etanol. Med en bas och etanol hade ca 60 % av silikonoljan brutits ned efter 72 h medan motsvarande nedbrytning tog ca 12 dagar med samma bas i vatten.

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1 INTRODUCTION

Silicones are widely used in consumer products such as oil, rubber, adhesives and soap. The term silicone is a generic name for polymers with a siloxane bond, meaning alternating silicon and oxygen atoms with substituents on the silicon. The most common form of these polymers is polydimethylsiloxane (PDMS) (figure 1). Oligomeric cycles of PDMS are also used in different applications. They are e.g. used as delivery vehicles for substances in cosmetics and similar products.[1] PDMS is also used in other biological applications such as intravenous bags, skin patches for drug delivery and in breast implants.[2]

Silicon and carbon are in the same column in the periodic table which indicates that they might be similar in terms of their chemistry. In some cases, they are. Silanes are very susceptible to nucleophilic substitution compared to their carbon analogues. On the other hand, Si-X bonds have different properties compared to C-X, such as ionic character and bond length.[3]

Some unique properties of Silicon come from back donation of the *d*-orbitals. The back donation is amongst other things used as an explanation for the flexibility of siloxane bonds (Si-O-Si), which is an important feature when it comes to silicone polymers.[4]

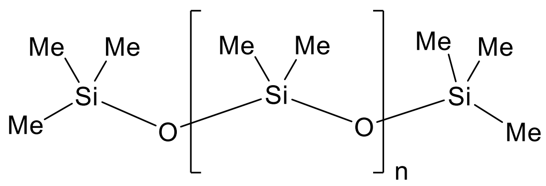

Figure 1. Polydimethylsiloxane.

There is a convenient way of notation for siloxanes which makes it easier to specify structures of polymeric and oligomeric siloxanes in text. There are 4 main letters that are used in combination with each other. They are M, D, T and Q, meaning monofunctional, difunctional, trifunctional and quadrifunctional. The units they refer to are shown in figure 2.

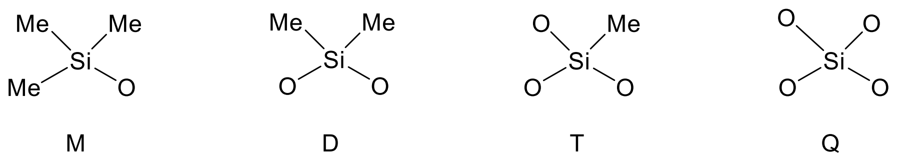

Figure 2. Notation for siloxane units.

This type of shorthand notation for methyl terminated polydimethylsiloxane in figure 1 would be MD_nM. As another example, the cyclic oligomeric siloxane with 3 siloxane units is called D_3 (figure 3).

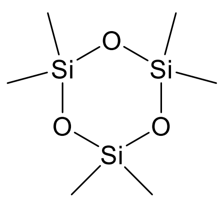

Figure 3. Hexamethylcyclotrisiloxane or D_3.

2 PDMS DEGRADATION

The degradation of PDMS in nature has been well studied since it is where many consumer products end up. It turns out that even though silicones are only produced synthetically, they degrade naturally. One pathway is through hydrolysis in soil. Different minerals act as alkaline catalysts, and the hydrolysis rate is different depending on the cation on the surface on the mineral. It was found that Ca^{2+} was 1.5 times more effective than Na^{+} on montmorillonite. The most abundant hydrolysis product is dimethylsilanediol (DMSD) from which the methyl groups can be oxidized to aldehyde and further to CO_2 by the bacterium *Arthrobacter* and fungus *Fusarium oxysporum schlechtendahl.*[5] Most of the DMSD and other hydrolysis products (small cyclic and linear oligomers) are evaporated into the atmosphere where they are oxidized by radical hydroxyl and nitrate groups. PDMS will also depolymerize under thermal conditions, although relatively high temperatures are needed (400-650 °C) which is good for some type of applications.

PDMS degradation could also be studied in processes where it is added for its antifoaming properties. One example why it would be useful is the production of tall oil, which is produced by skimming tall oil soap of the top of black liquor. The soap is acidified to produce crude tall oil (CTO) which in turn is distilled. The degradation of the trace amounts of PDMS might be interesting if the tall oil pitch (TOP) that is the residue of the distillation of CTO should be recycled for something where the silicones need to be removed. In this work PDMS degradation was investigated in different environments, including CTO and TOP.

2.1 Thermal degradation

A useful feature of PDMS is that it is relatively stable in high temperatures. Thermogravimetric analysis (TGA) shows that PDMS depolymerizes at 400-650 °C in inert atmosphere (figure 4 by Camino et al.[6]).[7,8] The polymer decomposes to cyclic oligomers which are volatilized. Researchers found it hard to perform reliable thermogravimetric analysis since trace amount of catalyst from the synthesis of the polymer would throw off the results. The products that form in inert atmosphere during degradation is mostly cyclic oligomers with hexamethylcyclotrisiloxane (D_3) being the most abundant. The mechanism of thermal degradation to cyclic siloxanes seems to be different than degradation by hydrolysis in the sense that in thermal conditions oligomers can split from within the polymer and not just from the ends (figure 5). The thermally weakest bond in PDMS is C-Si but since the products forming are cyclic, the bond that seems to be the one breaking is Si-O. The TGA analysis will yield different results if there is oxygen in the atmosphere since the silicone can oxidize to silica. Besides silica, there was additional CO_2 and water released when performing the experiment in air. The depolymerization starts at lower temperature in air (290 °C compared to 400 °C in nitrogen). The reason is thought to be that oxygen catalyzes the process.[6]

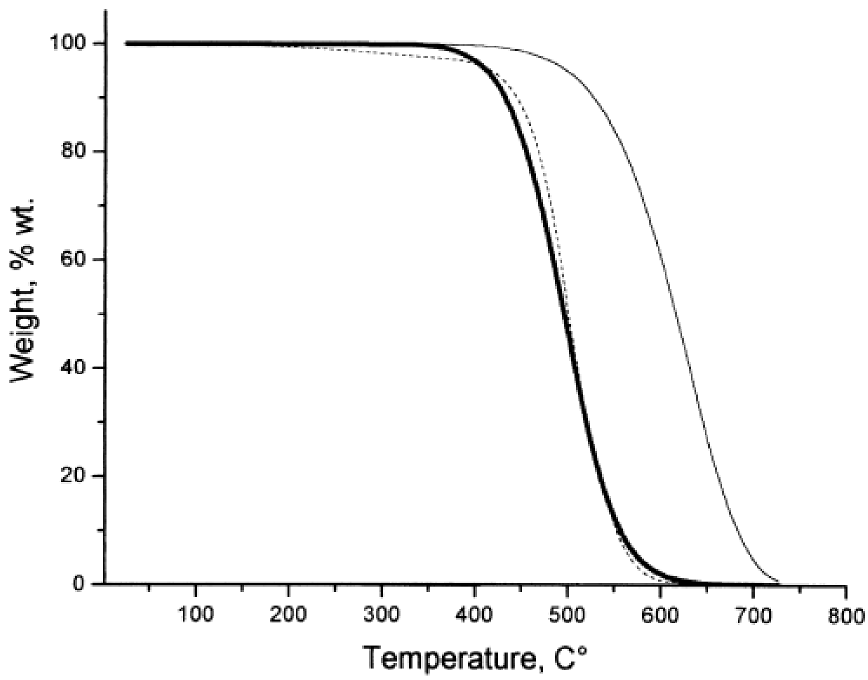

Figure 4. TGA curves of PDMS (N_2, 10 °min^{-1}). Experimental data: solid thick line, simulated: solid thin line, A= 0.5 x 10^6 s^{-1}, E= 26.76 kcal mol-1. Simulated optimized: dashed line, A= 0.25x10^7 s^{-1}, E= 25.11 kcal mol^{-1}.

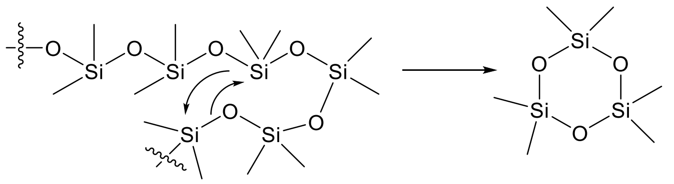

Figure 5. Mechanism of thermal decomposition of PDMS.

2.2 Hydrolysis dependence on pH

The hydrolysis of PDMS can be acid or base catalyzed. Ducom et al. did alkaline and acidic hydrolysis experiments and compared the rate of degradation in pH ranging from 2 to 11.[9] Three different silicone oils were tested with different terminal groups, Methyl, hydroxyl and vinyl. Different acids and bases were also used. The acids used were HNO_3 and HCl and the bases were NaOH and $Ca(OH)_2$. The general trend is that the hydrolysis is more effective under highly alkaline or highly acidic conditions. The more optimal of the two being alkaline conditions. The different cations were also found to factor into the rate of hydrolysis such that the Ca^{2+} was more effective than Na^+ in the alkaline experiment.

The general mechanism for PDMS hydrolysis in water is shown in figure 6. Since the reaction is reversible, polymerization also occurs to some extent.[10] The base and acid catalyzed reactions happen through nucleophilic substitution. The base catalyzed reaction is very similar the hydroxyl group attacks the silicon atom and splits of a monomer of DMSD (figure 7). For the acid catalyzed reaction, there is an electrophilic attack at the oxygen which will yield the same monomer split as for the base catalyzed reaction (figure 8).

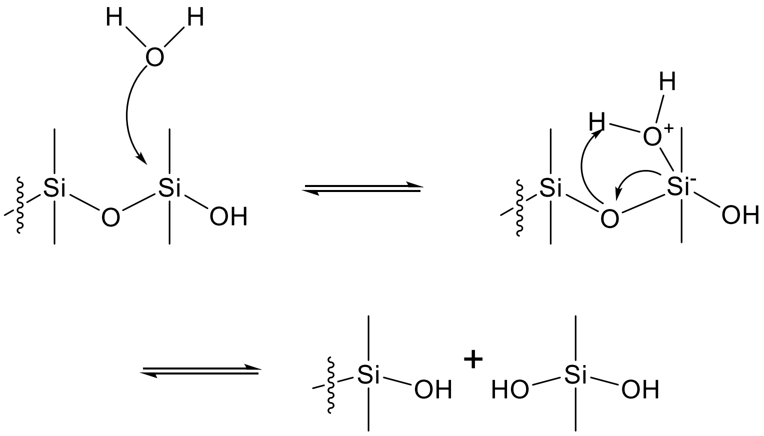

Figure 6. PDMS hydrolysis mechanism in water.

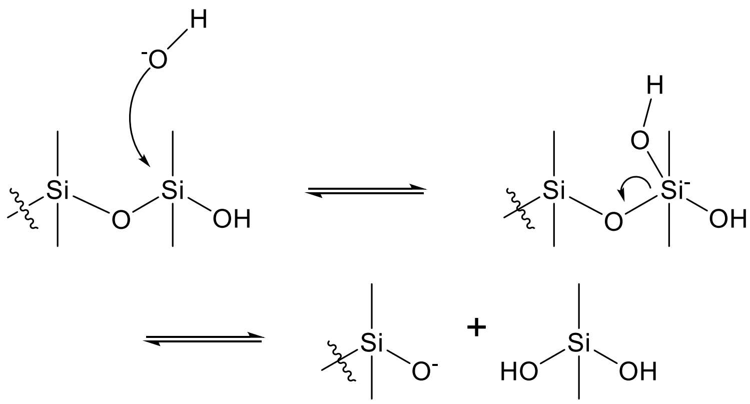

Figure 7. Base catalyzed hydrolysis of PDMS.

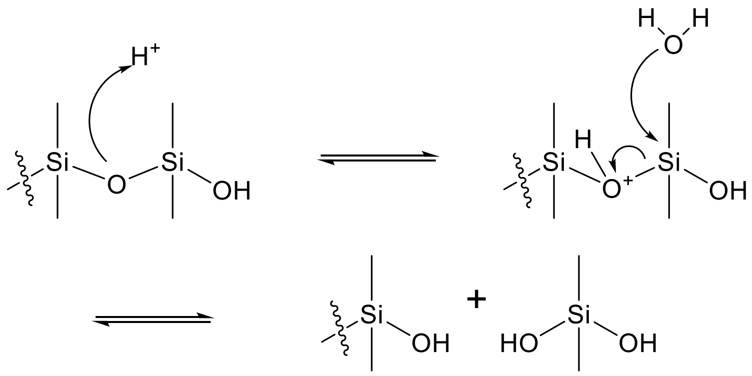

Figure 8. Acid catalyzed hydrolysis of PDMS.

2.3 Environmental degradation

When a product that is used as extensively and in such a wide range of applications as silicones, it is bound to end up in nature. Therefore studies has been conducted in order to explore if or how it degrades and whether it is toxic.[11] The high molecular weight silicones can be either solid as in sealants and rubber or fluid as in lubricants and antifoams. Silicon is only found in nature oxidized as different silicates. Therefore, any organosilicon structures are completely man-made. One might then expect that nature wouldn't be able to handle these materials very well. However, it has been found that silicones readily degrade in nature.

High molecular weight PDMS, which is the most common form of silicone, usually comes into the environment through the sludge from water treatment plants. This is because the polymers are hydrophobic and attach to the sludge rather than the water effluent. If the sludge is incinerated the polymers are oxidized and turn into CO_2 and silica. If the sludge is not incinerated and end up in the soil the PDMS will hydrolyze at the surface of minerals acting as catalysts. The rates of depolymerization through hydrolysis differ depending on factors such as type of cation of the catalyst, moisture level and clay type.[12] The higher the polarizing power of the cation, the faster the rate of hydrolysis. The rate is not constant throughout the process but the initial rate varies between 3 and 11 mg g^{-1} day^{-1} for Al^{3+}, Ca^{2+} and Na^{+}.[12] The polymer is hydrolyzed to dimethylsilanediol, which evaporates into the atmosphere where it is oxidized by OH and NO_3 radicals.[13] The volatilization of DMSD into the atmosphere can also happen through microbial conversion to CO_2.[14]

3 ANALYSIS

Analyzing silicones is not an easy task. There are a few different methods that are popular, depending on what information is needed and the type of silicones. They are inductively coupled plasma- atomic emission spectroscopy (ICP-AES), which is used to detect total amount of silicon without necessarily knowing the species of silicone. Gas chromatography coupled with mass spectroscopy (GC-MS) is a reliable method of analyzing smaller species and ^{29}Si nuclear magnetic resonance spectroscopy (NMR) is good also for larger polymers. Fourier transform infrared spectroscopy (FT-IR) is also used which is reliable for exact identification of smaller species of which there are reference spectra.[15] High pressure size-exclusion chromatography (HP-SEC) is useful for higher MW siloxanes.

For oligomeric siloxane structures a useful way of analyzing is to first separate the products by gas chromatography (GC) or supercritical fluid chromatography (SFC). The analysis part is then usually mass spectrometry or infrared. Infrared seems to be less reliable when the number of siloxane units exceeds 8 but the smaller ones are listed in the literature[16,15]. Other physical properties can be found in the litterature[17], such as melting and boiling point, density and refractive index.

Nuclear magnetic resonance spectroscopy (NMR) or specifically ^{29}Si NMR is a great way of analysis in that mono-, di-, and trifunctional units can be discerned. ^{1}H NMR is less practical since the methyl groups resonate at about the same frequency. High-performance liquid chromatography is a very convenient way of characterizing high MW siloxanes and gives a rough estimate of the average weight.

The polymers may also be degraded or depolymerized to find out information about substituents. The depolymerization products are then analyzed by GC. Some depolymerization procedures that can be used are alkali hydrolysis, fluorosilane derivatization and Alkoxy derivatization.[17] The alkali reaction will cleave siloxane bonds and form salts and liquids that can be separated by distillation. Fluorosilane derivatization is done with hydrofluoric acid (HF) or boron trifluoride. Heating is not needed but it will speed up the reaction. A disadvantage for the procedure is that HF is hazardous. Alkoxy derivatization is a way of depolymerization where PDMS is reacted with tetraethoxy silane in a 1:1 molar ratio with the siloxane units, with a base as a catalyst.

4 EXPERIMENTAL PROCEDURES

4.1 Materials and Analysis

The PDMS used was 50 cSt or 1000 cSt silicone oil aquired from Sigma-Aldrich®. Tall oil pitch was obtained from Neste and crude tall oil from Metsä Fibre. The HP-SEC analyses were performed on a Shimadzu LC-10AT liquid chromatograph combined with a Sedex 85 LT-ELSD. Two Jordi Gel DVB 500 columns with an internal diameter of 7.8 mm and with a length of 300 mm. All samples were diluted to 2 mg mL^{-1} and 1 mL of sample was transferred through a 0.2 µm PTFE filter to the HP-SEC vials. The eluent used was HPLC-grade THF with 1 % glacial acetic acid. An injection volume of 50 µL was used with 0.8 mL/min flow rate.

For GC analyses Clarus® 500 Gas Chromatograph from PerkinElmer with a short column, HP-1 Agilent Narrowbore. For GC-MS an HP 6890 Series with an Agilent 19091Z-002 HP-1 methylsiloxane capillary column was coupled with an HP 5973 MS detector. The GC samples were prepared by sillylation with a 150 µ mixture of pyridine:BSTFA:TMCS (1:4:1).

The ion trap used was an Agilent 1100 LC/MSD ion trap mass spectrometer equipped with an electrospray ionization source. The Q-TOF was a Bruker Daltonics micrOTOF quadrupole and time-of-flight mass spectrometer equipped with an electrospray ionization source. For the Q-TOF and ion trap analyses the samples were not treated in any other way than being diluted and analyzed after slowly increasing the concentration. The analyses were ran on positive node.

4.2 Preliminary experiments

The PDMS hydrolysis was expected to occur in alkaline and acidic environment. The focus was due to time constraint put on alkaline experiments and to get an idea of the rate some initial experiments were conducted. In the first experiment, 500 mg of silicone oil (1000 cSt, ~40 kDa) was added to 50 ml 0.1 M NaOH and heated to 90 °C for two hours with vigorous stirring applied. The mixture was acidified with H_2SO_4 and extracted with 3x60 ml $CHCl_3$ and after evaporation the oil was dissolved in HPLC grade THF. No hydrolysis was detected by HP-SEC. The experiment was repeated for 24 hours, but there was still no hydrolysis detected. The HP-SEC chromatograms are shown in appendix A.

In the second experiment, a solution of toluene and 0. 1 M NaOH (1:2) was used with a phase transfer catalyst, tetra butyl ammonium fluoride (120 mg). The oil (500 mg) was added and the mixture heated to 80 °C for 24 hours. The mixture was extracted with 2x50 ml toluene and evaporated. The residue was dissolved in HPLC grade THF and analyzed with HP-SEC. The chromatogram is shown in appendix A.

4.3 Alkaline hydrolysis in THF and NaOH

PDMS (500 mg) was dissolved in 60 ml THF and 15 ml 0.1 M NaOH was added. The mixture was heated to 55 °C and stirred with a magnetic stirrer for one week. Samples of 10 ml were taken with pipette after 1, 3 and 7 days. The samples were extracted with 2 x 50 ml chloroform and the combined organic phases were evaporated and dried. The remaining oil was dissolved in THF for analysis with HP-SEC and short column GC.

4.4 Alkaline hydrolysis of PDMS in EtOH and KOH

PDMS (200 mg) was added to a 100 ml mixture of EtOH and 1 M KOH (1:9). The mixture was heated to 70 °C and stirred at 1000 rpm or slightly below. The oil dissolved better after heating. After the appropriate reaction time (14, 48, and 72 h) in separate experiments, the mixture was cooled to room temperature and acidified with H_2SO_4 (pH <2). Water was added to dissolve the salt. Extraction was then performed with 3 x 70 ml $CHCl_3$. After extraction the organic phases were combined, evaporated and dried. The residue was dissolved in THF for analysis with HP-SEC and GC-MS

4.5 Alkaline hydrolysis in aqueous KOH

PDMS (200 mg) was added to 100 ml aqueous KOH. The mixture was heated to 70 °C and the oil did not dissolve at this temperature. Reaction times for these experiments were 24, 48 and 72 h and then 11 and 16 days. Extraction was performed with 3 x 70 ml $CHCl_3$ and the organic phases were combined for evaporation. The residue was dissolved in THF for analysis with HP-SEC.

4.6 Alkaline hydrolysis of 50 cSt PDMS in KOH and EtOH

A lower MW oil was also hydrolyzed for comparison. A different procedure was used for this experiment. The 50 cSt silicone oil (10 mg) was hydrolyzed in a 20 ml mixture of EtOH and 0.5 M KOH (9:1). The variable that was changed was the temperature and all experiments were conducted for 45 min. The temperature was varied between 25, 45 and 70 °C. The mixtures were heated in an oven and shaken vigorously every 10 minutes. The workup consisted of adding 3 ml distilled water and acidifying with phosphoric acid. The extraction was performed with 2 x 5 ml hexane. The combined organic phases were washed with 1 ml distilled water. After evaporation the residue was dissolved in THF and analyzed with HP-SEC and GC.

4.7 Alkaline hydrolysis of PDMS in EtOH and KOH spiked with crude tall oil

To get a picture of how the crude tall oil (CTO) and tall oil pitch (TOP) influence the rate of hydrolysis, 200 mg of PDMS and 200 mg CTO was mixed with EtOH and 1 M KOH (9:1). The CTO dissolved well. The mixtures were heated and stirred vigorously for 25, 48 and 72 h. The mixtures were then cooled to room temperature and 100 ml distilled water was added, after which they were extracted with 2x70 ml $CHCl_3$. The extraction was somewhat problematic with the emulsion of ethanol, water and chloroform. The organic phase was evaporated and analyzed with HP-SEC.

4.8 Alkaline hydrolysis of PDMS in EtOH and KOH spiked with tall oil pitch

Similarly, to the CTO experiment, 200 mg of tall oil pitch (TOP) was mixed with 200 mg of PDMS in EtOH and 1 M KOH. Initially the TOP didn't dissolve very well but after a few minutes at 70 °C it was completely dissolved. After cool down to room temperature, 100 ml of distilled water was added and the mixture was extracted with 2x70 ml $CHCl_3$. After evaporation the organic phase was analyzed with HP-SEC.

4.9 Acidic hydrolysis of PDMS

For the acid catalyzed experiments 200 mg PDMS was added to aqueous solution of H_2SO_4 (0.48 mM, pH ~3). The mixture was heated to 70 °C and stirred at 1000 rpm for 1-3 days. The mixture was extracted with 3x70 ml $CHCl_3$ after which the organic phase was evaporated and dried. The residue was measured gravimetrically and analyzed with HP-SEC after it was dissolved in THF. Since there seemed to be no hydrolysis after 3 days the experiments were repeated using 1 M sulfuric acid.

5 RESULTS AND DISCUSSION

5.1 Alkaline hydrolysis in THF and NaOH

The initial expectations for the hydrolysis experiments were that the peak in the HP-SEC graph would shift to the right, showing that the average molecular weight would get reduced assuming that hydrolysis would occur from the end of the polymer. If the polymer would split randomly, the HP-SEC should relatively quickly show a very flat peak shifted to the right since the weight of the polymers would be very diverse.

The experiment with PDMS in 0.1 M NaOH and THF (1:4) showed that hydrolysis was occuring but there was no significant shift in the peaks in the HP-SEC diagram (figure 9). The concentrations of the samples were calculated according to the weight of the starting material so the area of the peak will correspond to the amount of the polymer left.

The peak does seem to be more flat which might indicate a shift in molecular weight but the most clear sign of degradation was the fact that more starting material was missing as the reaction time was increased. The degradation rate shown in figure 10 was calculated from the areas of the peaks of the HP-SEC chromatogram.

Analysis with short-column GC (figure 11) showed no signs of oligomers suggesting that the product of the hydrolysis is, in accordance with the litterature,[18] mostly dimethylsilanediol (DMSD) which would be extracted to the water phase.

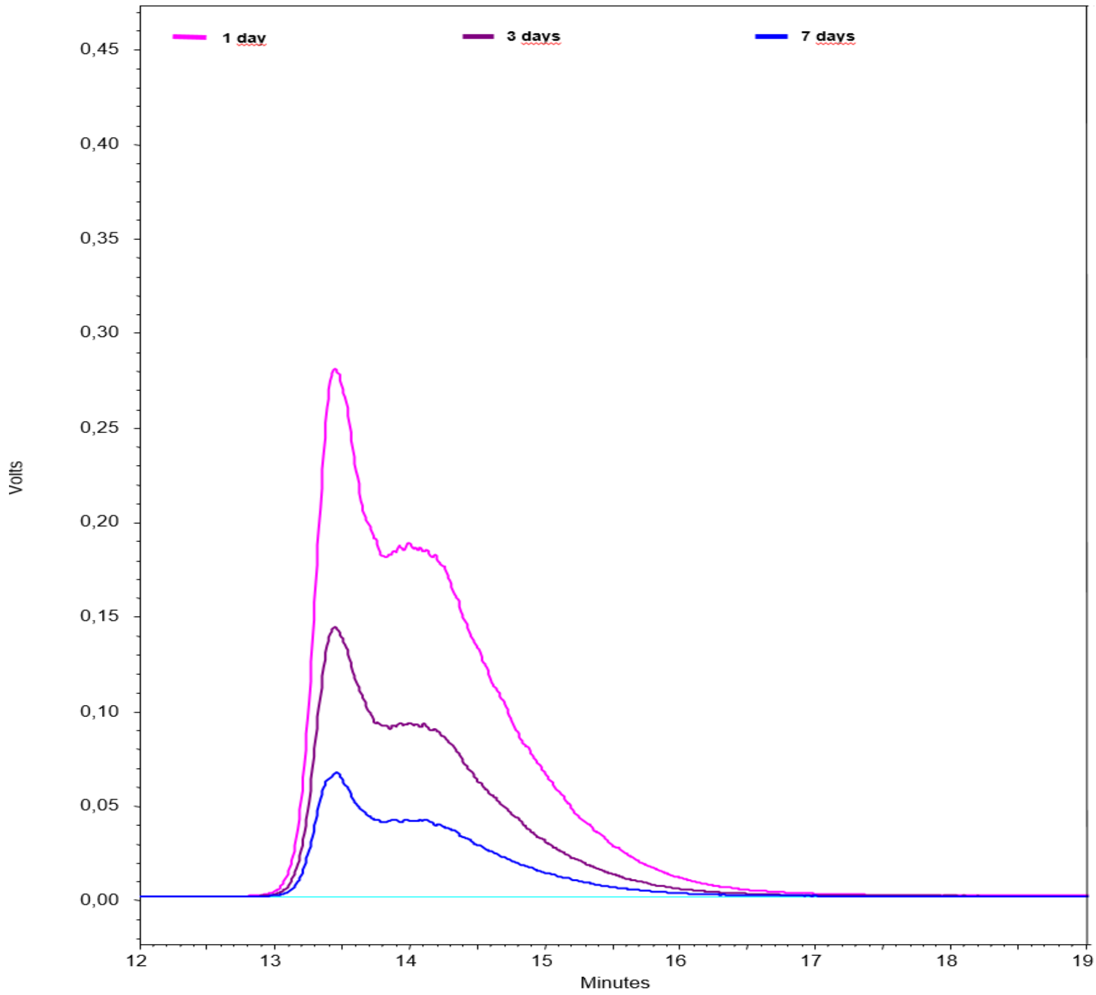

Figure 9. HP-SEC chromatogram of PDMS in NaOH: THF (1:4).

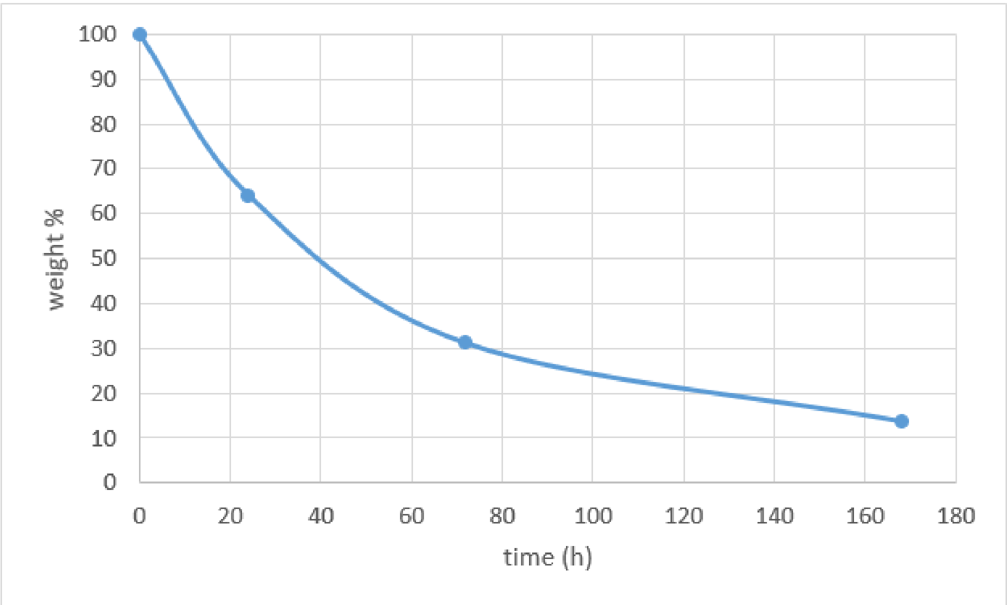

Figure 10. Weight % of PDMS remaining vs time of hydrolysis in NaOH: THF (1:4) calculated from the areas obtained from the HP-SEC chromatogram.

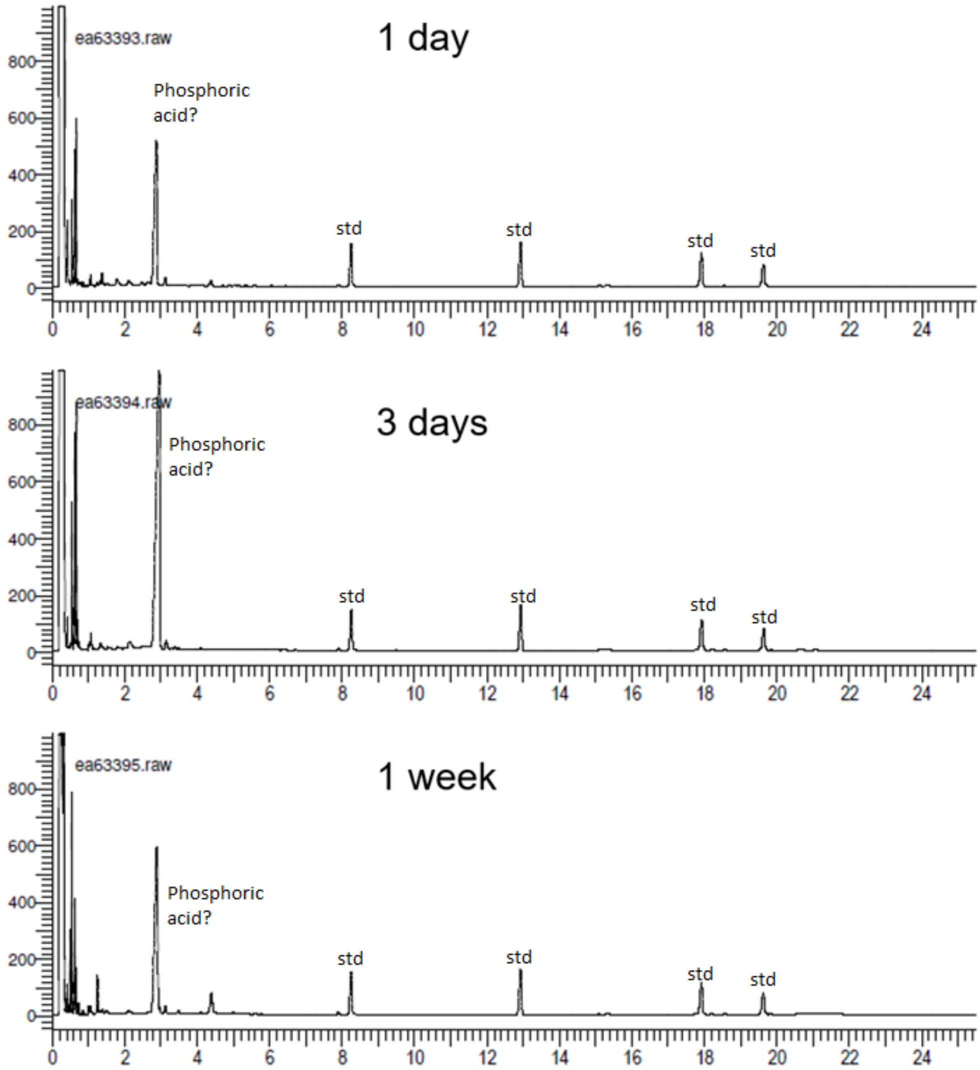

Figure 11. Short-column GC analysis of PDMS in NaOH: THF (1:4).

5.2 Alkaline Hydrolysis of PDMS in EtOH and KOH

The hydrolysis in ethanol and KOH was more effective than aqueous KOH, which is to be expected since PDMS is more soluble in EtOH than water. There was a slight shift in the HP-SEC peak after 72 h, and the exclusion peak to the far left was missing (figure 12). During extraction all DMSD would go to the water phase, so after evaporation and drying of the organic phase the weight of the remainder could be compared to the weight of the starting material to yield a curve corresponding to the rate of hydrolysis.

The gravimetric loss of the workup was measured to 5 % by performing a work up immediately. The gravimetric analysis yielded a curve which indicated that about 60 % of the polymer had degraded after 3 days. When comparing the area in the HP-SEC graph, which should be quantitative, the ammount of PDMS left was calculated to 23.6 %. The areas are shown in appendix B.

The average molecular weight shift as approximated with a calibration curve from GPC (Appendix E). The approximated average after 72 h of hydrolysis was 21 000 Da. The calibration data is shown in appendix E. Since the average of the total MW on the starting material was 39 106 Da, the gravimetrical analysis of 60 % degradation seems more accurate than the 76 % according to the calculation of the HP-SEC area.

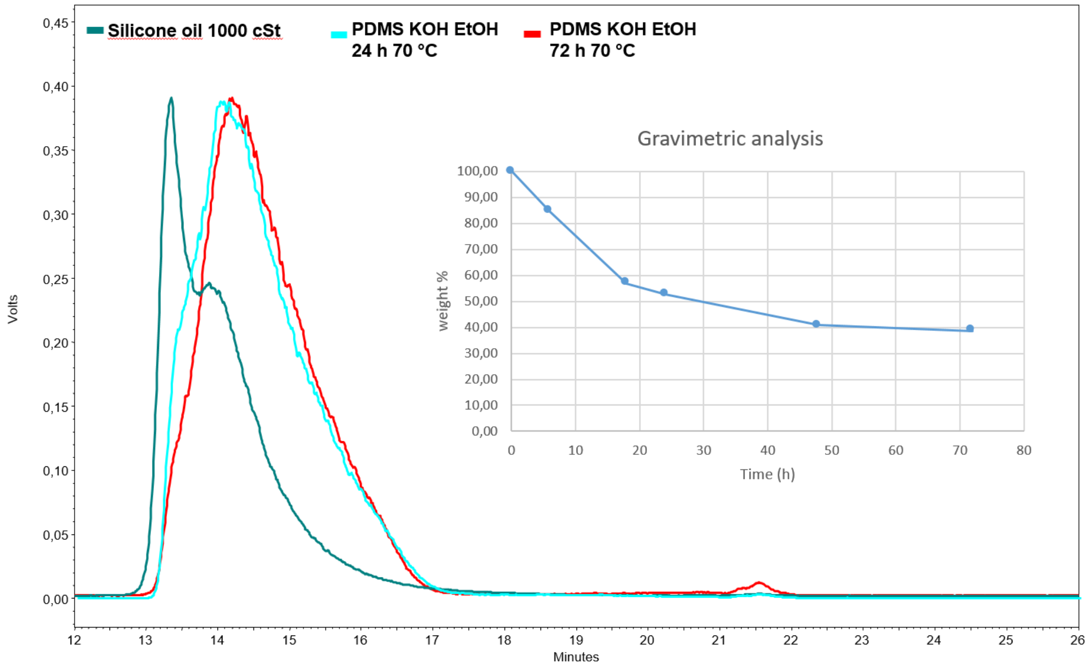

Figure 12. Normalized HP-SEC curve of PDMS and PDMS hydrolyzed in EtOH/KOH (9:1) at 70 °C for 24 and 72 h. Gravimetric curve showing how much weight-% was measured after extraction.

5.3 Alkaline hydrolysis in aqueous KOH

The aqueous experiment was conducted from 48 h to 16 days. Even after 16 days there was high molecular weight polymer left although gravimetrically there was only a few percent of starting material left (figure 13). This suggests that the high MW polymer is shielded in droplets and eaten from the outside, consuming the polymers at the surface. This would explain why there is no shift in the peak, because there will not be much of lower weight polymer except in the case for 16 days. The reason why there is some lower MW polymer found in the 16-day experiment (the flat peak at 18-23 min in figure 13) might be due to the fact that when the droplets decrease in size, the surface to volume ratio increases. Since there would be lower weight polymer on the surfaces of the droplets, the amount will be relatively higher.

The products of the 16-day experiment was also analyzed with an LC-MSD-Trap and QTOF mass spectrometer since there was lower MW material as seen in figure 13. There were some masses in the range of 300 to 800 Da. They were believed to correspond to depolymerization products of PDMS which might have reacted with EtOH, and traces of K, Na and Mg from water. There was however no positive identification of species. The mass spectra can be found in appendix C and D.

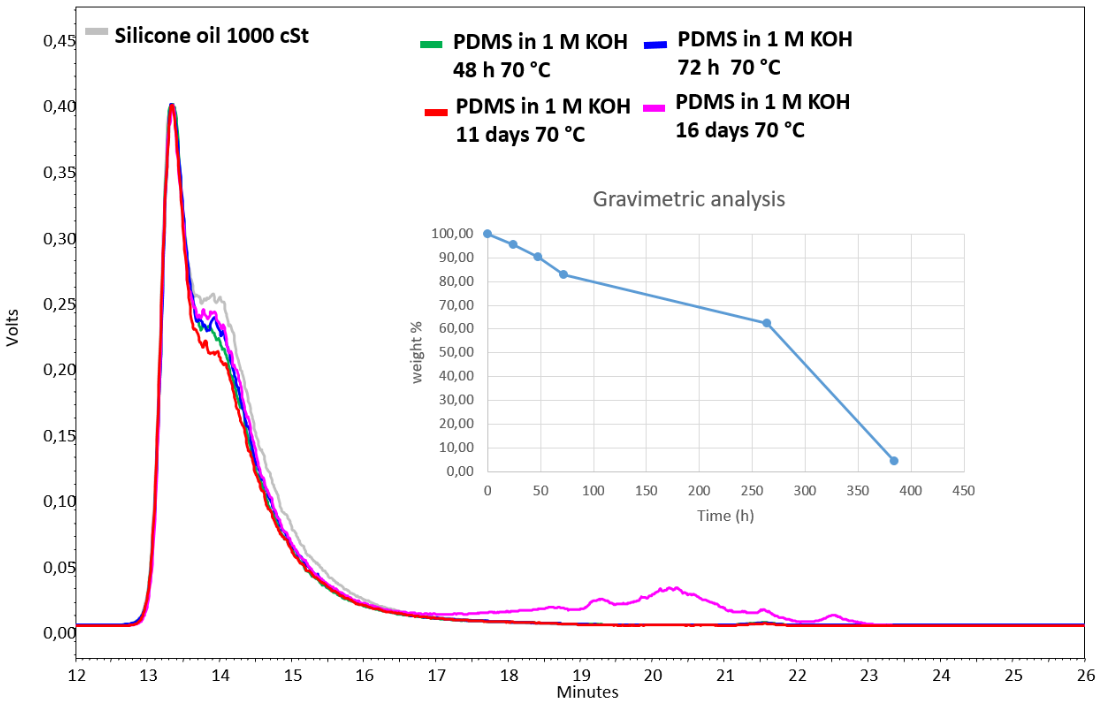

Figure 13. Normalized HP-SEC chromatogram and gravimetric graph of PDMS hydrolysis in aqueous KOH.

5.4 Alkaline hydrolysis of 50 cSt PDMS in KOH and EtOH

The HP-SEC analysis of the hydrolysis of the lower MW PDMS (2-5 kDa) is shown in figure 14. With more hydrolysis (generated by higher temperature) the peak is not only decreasing in size but becoming thinner. This suggests that the lower weight polymers are hydrolyzing faster. At 70 °C for 45 min there is no polymer left at <3 000 Da corresponding to >18 min in the chromatogram. The reason might be that the dissolution is more effective with lower MW chains and therefore the hydrolysis is faster. This explains why there are no oligomers found in the HP-SEC analyses since the oligomers would degrade faster. The short column GC chromatogram (figure 15) shows clearly that the lower MW material is hydrolyzing faster since the peaks 8-18 min are disappearing before the peaks at 18-24 min.

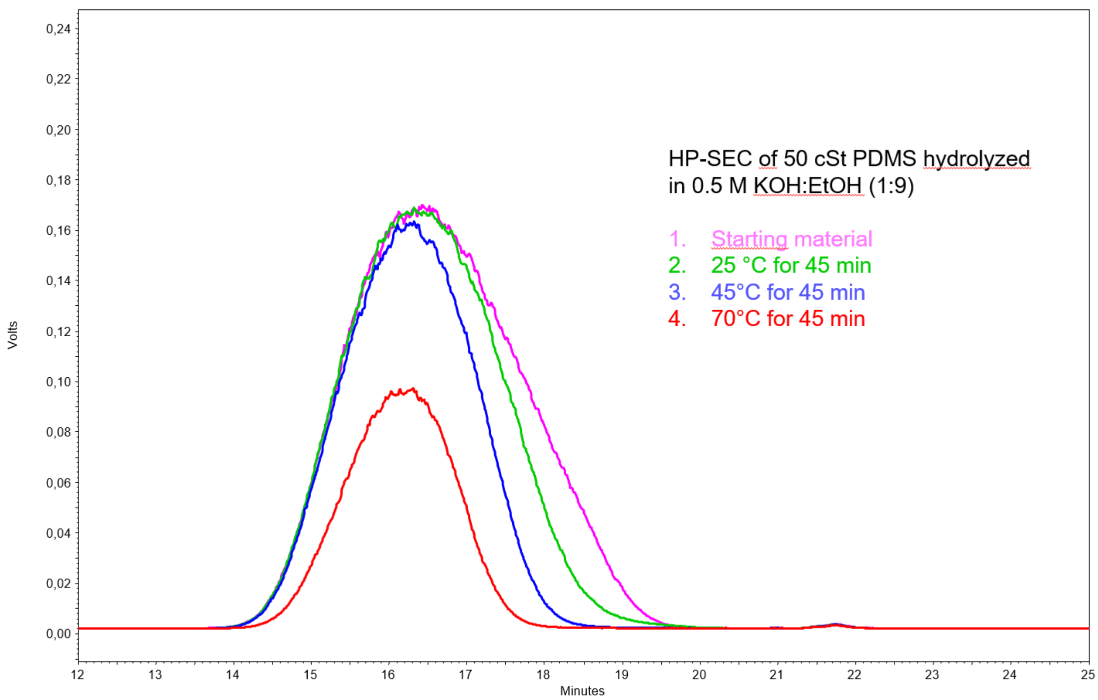

Figure 14. HP-SEC chromatogram of 50 cSt PDMS hydrolyzed in 0.5 M KOH:EtOH (1:9).

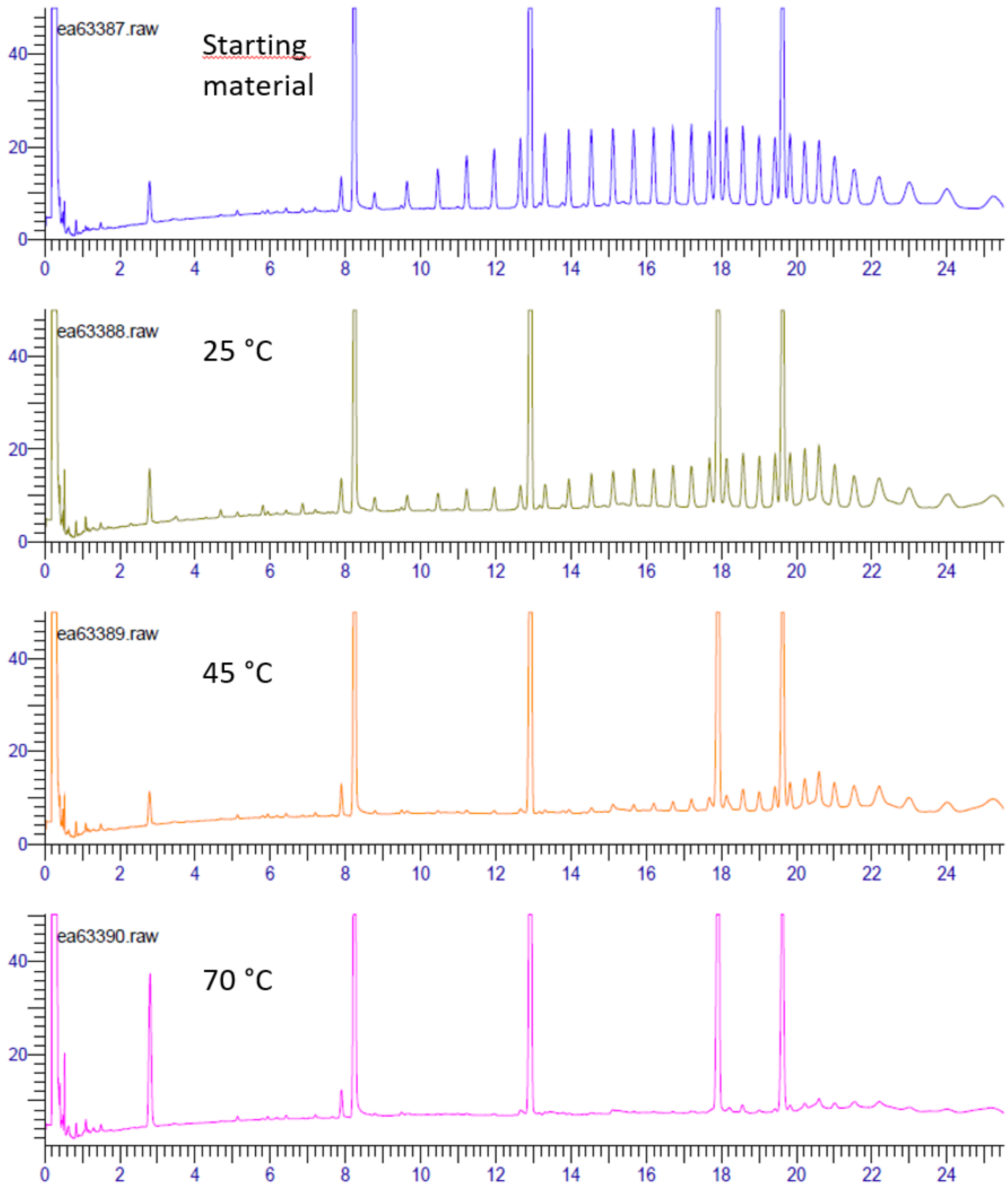

Figure 15. Short column GC chromatogram of 50 cSt PDMS hydrolyzed in 0.5 M KOH:EtOH (1:9) for 45 min at 25, 45 and 70 °C.

5.5 Alkaline hydrolysis of PDMS in EtOH and KOH spiked with crude tall oil

The hydrolysis of PDMS in EtOH and KOH spiked with crude tall oil (CTO) was investigated to see how the hydrolysis of PDMS would be affected by the tall oil. The resulting HP-SEC chromatograms are shown in figure 16. PDMS is clearly decreasing as the time for the experiments increase. The other components, sterols and fatty acids at 20- 24 min in the chromatogram, seemed to vary more randomly. This is probably because the workup was slightly different between the experiments since the emulsion of ethanol, water and chloroform was problematic to extract. The resin acid peaks at 23 min also varies slightly but is the most stable. The relation between the sterol peak and resin acid peak is about the same in the 24 h and 48 h experiments but changes after 72 h.

As expected, the rate of PDMS degradation (figure 17) is higher with only 10.0 % left after 72 h compared to the same experiment without CTO where there were almost 40 % left. Although the procedure was slightly problematic, it is evident that the hydrolysis is faster with CTO present. One should keep in mind that the 1:1 ratio of PDMS and CTO is nowhere near representative of the amount of silicones left in CTO from soap cooking. On the other hand, in this experiment EtOH might help with dissolution which probably makes the process of degradation faster. If there would be oligomeric structures of PDMS they would show up behind the peaks of the sterols, fatty acids and resin acids, however as explained in chapter 5.4 they would probably hydrolyze too fast to be spotted on HP-SEC.

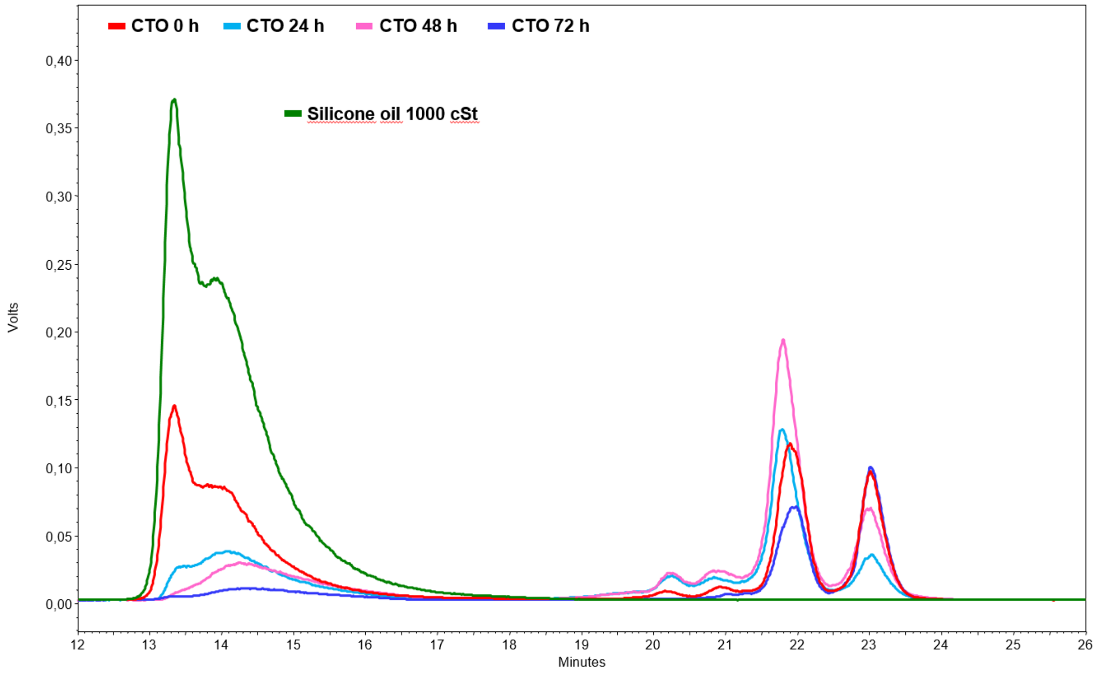

Figure 16. HP-SEC chromatogram of CTO and PDMS (1:1) in EtOH and 1 M KOH (9:1).

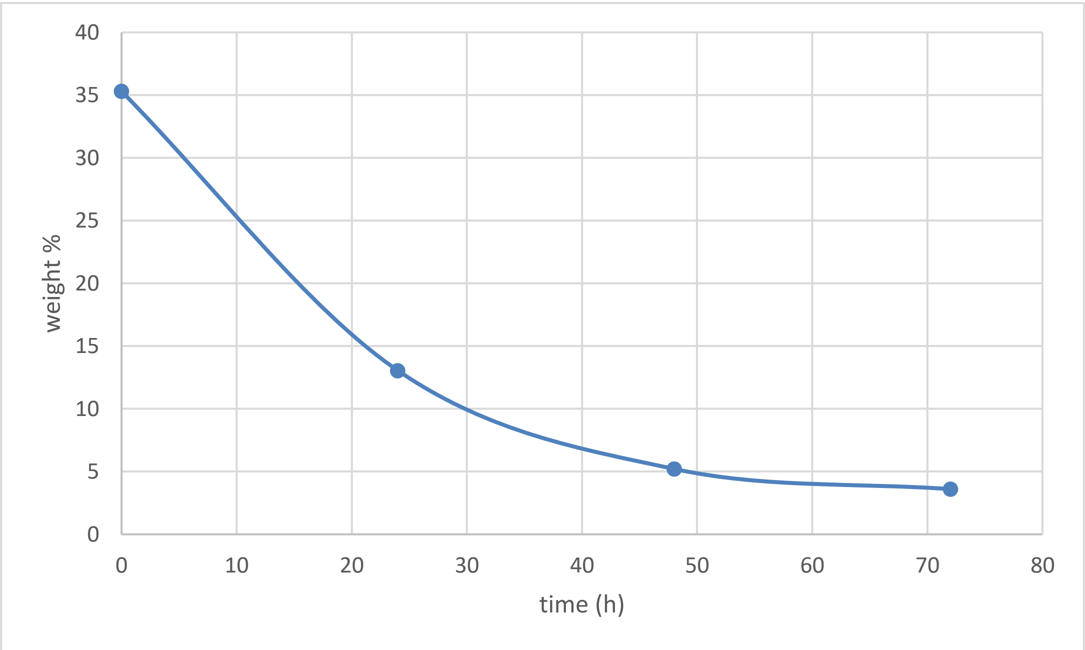

Figure 17. Weight % of PDMS left vs time of hydrolysis with CTO in EtOH: KOH (9:1). Percentages were calculated from the area of the PDMS peak. The 48-h curve was normalized to the resin acid peak at 23 min of the 24 h curve before the calculations.

5.6 Alkaline hydrolysis of PDMS in EtOH and KOH spiked with tall oil pitch

The resulting HP-SEC analysis of the hydrolysis experiment of PDMS with TOP in a 1:1 ratio is shown in figure 18. The chromatogram shows that the steryl esters at 20 min that are found initially in TOP disappear, which is to be expected since they should hydrolyze in the alkaline environment to sterols that show up at 22 min. Similarly to the experiment with CTO the hydrolysis seems to be faster, with 15.8 % left after three days (figure19) compared to 40 % without TOP.

The sterol peak at 22 min seems to change in relation to the resin acid peak at 23 min for the 72 h experiment compared to the other two. Between the 24 h and 48 h experiments the relation is about the same. The reason might be because of differences in workup or some other reactions.

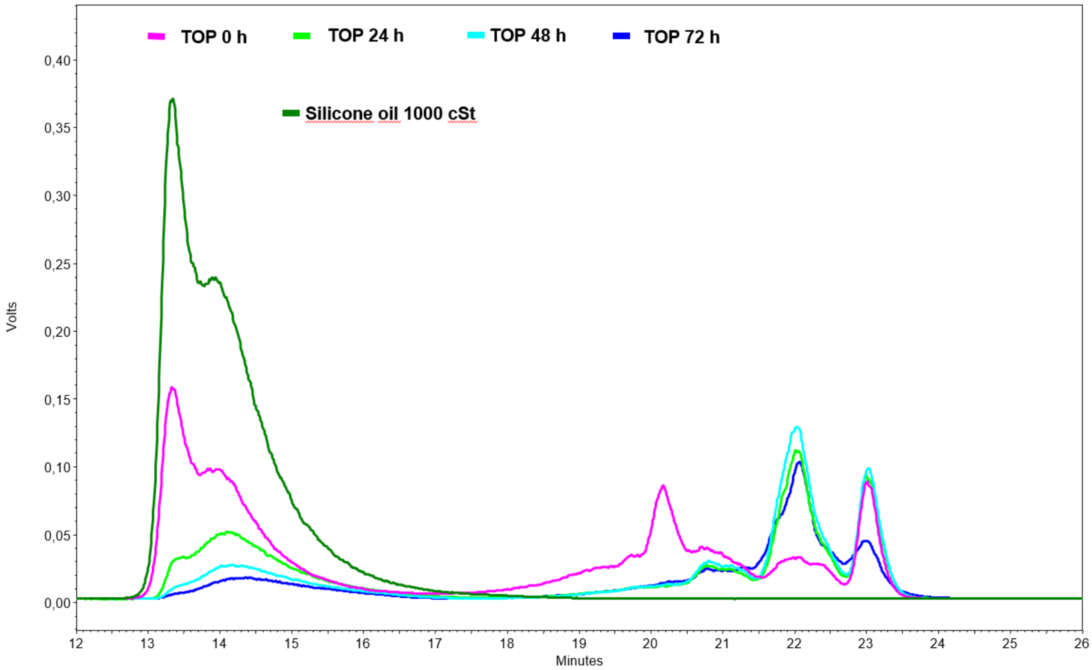

Figure 18. HP-SEC chromatogram of TOP and PDMS (1:1) in EtOH: KOH (9:1)

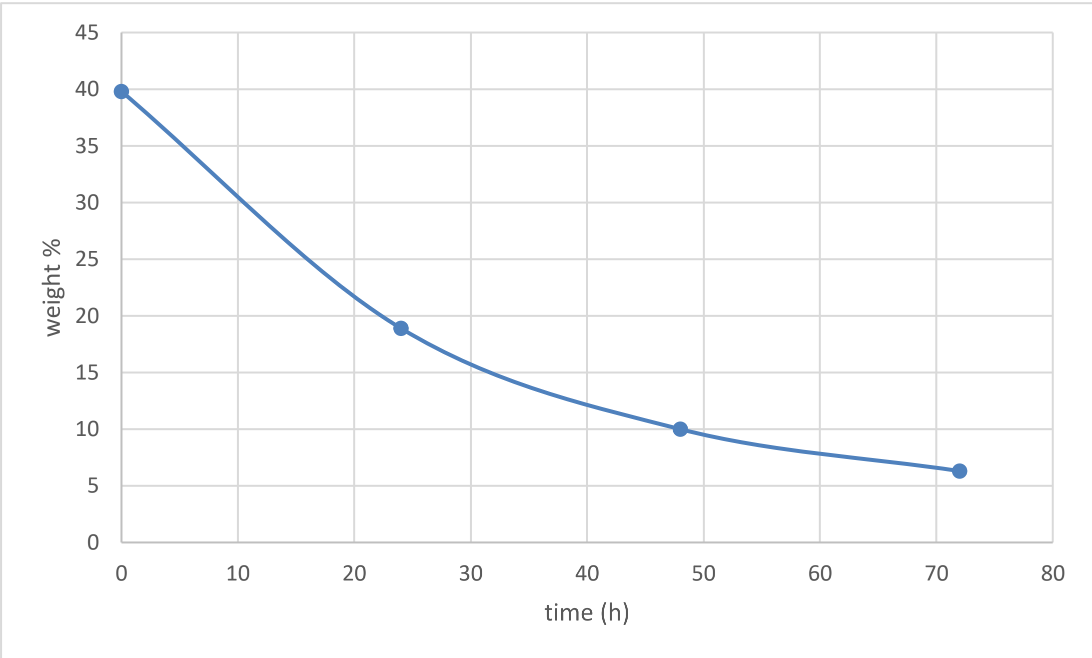

Figure 19. Weight % of PDMS left vs time of hydrolysis with TOP in EtOH: KOH (9:1) calculated from the areas of the HP-SEC chromatogram.

5.7 Acidic hydrolysis of PDMS

The acidic hydrolysis was probably too slow to notice any significant degradation in three days. The HP-SEC chromatogram (figure 20) indicated that hydrolysis occurred since the shape of the peaks were changing. There was no significant amount of degradation because the calculation from comparing the areas showed that there was ~80 % left after 24 h and even more at 72 h (figure 21). This is probably because of the error from the workup. There is most likely not a big difference between one and three days. The gravimetric analysis showed a similar result (figure 22). The fact that the curves are not showing a clear descent is not entirely unexpected when comparing to the length of the alkali experiment in aqueous environment, which showed that high MW PDMS was left after 16 days. The peak in the chromatogram in figure 20 seems to get thinner and shift to the left which suggests that there might be re-polymerization occurring.

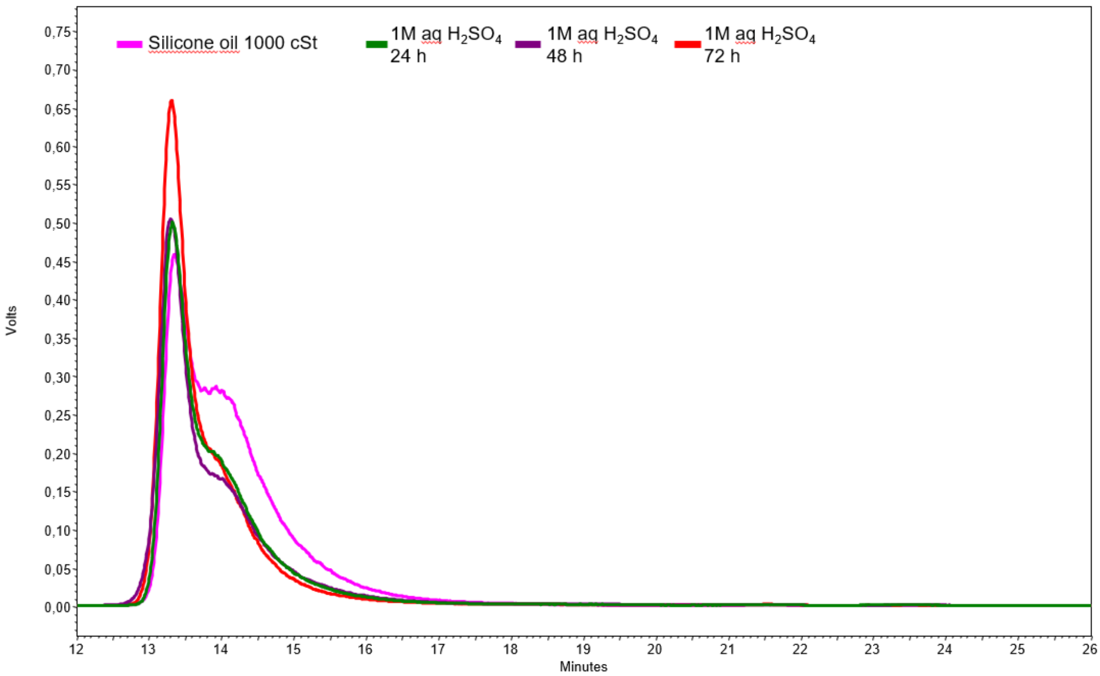

Figure 20. HP-SEC chromatogram of PDMS in 1 M H_2SO_4.

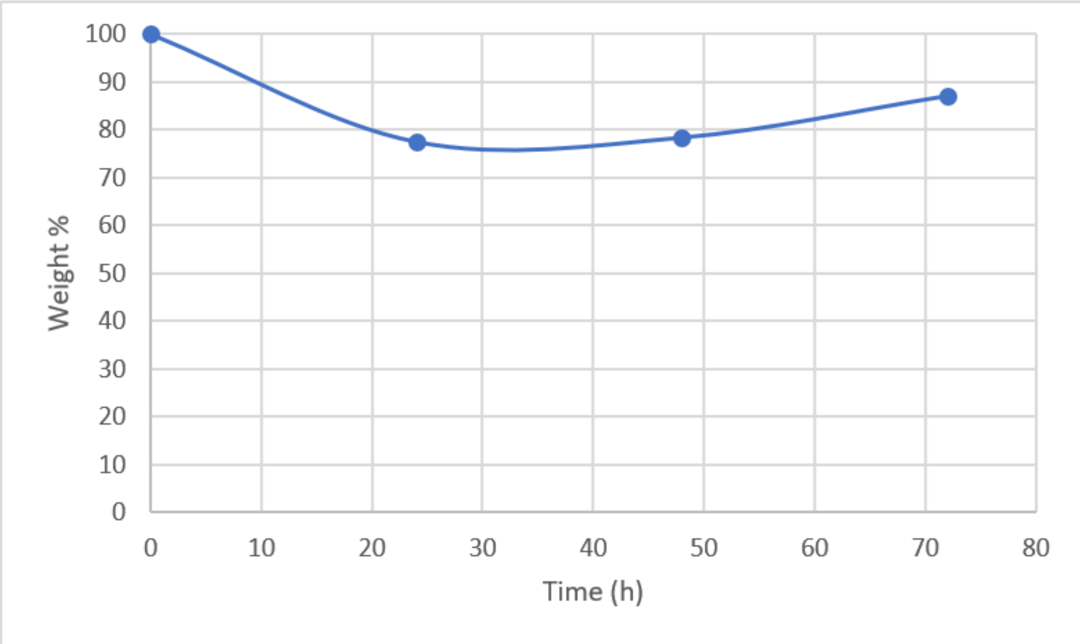

Figure 21. PDMS degradation in 1 M H_2SO_4 calculated from the area of the HP-SEC chromatogram.

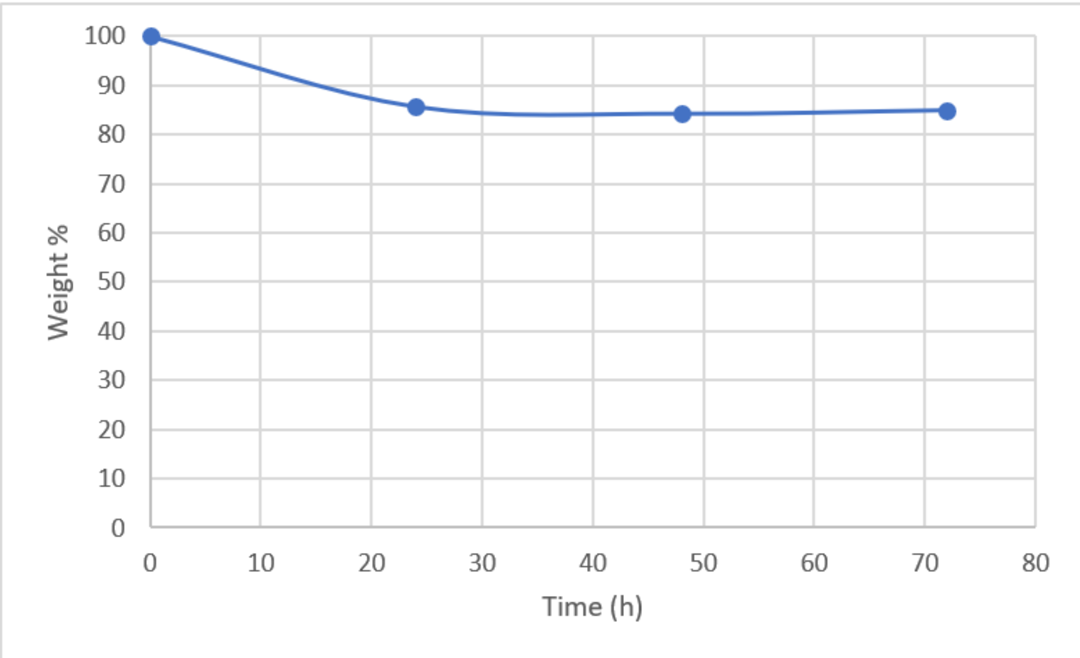

Figure 22. Gravimetric analysis of PDMS degradation in 1 M H_2SO_4.

6 CONCLUSION

It is evident that the hydrolysis is occurring from the end of the polymer chains and splits monomers of DMSD. The fact that there is little to no shift towards lower MW of the peak from the starting material in the HP-SEC chromatograms might be explained by the polymer being protected inside droplets, so the polymers at the surfaces of the droplets will be consumed first especially in aqueous environment. There is very little starting material left as measured gravimetrically and by calculating the area of the peak in HP-SEC, which means that the polymer is indeed degrading. Since the material is missing gravimetrically as well, some of the material has to be extracted to the water phase and that indicates that the main hydrolysis product is DMSD which is water soluble.

When the hydrolysis experiments were conducted in organic solvents there was a much faster rate of hydrolysis which is expected considering that the oil will dissolve much more readily. There are many factors that might cause the results to be slightly inaccurate, such as temperature control, stirring and extraction not being very exact. The workup was not optimized, especially in the experiments with CTO and TOP samples were the extraction proved more difficult compared to the same experiments were CTO and TOP were excluded.

The curves of degradation through alkaline hydrolysis, both calculated from HP-SEC and measured gravimetrically, are not linear but the rate of degradation seems to subside over time. This could be due to the hydrolysis reaction being reversible and the concentration of DMSD is increasing, so the rate of re-polymerization would increase. A more likely reason might be that there is only about 3.5 equivalents of OH^- ions to siloxane units, which means that the change in pH might affect the rate since the concentration of OH^- ions is reduced.

Even though the experiments conducted were not optimized very well, some conclusions are confidently drawn. TOP and CTO influence the rate of hydrolysis such that it will be faster. The reason might be that there is some component in the CTO/TOP that catalyze the reaction. Another reason might be that the component(s) help dissolve the PDMS. It is unclear how accurate the experiments are and how much faster the hydrolysis is. It should also be noted that there are components in CTO and TOP that would consume the OH^- ions, e.g. in the hydrolysis of the steryl esters.

The only indication of lower MW products of the hydrolysis were found in the 16 day long experiment in 1 M KOH. The mass spectra acquired from analysis with Q-TOF and Ion trap mass spectrometers could not identified as any specific species, but they might contain Mg, K or Na and ethoxy groups which makes identification complicated.

7 SUMMARY IN SWEDISH – SVENSK SAMMANFATTNING

7.1 Sönderfall av polydimetylsiloxan

Silikon är ett samlingsnamn för en typ av polymer som består av kiselatomer med olika organiska substituenter som är bundna till varandra med syrebryggor. Den vanligaste typen av silikon är polydimetylsiloxan (PDMS) som har två metylgrupper bundna till varje kisel. De används i flera olika applikationer eftersom de är flexibla och värmetåliga. De används till bl.a. lim, tätning, smörjmedel och även i medicinska sammanhang i plåster som transporterar medicin och i bröstimplantat. PDMS används även för att förhindra bildande av skum vid tillverkning av tallolja som innebär att såpa tas från översta lagret av svartlut och surgörs med svavelsyra. Sedan destilleras den råa talloljan (crude tall oil, CTO) vidare till tallolja. Återstoden från destillationen (tall oil pitch, TOP) kunde eventuellt återanvändas och om silikonet behöver tas bort så är det skäl att studera hur hydrolysen sker i en sådan miljö.

Det har blivit väl undersökt hur PDMS bryts ner i miljön eftersom det förekommer i många konsumentprodukter. PDMS kommer oftast ut i miljön via reningsverk. Eftersom polymerkedjorna ofta har hög molekylvikt (>400 siloxanenheter) och inte är vattenlösliga binds de till slammet. Om slammet bränns upp oxideras polymeren till koldioxid och kiseldioxid. Om slammet inte bränns upp och hamnar i jorden hydrolyseras polymeren och spjälkar dimethylsilanediol (DMSD) från ändorna. DMSD evaporerar och oxideras av OH och NO_3 radikaler. Mikrober i jorden kan även bryta ner DMSD och bilda koldioxid av metylgrupperna. Hydrolysen i jordenkatalyseras av mineraler. Desto mera polariserande katjon desto effektivare katalys. För Al^{3+}, Ca^{2+} och Na^{+} katjonerna är den initiala hastigheten mellan 3 och 11 mg g^{-1} dag^{-1}.

7.1.1 Hydrolysexperiment med PDMS

Den generella proceduren för experimenten var att lösa upp PDMS i EtOH med antingen en bas eller en syra som katalysator. Experimenten utfördes också utan organiskt lösningsmedel. Den främsta analysmetoden som användes var HP-SEC och det förväntades att hitta en förskjutning av piken för utgångsmaterialet i kromatogrammet mot lägre molekylvikt. Andra analysmetoder som användes var GC, Q-TOF och ion trap masspektrometri. Experiment uppsättningen bestod i en 250 ml rundkolv med 200 mg PDMS och tillsatt lösningsmedel. Basen som användes var antingen NaOH eller KOH, som syra användes H_2SO_4 och etanol, toluen och THF användes som organiska lösningsmedel. Etanol blev det lösningsmedel som användes främst med 10 % 1 M KOH. En magnetomrörare användes (ca 1000 rpm) och blandningen värmdes upp i oljebad till 70 °C med en kylare. Upparbetningen bestod i extraktion med kloroform och de organiska faserna kombinerades och evaporerades. Efter evaporationen torkades återstoden och löstes upp i THF för HP-SEC-analys.

För att få en inblick i effekten av CTO och TOP på hydrolysen av PDMS tillsattes de i 1:1 förhållande med PDMS och experimenten med 10 % 1 M KOH i etanol upprepades. Tiden för experimenten med EtOH och KOH var ett, två och tre dygn för att ge en bild av degraderingen. För att få en bild av hur mycket utgångsmaterial som tappades vid upparbetningen utfördes denna även genast utan att vänta på någon hydrolys. I experimenten med PDMS i EtOH och KOH var det endast ca 5 % svinn, medan det var ca 70 % i experimenten med CTO och TOP.

7.1.2 Resultat och konklusion

De tydligaste tecknen på att hydrolys påvisades var att utgångsmaterial gravimetriskt saknades efter lägre tid och att arean för piken av utgångsmaterialet i HP-SEC kromatogrammen minskade.

Det visades att hydrolysen av PDMS sker från ändan av polymerkedjan i vattenhaltig miljö eftersom det inte hittades någon förskjutning i HP-SEC piken som motsvarar kluven PDMS. Det samma gällde vid användning av organiskt lösningsmedel även om där hittades en förskjutning i kromatogrammet. Inga lågmolekylära siloxaner hittades med GC. Efter 16 dagar lång hydrolys i 1 M KOH, där det endast fanns några procent kvar av utgångsmaterialet, kunde man tydligt se polymer av hög molekylvikt. Detta tyder också på att det formas droppar i vattnet som skyddar polymeren inuti och hydrolyseras vid droppens yta. Efter 16 dagar hittades det även spår i HP-SEC kromatogrammet av vad som troligen är oligomerer eller polymerer med lägre molekylvikt. Detta beror troligen på att förhållandet mellan ytan, där det finns kortare polymerer, och volymen av skyddad polymer växer när dropparna minskar. Masspektrometriska analyser med Q-TOF och ion trap visade att massorna låg i området 300-800 Da, vilket är konsekvent med cykliska eller linjära siloxaner med upp till 9 siloxanenheter. Ingen exakt massa identifierades men de är troligen någon form av cykliska eller linjära oligomerer av PDMS som eventuellt har bildat salter med Mg, K eller Na.

Hydrolysen i organiska lösningsmedel var mycket mera effektiv och detta beror troligtvis på att oljan är bättre upplöst. Det visade sig även att CTO och TOP snabbade upp hastigheten och CTO var effektivast. Det kan bero på att det finns något ämne som katalyserar reaktionen eftersom mängden TOP/CTO var lika stor som mängden PDMS är det inte lika troligt att de hjälper med lösligheten.

Degraderingskurvorna verkar avta med tiden i samtliga experiment är troligen att hydrolysen är reversibel. Eftersom det efterhand bildas mera DMSD så kommer det att finnas mera material som kan polymerisera. En annan faktor som kan påverka är att i EtOH experimenten med 10 ml KOH finns endast ca 3,5 ekvivalenter hydroxidjoner per siloxanenhet. Det ser även ut som att molekylvikten stiger i experimenten i sur miljö när man tittar på HP-SEC.

Det är oklart hur exakta resultaten är i och med att det finns en hel del faktorer som påverkar resultaten. Största orsaken till eventuella fel antas vara upparbetningen där material förloras, särskilt i experimenten med CTO och TOP där det förlorades ca 60%. Omrörning och temperaturkontroll var heller inte exakta.

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9 APPENDICES

Appendix A. HP-SEC analyses

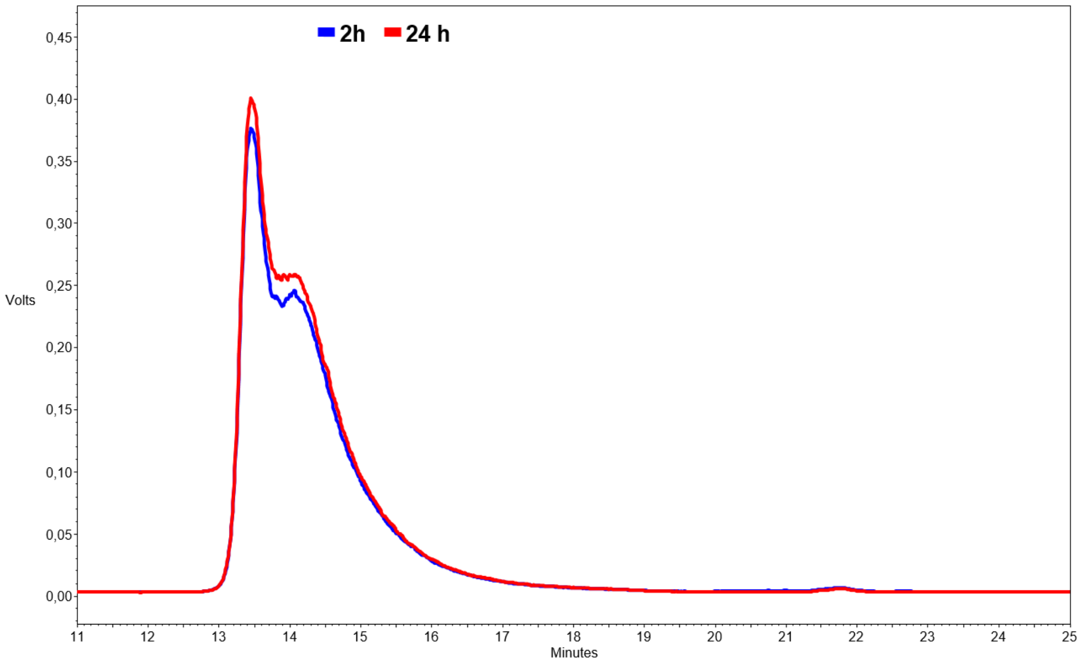


Figure A1. HP-SEC analysis of PDMS in 0.1 M NaOH for 2 h and 24 h at 90 °C.

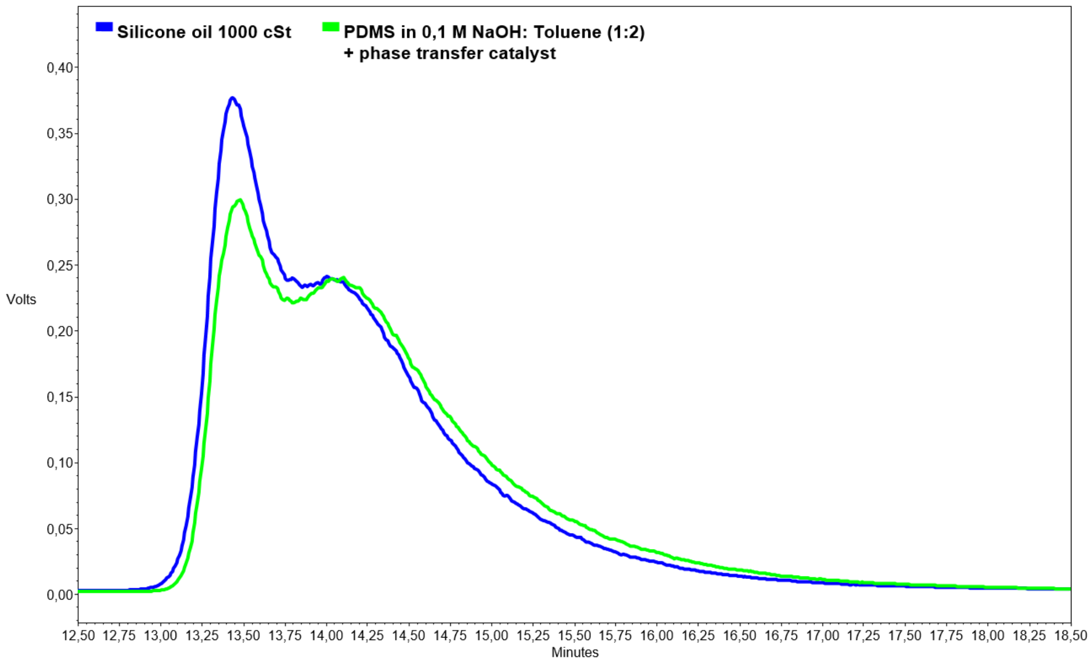


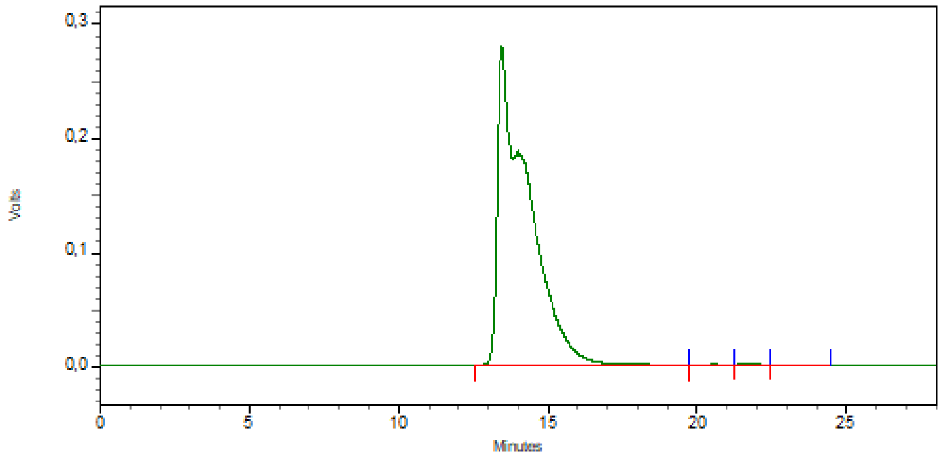
Figure A2. HP-SEC chromatogram of PDMS in 0.1 M NaOH: Toluene (1:2) with a phase transfer catalyst at 80 °C for 24 h.

Appendix B. HP-SEC areas.

C:\Data\JH\D5\jh_sec5_418-Rep1.dat AO-I-30a

Jordi Gel DVB 500Å 50 x 7.8 mm (guard) +
2 x Jordi Gel DVB 500Å 300 x 7.8 mm
ELSD 40C Gain 3 (inj 50 ul)

C:\Data\JH\D5\Sec_0-8_28min_calc_tst.met



Detector D

Pk #	Retention Time	Area	Area Percent	Height
1	14,95	19905982	99,4	69329
2	20,63	28302	0,1	479
3	21,75	53644	0,3	1641
4	23,32	29502	0,1	311
Totals		20017431	100,0	71760

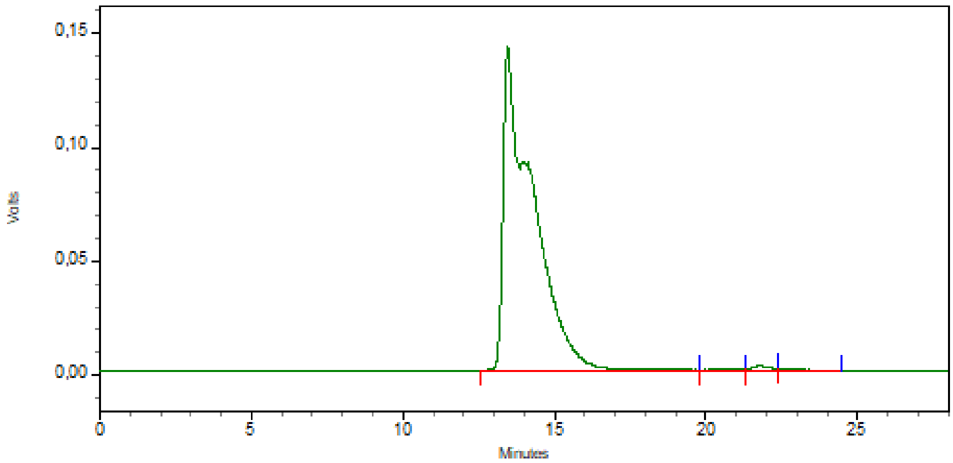
Figure B1. HP-SEC area of PDMS in THF and NaOH for 24 h.

Appendix B. HP-SEC areas.

C:\Data\JH\D5\jh_sec5_419-Rep1.dat AO-I-30b

Jordi Gel DVB 500Å 50 x 7.8 mm (guard) +
2 x Jordi Gel DVB 500Å 300 x 7.8 mm
ELSD 40C Gain 3 (inj 50 ul)

C:\Data\JH\D5\Sec_0-8_28min_calc_tst.met



Detector D

Pk #	Retention Time	Area	Area Percent	Height
1	14,98	9672570	98,7	30933
2	20,63	16348	0,2	185
3	21,77	78868	0,8	2239
4	23,32	28367	0,3	111
Totals		9796152	100,0	33467

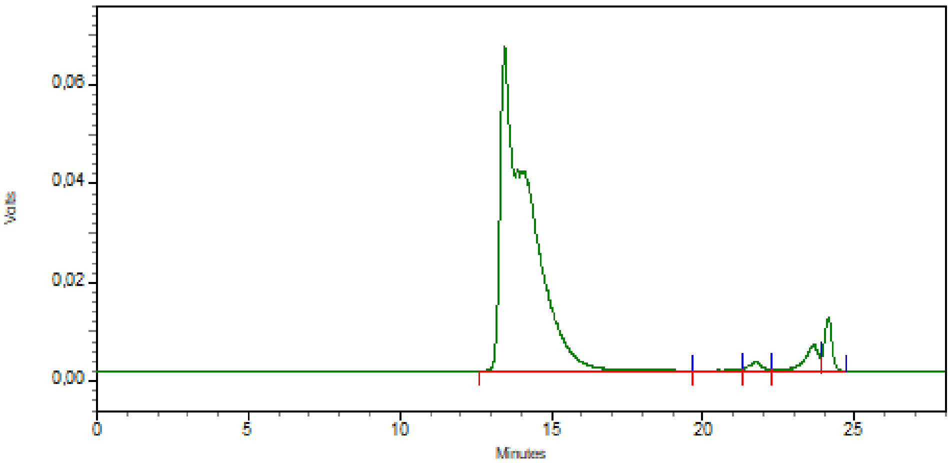
Figure B2. HP-SEC area of PDMS in THF and NaOH for 3 days.

Appendix B. HP-SEC areas.

C:\Data\JH\D5\jh_sec5_420-Rep1.dat AO-I-30c

Jordi Gel DVB 500Å 50 x 7.8 mm (guard) +
2 x Jordi Gel DVB 500Å 300 x 7.8 mm
ELSD 40C Gain 3 (inj 50 ul)

C:\Data\JH\D5\Sec_0-8_28min_calc_tst.met



Detector D

Pk #	Retention Time	Area	Area Percent	Height
1	14,98	4281815	91,5	13195
2	20,61	7058	0,2	38
3	21,76	48487	1,0	1773
4	23,32	159735	3,4	1902
5	24,15	180247	3,9	10411
Totals		4677341	100,0	27318

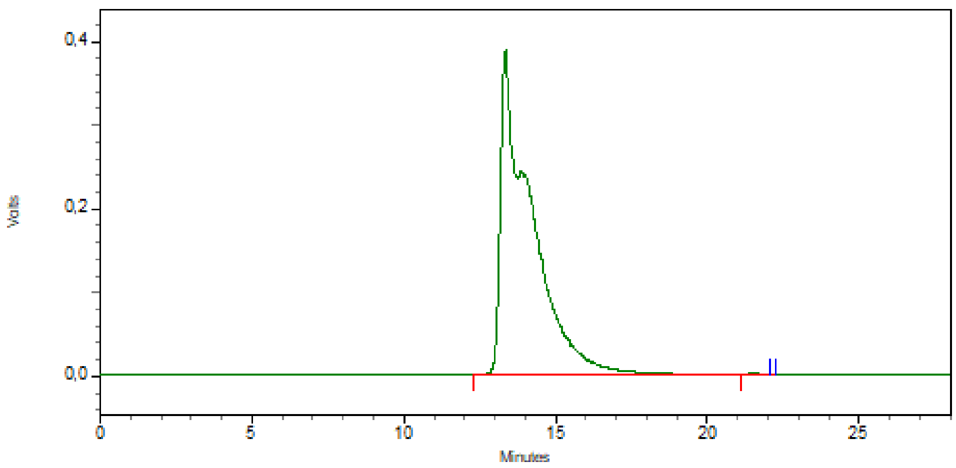
Figure B3. HP-SEC area of PDMS in THF and NaOH for 7 days.

Appendix B. HP-SEC areas.

C:\Data\JH\D5\jh_sec5_455-Rep1.dat Silicone oil 1000 cSt 2 mg/ml

Jordi Gel DVB 500Å 50 x 7.8 mm (guard) +
2 x Jordi Gel DVB 500Å 300 x 7.8 mm
ELSD 40C Gain 3 (inj 50 ul)

C:\Data\JH\D5\Sec_0-8_28min_calc_tst.met



Detector D

Pk #	Retention Time	Area	Area Percent	Height
1	14,95	27178558	99,9	75578
2	21,77	29112	0,1	364
Totals		27207670	100,0	75942

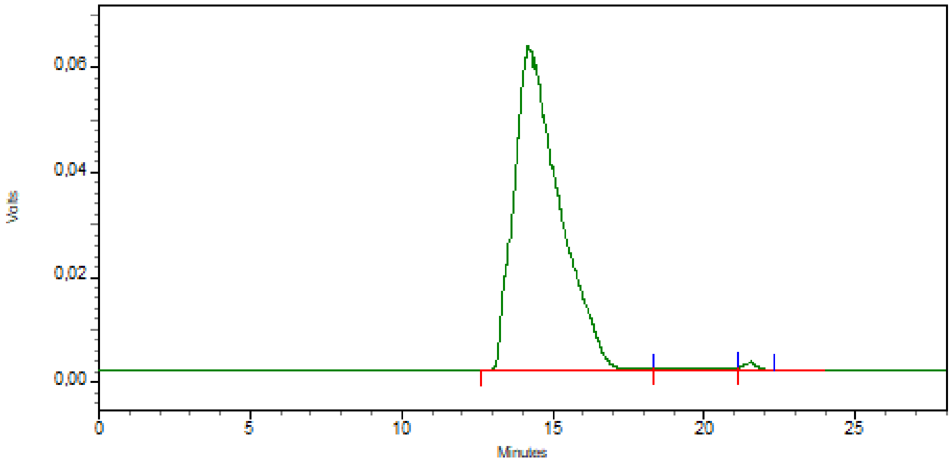
Figure B4. HP-SEC area of PDMS starting material reference for PDMS in EtOH:KOH (9:1)

Appendix B. HP-SEC areas.

C:\Data\JH\D5\jh_sec5_454-Rep2.dat AO-I-45 (2 mg/ml starting material)

Jordi Gel DVB 500Å 50 x 7.8 mm (guard) +
2 x Jordi Gel DVB 500Å 300 x 7.8 mm
ELSD 40C Gain 3 (inj 50 ul)

C:\Data\JH\D5\Sec 0-8 28min calc tst.met



Detector D

Pk #	Retention Time	Area	Area Percent	Height
1	14,98	6411694	98,7	38419
2	20,63	43517	0,7	362
3	21,77	43547	0,7	591
Totals		6498759	100,0	39372

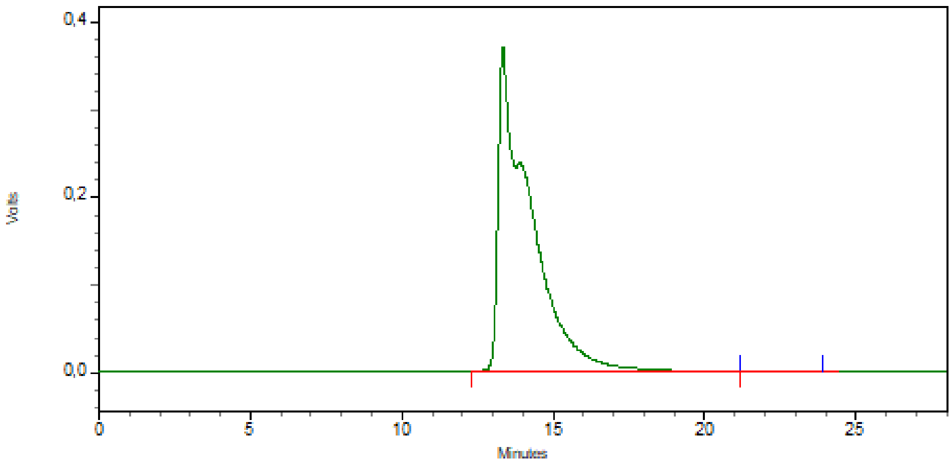
Figure B5. HP-SEC area of PDMS in EtOH: KOH (9:1) at 70 °C for 72 h.

Appendix B. HP-SEC areas.

C:\Data\JH\D5\jh_sec5_569-Rep2.dat Silicone oil 1000 cSt 2 mg/ml

Jordi Gel DVB 500Å 50 x 7.8 mm (guard) +
2 x Jordi Gel DVB 500Å 300 x 7.8 mm
ELSD 40C Gain 3 (inj 50 ul)

C:\Data\JH\D5\Sec_0-8_28min_calc_tst.met



Detector D

Pk #	Retention Time	Area	Area Percent	Height
1	14,95	26792062	100,0	77271
2	21,76	3423	0,0	40
Totals		26795485	100,0	77311

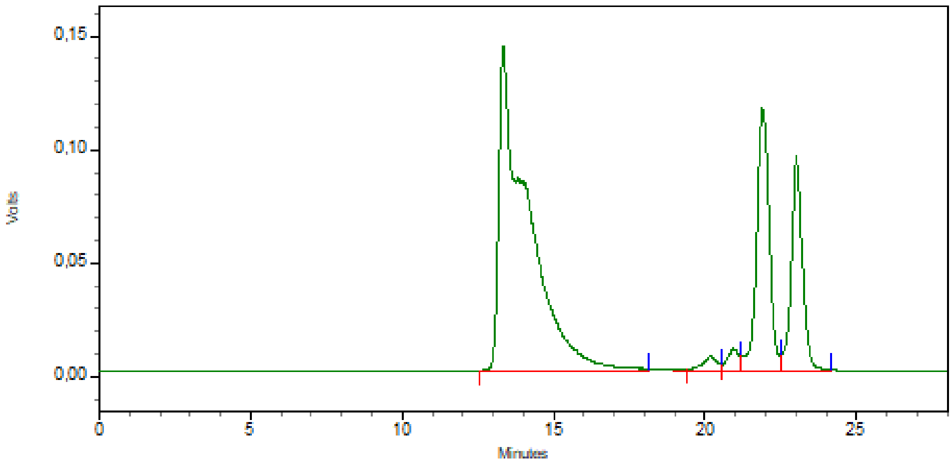
Figure B6. Starting material reference for CTO and TOP experiments.

Appendix B. HP-SEC areas.

C:\Data\JH\D5\jh_sec5_560.dat AO-I-70 (2 mg/ml)

Jordi Gel DVB 500Å 50 x 7.8 mm (guard) +
2 x Jordi Gel DVB 500Å 300 x 7.8 mm
ELSD 40C Gain 3 (inj 50 ul)

C:\Data\JH\D5\Sec_0-8_28min_calc_tst.met



Detector D

Pk #	Retention Time	Area	Area Percent	Height
1	13,34	9452379	60,3	142604
2	20,16	210612	1,3	6455
3	20,92	260373	1,7	9578
4	21,89	3340007	21,3	114655
5	23,01	2407237	15,4	94482
Totals		15670607	100,0	367773

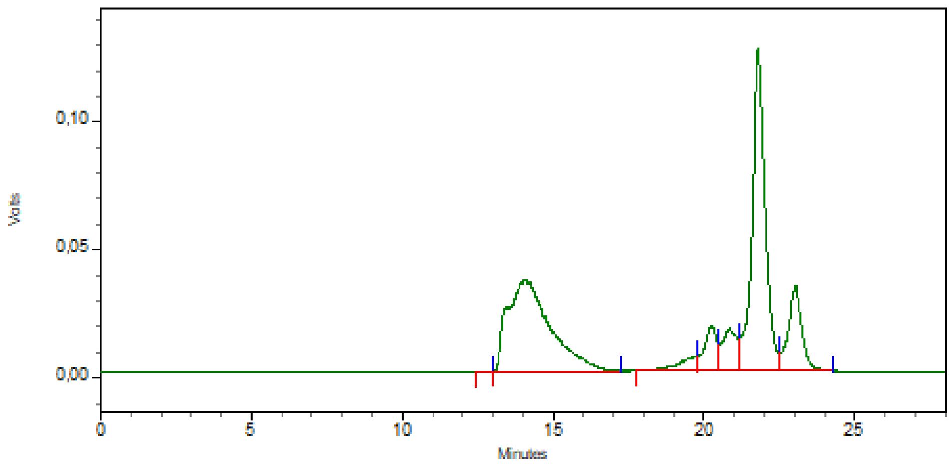
Figure B7. CTO and PDMS in EtOH: KOH at 70 °C for 0 h.

Appendix B. HP-SEC areas.

C:\Data\JH\D5\jh_sec5_556.dat AO-I-65 (2 mg/ml)

Jordi Gel DVB 500Å 50 x 7.8 mm (guard) +
2 x Jordi Gel DVB 500Å 300 x 7.8 mm
ELSD 40C Gain 3 (inj 50 ul)

C:\Data\JH\D5\Sec_0-8_28min_calc_tst.met



Detector D

Pk #	Retention Time	Area	Area Percent	Height
1	12,50	1357	0,0	75
2	14,07	3497228	36,4	35853
3	19,73	232104	2,4	5719
4	20,24	511977	5,3	17558
5	20,84	529511	5,5	16394
6	21,78	3821069	39,7	125770
7	23,03	1026994	10,7	33225
Totals		9620240	100,0	234595

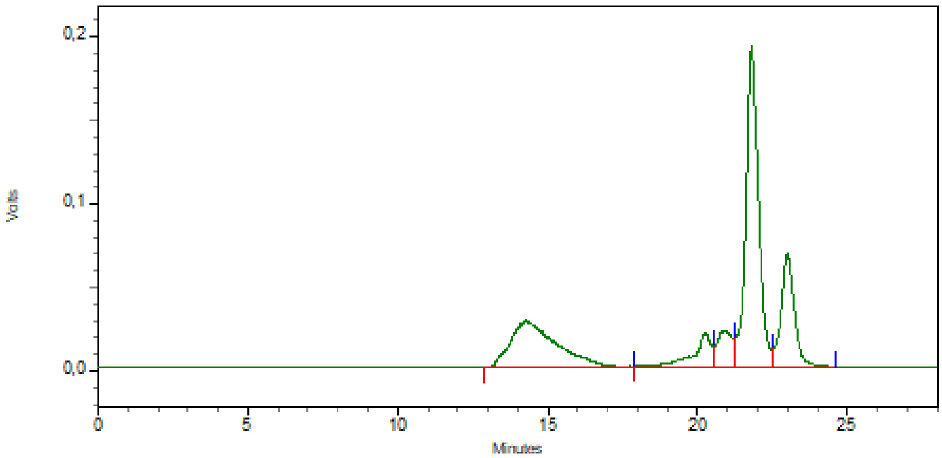
Figure B8. CTO and PDMS in EtOH: KOH at 70 °C for 24 h.

Appendix B. HP-SEC areas.

C:\Data\JH\D5\jh_sec5_557.dat AO-I-66 (2 mg/ml)

Jordi Gel DVB 500Å 50 x 7.8 mm (guard) +
2 x Jordi Gel DVB 500Å 300 x 7.8 mm
ELSD 40C Gain 3 (inj 50 ul)

C:\Data\JH\D5\Sec_0-8_28min_calc_tst.met



Detector D

Pk #	Retention Time	Area	Area Percent	Height
1	14,25	2878349	23,7	27547
2	20,21	861347	7,1	20042
3	20,83	768917	6,3	21505
4	21,79	5531837	45,5	191297
5	22,97	2108565	17,4	66920
Totals		12149015	100,0	327311

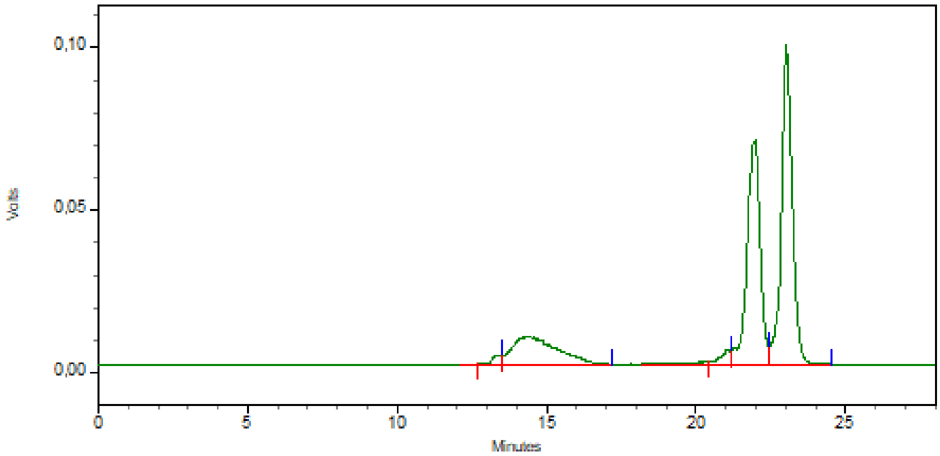
Figure B9. CTO and PDMS in EtOH: KOH at 70 °C for 48 h.

Appendix B. HP-SEC areas.

C:\Data\JH\D5\jh_sec5_558.dat AO-I-68 (2 mg/ml)

Jordi Gel DVB 500Å 50 x 7.8 mm (guard) +
2 x Jordi Gel DVB 500Å 300 x 7.8 mm
ELSD 40C Gain 3 (inj 50 ul)

C:\Data\JH\D5\Sec_0-8_28min_calc_tst.met



Detector D

Pk #	Retention Time	Area	Area Percent	Height
1	13,32	65094	1,2	2904
2	14,32	894562	15,8	8730
3	21,01	97676	1,7	4411
4	21,92	2116159	37,4	68231
5	23,02	2486392	43,9	98040
Totals		5659882	100,0	182316

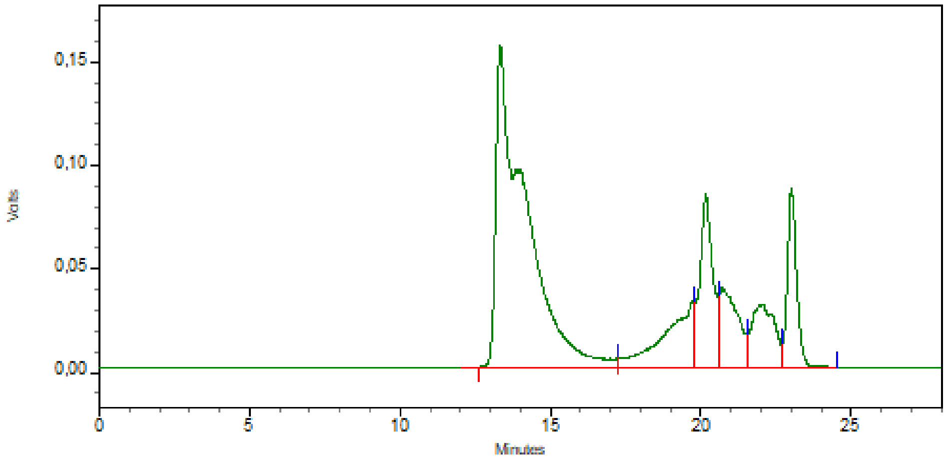
Figure B10. CTO and PDMS in EtOH: KOH at 70 °C for 72 h.

Appendix B. HP-SEC areas.

C:\Data\JH\D5\jh_sec5_563.dat AO-I-74 (2 mg/ml)

Jordi Gel DVB 500Å 50 x 7.8 mm (guard) +
2 x Jordi Gel DVB 500Å 300 x 7.8 mm
ELSD 40C Gain 3 (inj 50 ul)

C:\Data\JH\D5\Sec_0-8_28min_calc_tst.met



Detector D

Pk #	Retention Time	Area	Area Percent	Height
1	14,98	10660147	52,4	28120
2	19,72	2079480	10,2	31859
3	20,16	2488406	12,2	82861
4	20,70	1691839	8,3	37998
5	21,98	1574442	7,7	30148
6	23,01	1840511	9,1	85921
Totals		20334824	100,0	296908

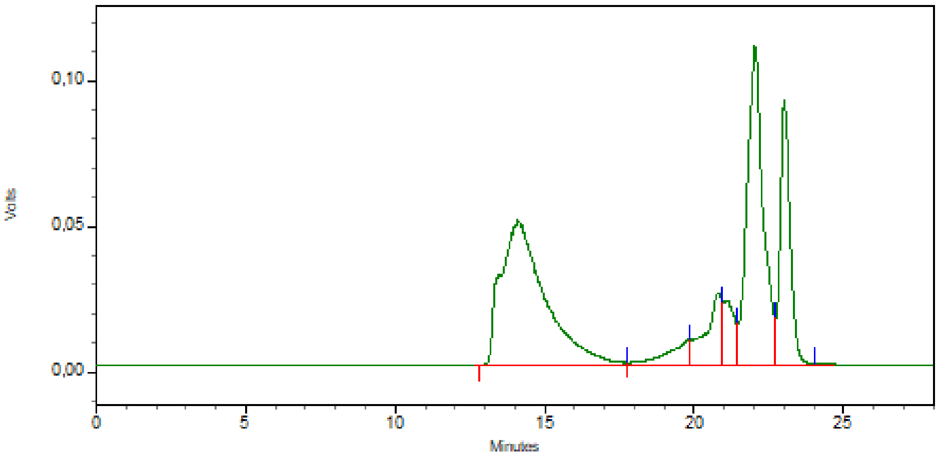
Figure B11. TOP and PDMS in EtOH: KOH at 70 °C for 0 h.

Appendix B. HP-SEC areas.

C:\Data\JH\D5\jh_sec5_561.dat AO-I-71 (2 mg/ml)

Jordi Gel DVB 500Å 50 x 7.8 mm (guard) +
2 x Jordi Gel DVB 500Å 300 x 7.8 mm
ELSD 40C Gain 3 (inj 50 ul)

C:\Data\JH\D5\Sec_0-8_28min_calc_tst.met



Detector D

Pk #	Retention Time	Area	Area Percent	Height
1	14,10	5047207	38,4	49455
2	19,80	433824	3,3	8625
3	20,77	930017	7,1	24391
4	20,98	551899	4,2	22048
5	22,02	4083762	31,1	109475
6	23,00	2090650	15,9	90159
Totals		13137359	100,0	304154

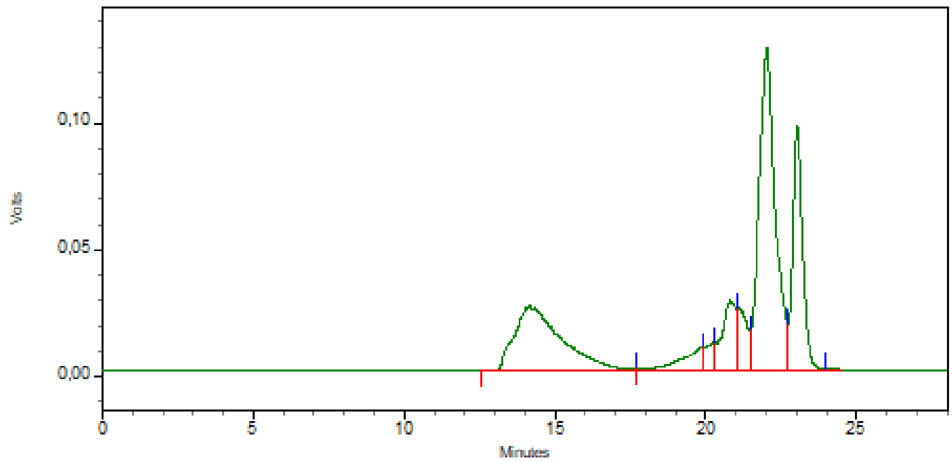
Figure B12. TOP and PDMS in EtOH: KOH at 70 °C for 24 h.

Appendix B. HP-SEC areas.

C:\Data\JH\D5\jh_sec5_562.dat AO-I-73 (2 mg/ml)

Jordi Gel DVB 500Å 50 x 7.8 mm (guard) +
2 x Jordi Gel DVB 500Å 300 x 7.8 mm
ELSD 40C Gain 3 (inj 50 ul)

C:\Data\JH\D5\Sec_0-8_28min_calc_tst.met



Detector D

Pk #	Retention Time	Area	Area Percent	Height
1	14,95	2679671	22,9	15036
2	19,85	416905	3,6	8987
3	20,23	218764	1,9	10945
4	20,81	870179	7,4	27563
5	21,05	558821	4,8	24337
6	22,02	4760882	40,7	126854
7	23,03	2201302	18,8	95989
Totals		11706524	100,0	309711

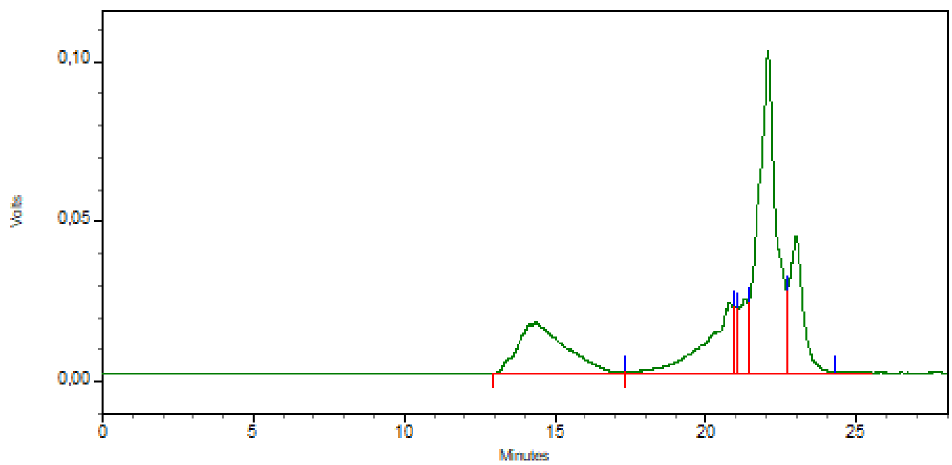
Figure B13. TOP and PDMS in EtOH: KOH at 70 °C for 48 h.

Appendix B. HP-SEC areas.

C:\Data\JH\D5\jh_sec5_559.dat AO-I-69 (2 mg/ml)

Jordi Gel DVB 500Å 50 x 7.8 mm (guard) +
2 x Jordi Gel DVB 500Å 300 x 7.8 mm
ELSD 40C Gain 3 (inj 50 ul)

C:\Data\JH\D5\Sec_0-8_28min_calc_tst.met



Detector D

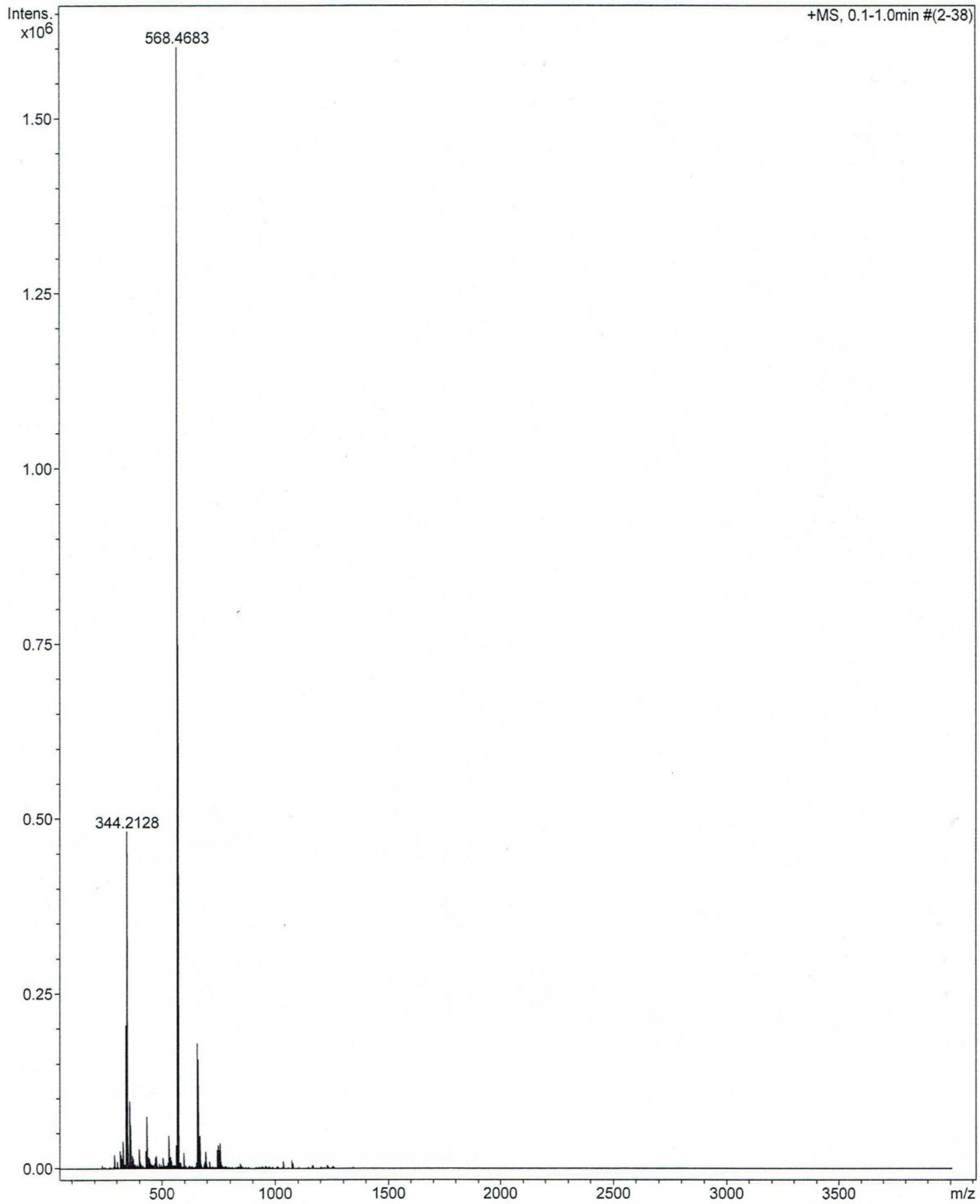
Pk #	Retention Time	Area	Area Percent	Height
1	14,36	1697690	18,7	15612
2	20,77	1313745	14,5	21952
3	20,93	218313	2,4	21009
4	21,29	426313	4,7	23224
5	22,06	4106569	45,2	100505
6	22,99	1318019	14,5	42506
Totals		9080647	100,0	224808

Figure B14. TOP and PDMS in EtOH: KOH at 70 °C for 72 h.

APPENDIX C. Q-TOF mass spectra of PDMS in 1 M KOH for 16 days.

Generic Display Report

Analysis Info		Acquisition Date	3/7/2019 2:06:39 PM
Analysis Name	D:\Data\SabineRendon\190307 AO-I-54b.d		
Method	tunepos_wide.m	Operator	Bruker07
Sample Name	190307 AO-I-54b	Instrument	micrOTOF-Q
Comment			



Bruker Compass DataAnalysis 4.0 printed: 3/7/2019 2:39:42 PM Page 1 of 1

APPENDIX C. Q-TOF mass spectra of PDMS in 1 M KOH for 16 days.

Generic Display Report

Analysis Info

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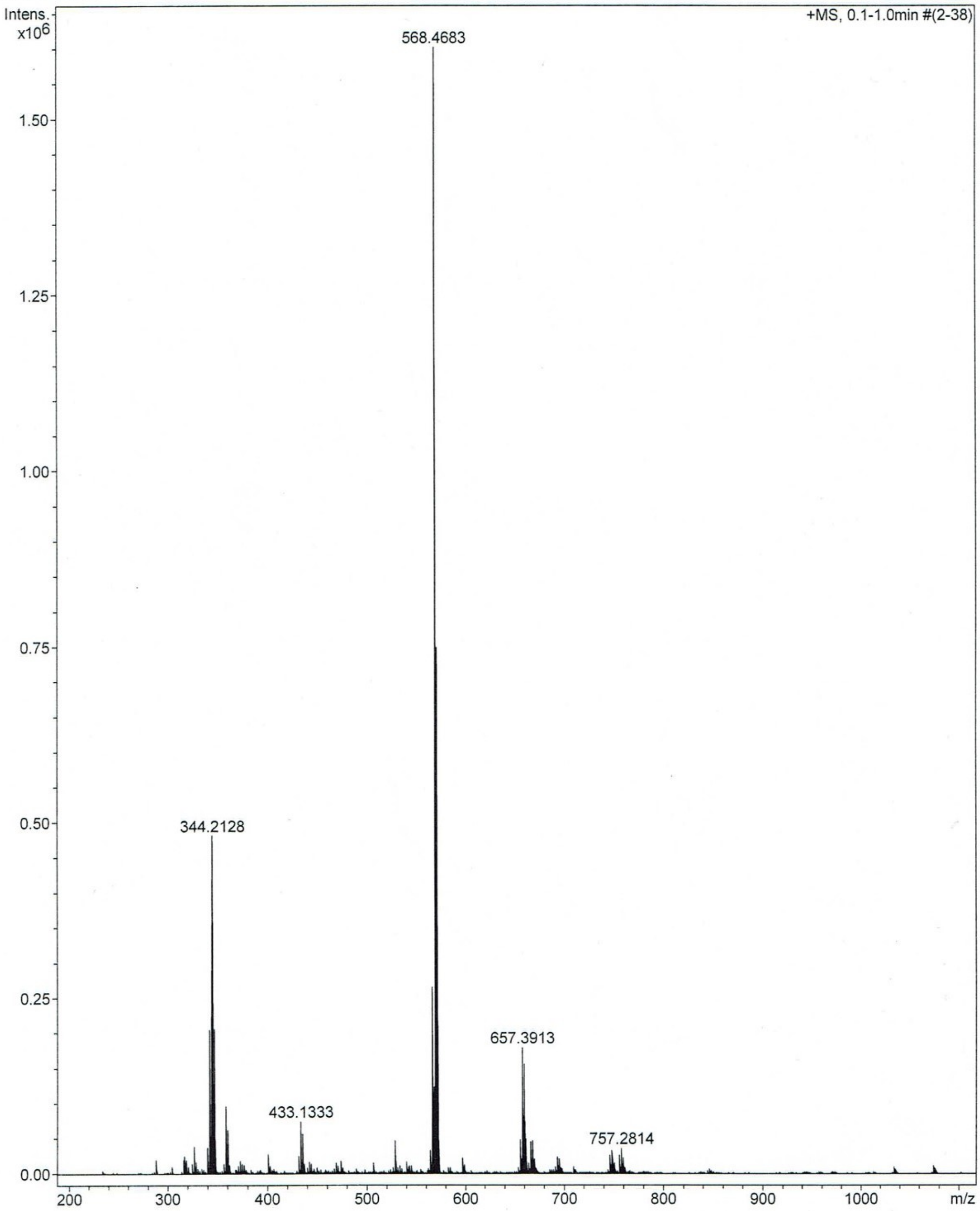
Sample Name	190307 AO-I-54b	Instrument	micrOTOF-Q
Comment			



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APPENDIX C. Q-TOF mass spectra of PDMS in 1 M KOH for 16 days.

Generic Display Report

Analysis Info

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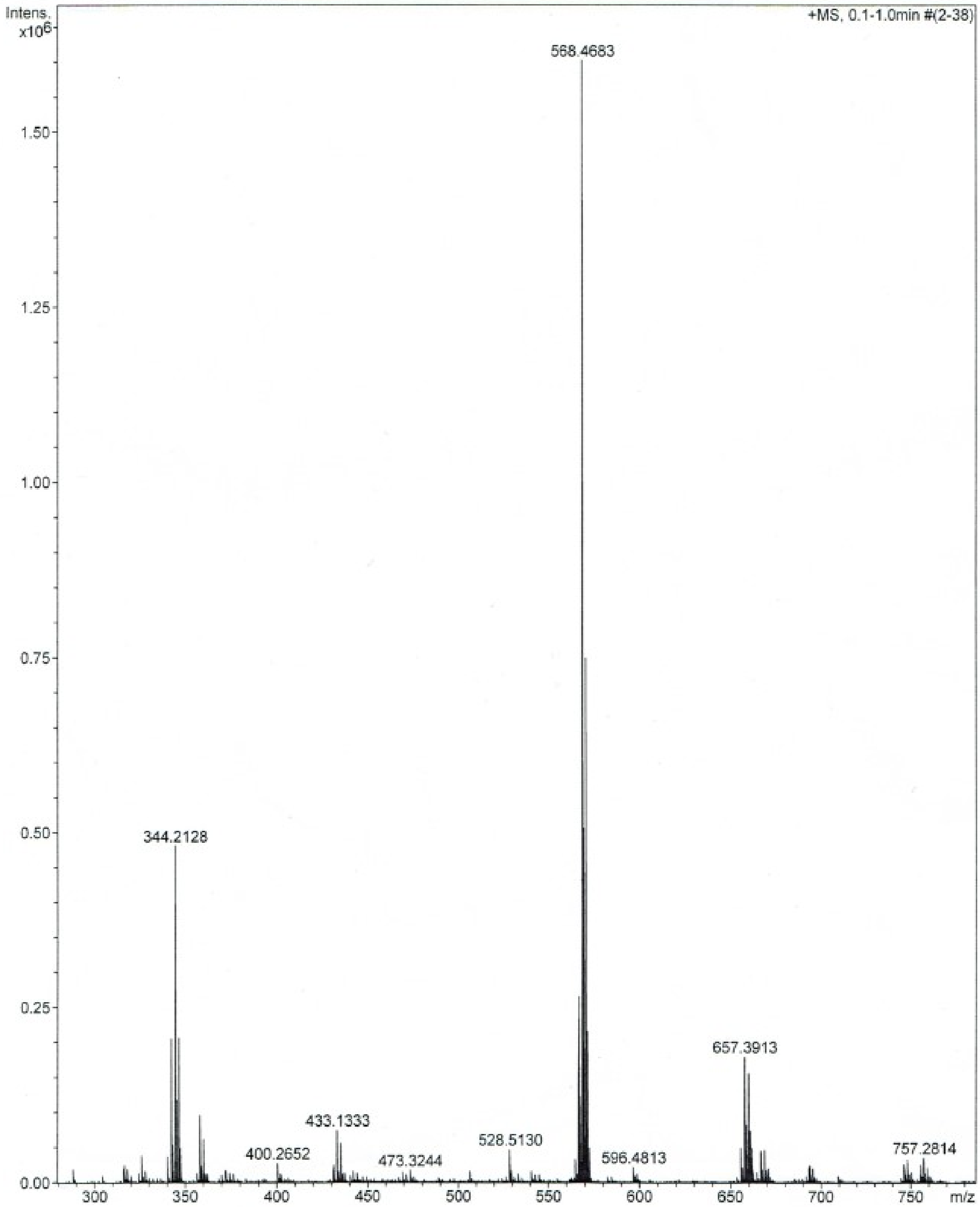
Method	tunepos_wide.m	Operator	Bruker07
Sample Name	190307 AO-I-54b	Instrument	micrOTOF-Q
Comment			



Bruker Compass DataAnalysis 4.0 printed: 3/7/2019 2:41:07 PM Page 1 of 1

APPENDIX C. Q-TOF mass spectra of PDMS in 1 M KOH for 16 days.

Generic Display Report

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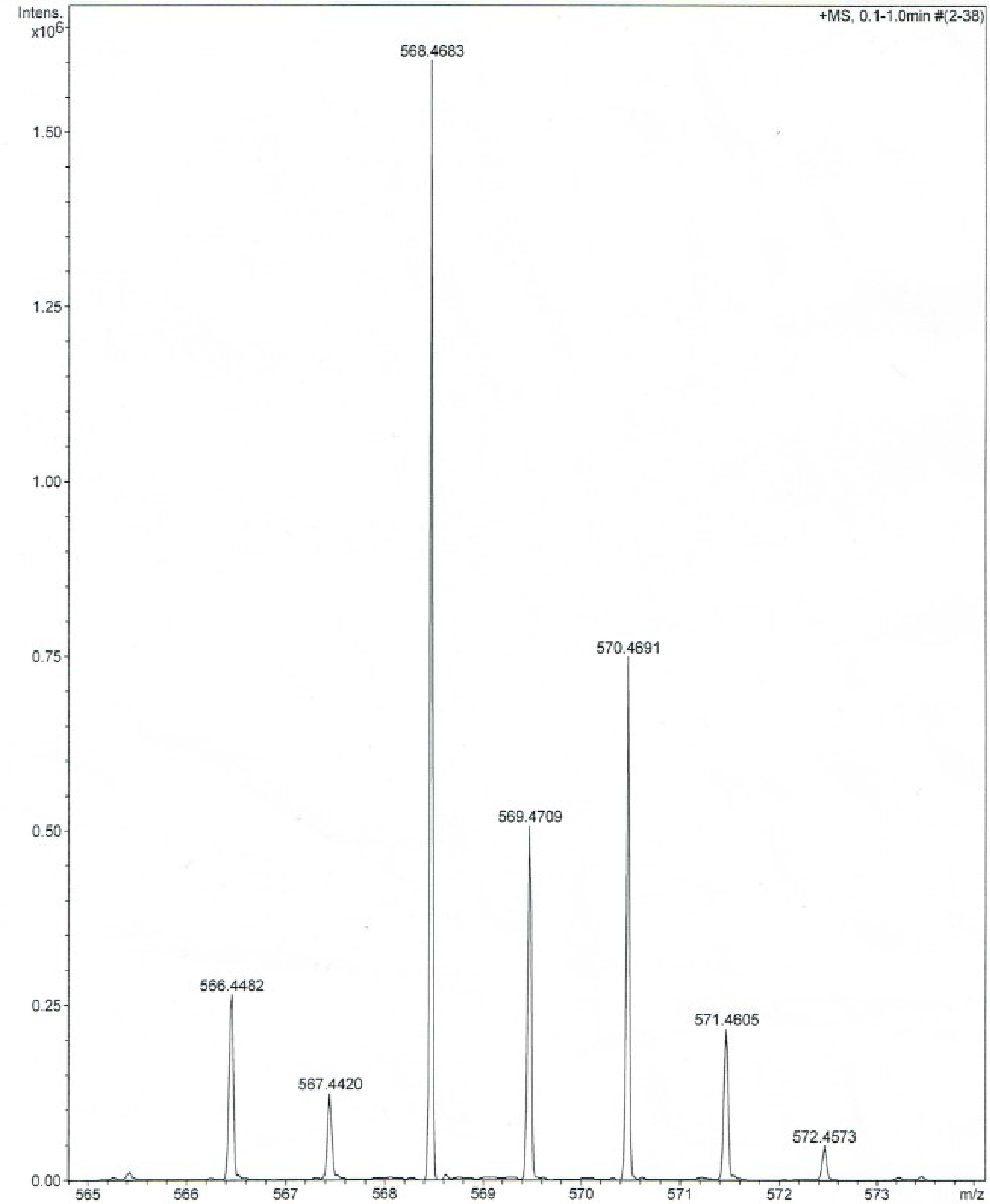
Method	tunepos_wide.m	Operator	Bruker07
Sample Name	190307 AO-I-54b	Instrument	micrOTOF-Q
Comment			



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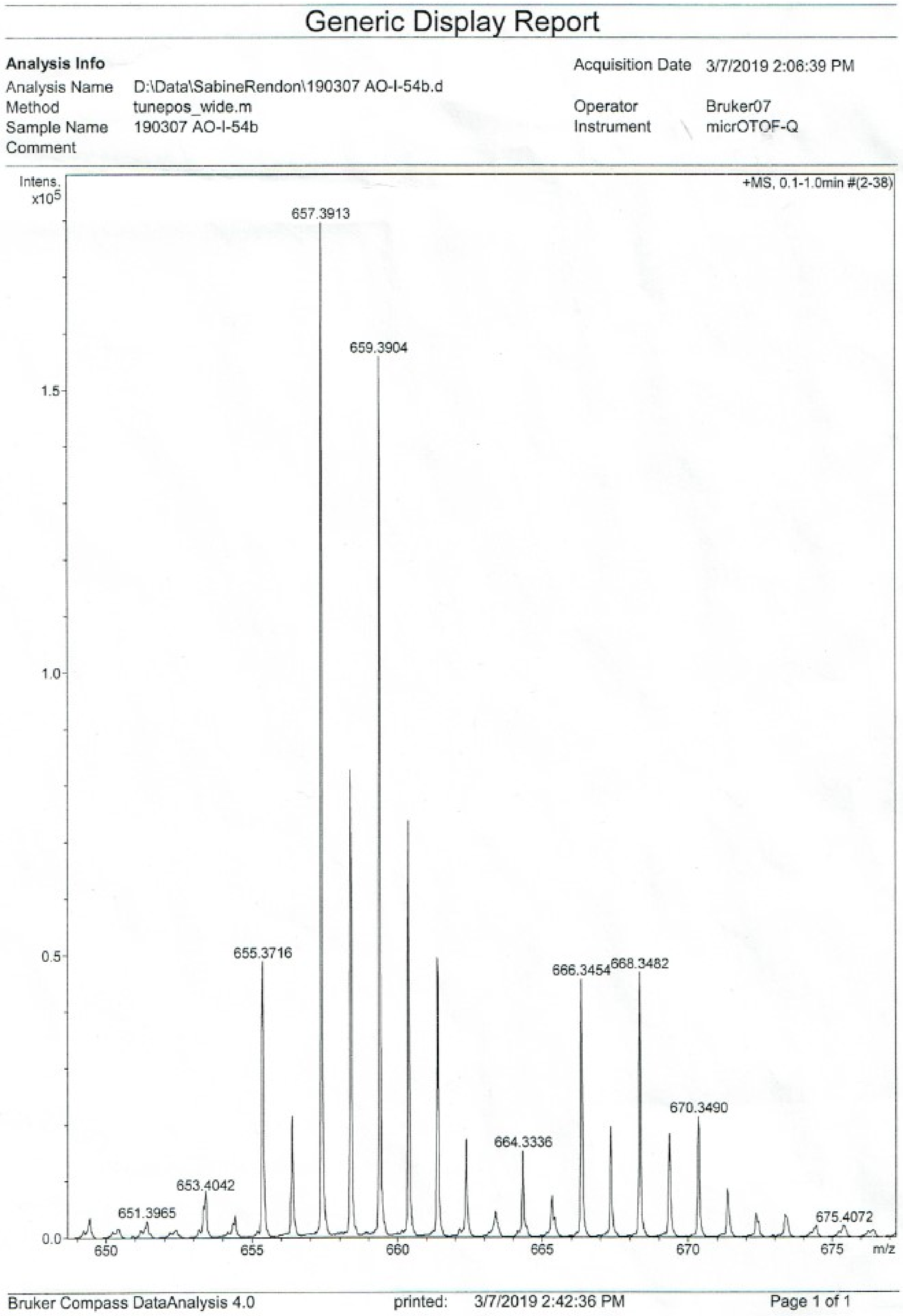
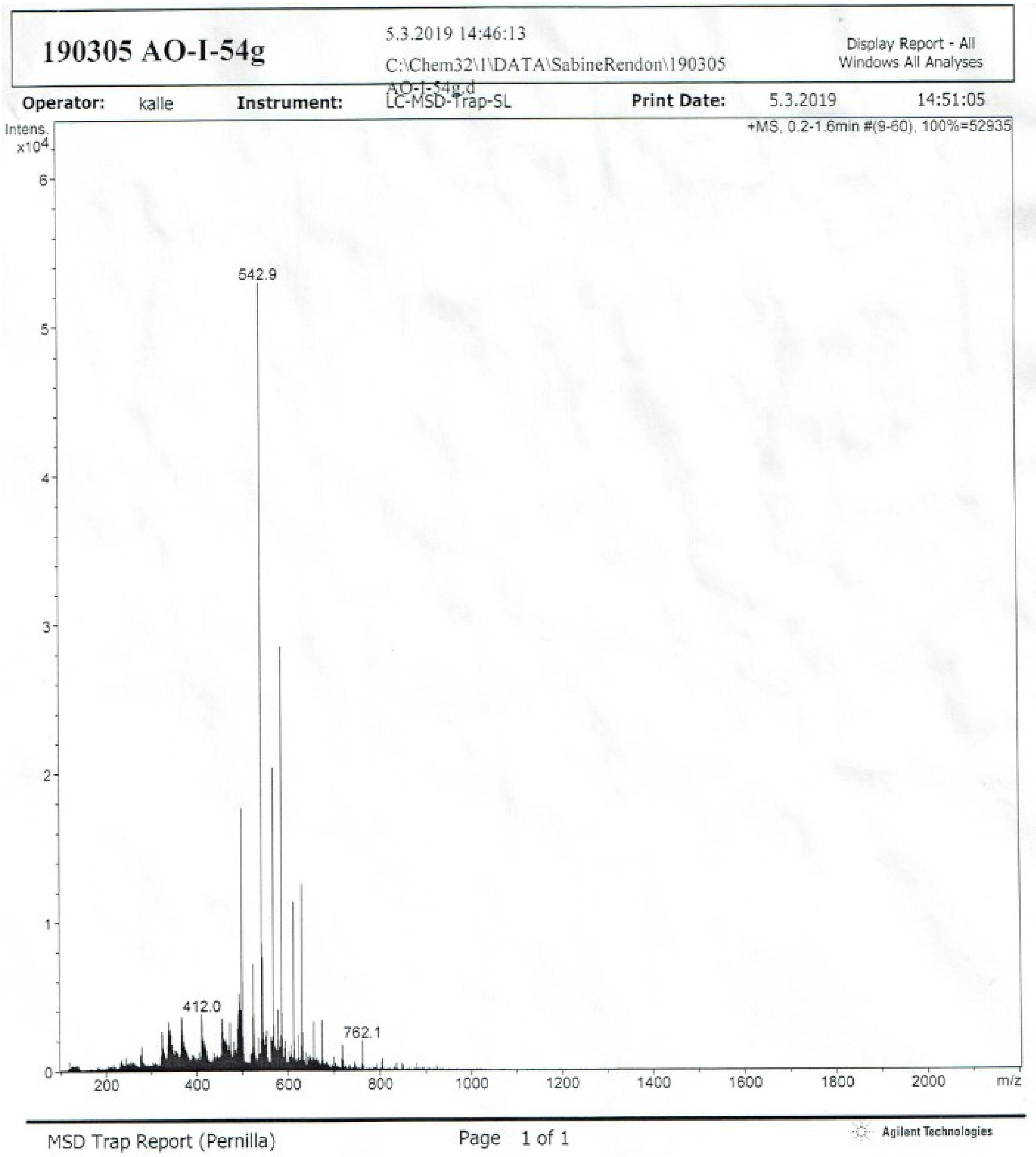
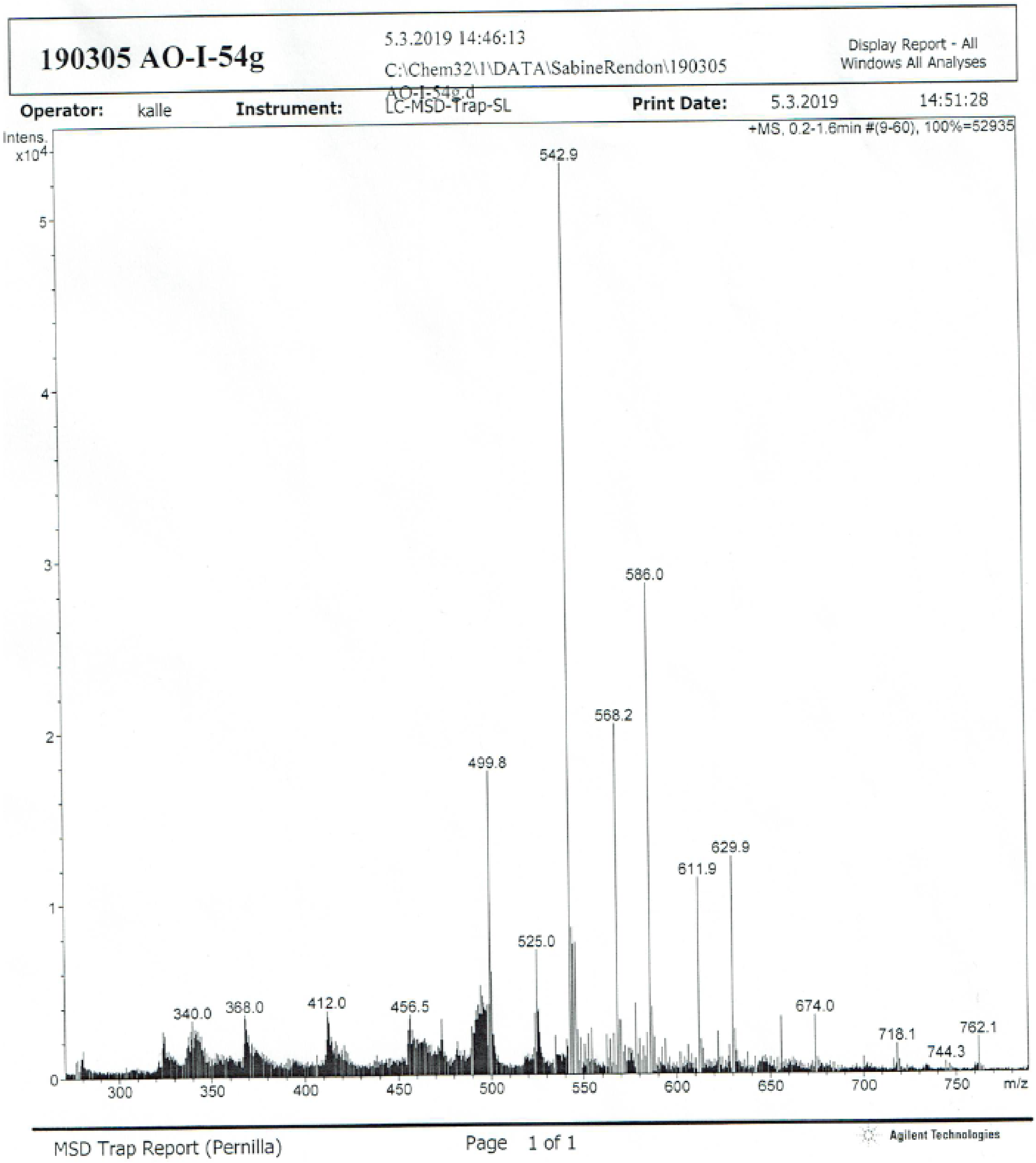
APPENDIX C. Q-TOF mass spectra of PDMS in 1 M KOH for 16 days.



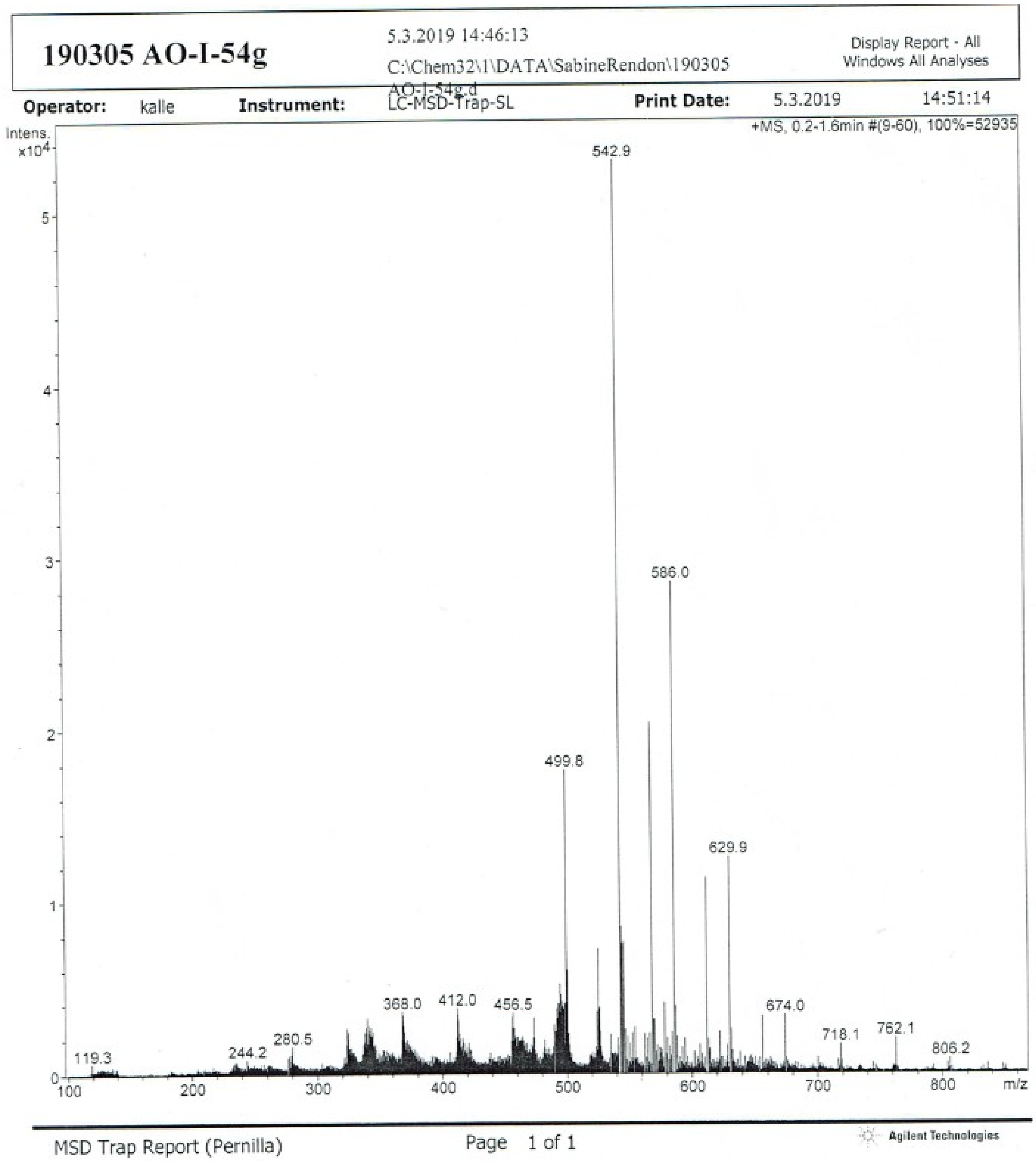
APPENDIX D. Ion-trap mass spectra of PDMS in 1 M KOH for 16 days.



APPENDIX D. Ion-trap mass spectra of PDMS in 1 M KOH for 16 days.



APPENDIX D. Ion-trap mass spectra of PDMS in 1 M KOH for 16 days.



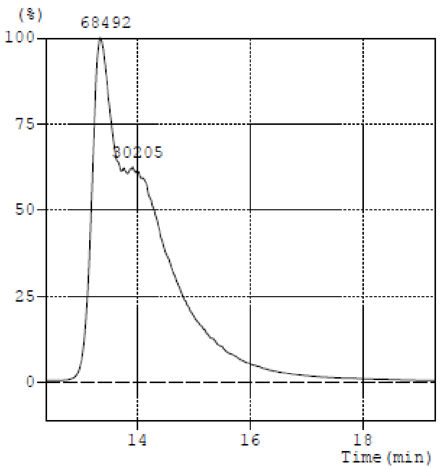
APPENDIX E. GPC Report

GPC Report Version 1.03

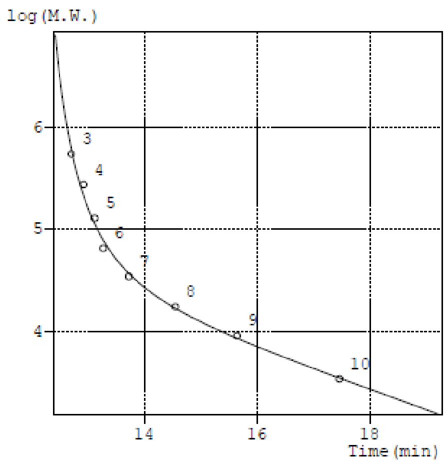
*** Title ***

Developer :
Date/Time : 19.05.06 11:49:14
Comment :
System No. : 1
Channel No. : 1
Report No. : 1
Method File : 14032019.GMT
Data File : SILICON.D01
Sample Name : Silicone oil 1000 cSt
Sample ID :
Type : U

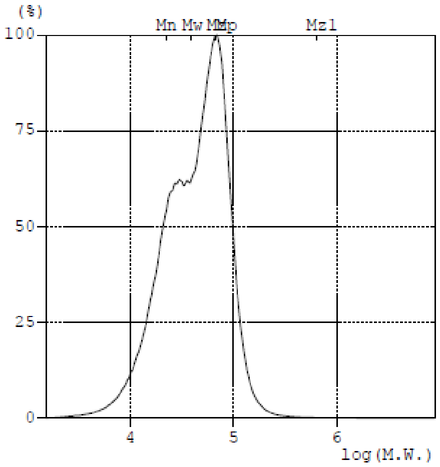
** Chromatogram **



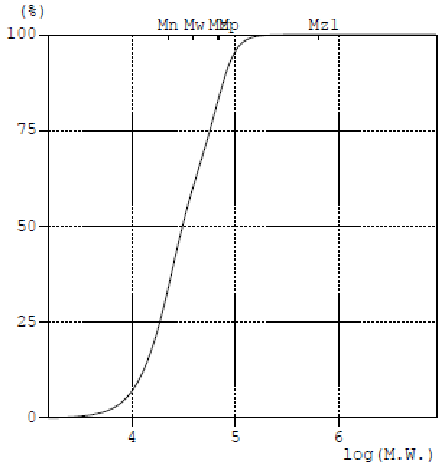
** Calibration Curve **



** Differential M.W. Curve **



** Integral M.W. Curve **



*** Peak No.1 ***

[Ave. Molecular Weight]

Number-A.M.W.(Mn)	:	54 260
Weight-A.M.W.(Mw)	:	62 326
Z-A.M.W.(Mz)	:	84 272
(Z+1)-A.M.W.(Mz1)	:	684 890
Mw/Mn	:	1,14866
Mv/Mn	:	0,00000
Mz/Mw	:	1,35211

*** Peak No.2 ***

APPENDIX E. GPC Report

```
[ Ave. Molecular Weight ]
     Number-A.M.W.(Mn)    :      14 815
     Weight-A.M.W.(Mw)    :      18 873
     Z-A.M.W.(Mz)         :      21 725
     (Z+1)-A.M.W.(Mz1)    :      23 725
     Mw/Mn                :          1,27395
     Mv/Mn                :          0,00000
     Mz/Mw                :          1,15109

*** Ave. Molecular Weight(Total) ***
          Number-A.M.W.(Mn)  :      22 395
          Weight-A.M.W.(Mw)  :      39 106
          Z-A.M.W.(Mz)       :      68 141
          (Z+1)-A.M.W.(Mz1)  :     630 524
          Mw/Mn              :          1,74616
          Mv/Mn              :          0,00000
          Mz/Mw              :          1,74248

*** GPC Method ***
 ** Header **
     Operator  :
     Date/Time : 19.05.05 17:19:46
     Comment   : 2 x Jordigel DVB 500A
                 TPK 12 PS-standarder
                 T.LIMIT 11,5 min

 ** LC Parameter **
     Flow(ml/min)   :
     Temperature(C) :   40,000

 ** GPC Parameter **
          Name        :
          Q Factor    : 1,000
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          Vis. Coeff. :  a =   0,000
                         k =   0,000
     ** polymer B **
          Vis. Coeff. :  a =   0,000
                         k =   0,000

 ** Quantitative Parameters **
     Correction with I.S. : OFF
     Correction with Delay Time : OFF
     Sensitivity Correction(RID) : OFF
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APPENDIX E. GPC Report

** Calibration Curve Table **

	R.T(min)	Molecular Weight	Active	Virtual
1	11,903	2 520 000	OFF	OFF
2	12,353	1 210 000	OFF	OFF
3	12,702	552 000	ON	OFF
4	12,921	277 000	ON	OFF
5	13,118	130 000	ON	OFF
6	13,271	66 000	ON	OFF
7	13,726	34 800	ON	OFF
8	14,550	17 600	ON	OFF
9	15,648	9 130	ON	OFF
10	17,466	3 470	ON	OFF
11	19,690	1 250	ON	OFF
12	20,739	786	ON	OFF
13	21,045	682	ON	OFF
14	21,377	578	ON	OFF
15	21,782	474	ON	OFF
16	22,280	370	ON	OFF

*** Peak Information(Total) ***

	Time	Molecular Weight	Height
Start	12,400	1,05151E+07	-2
Top	13,345	68 492	454796
End	19,275	1 540	33

*** Slice Data (Total) ***

Slice #	Time	Elution Volume	Molecular Weight	Height	Sub Total	%
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2	12,44	0,000	6,41871E+06	44	21459020	99,99
3	12,46	0,000	4,73788E+06	40	21458976	99,99
4	12,49	0,000	3,60185E+06	23	21458937	99,99
5	12,51	0,000	2,77267E+06	61	21458914	99,99
6	12,54	0,000	2,18717E+06	90	21458853	99,99
7	12,56	0,000	1,74252E+06	114	21458764	99,99
8	12,59	0,000	1,41695E+06	159	21458649	99,99
9	12,61	0,000	1,16140E+06	232	21458490	99,99
10	12,64	0,000	968 523	287	21458258	99,99
11	12,66	0,000	812 859	329	21457971	99,99
12	12,69	0,000	692 319	426	21457643	99,99
13	12,71	0,000	592 715	578	21457217	99,99
14	12,74	0,000	513 883	747	21456639	99,98
15	12,76	0,000	447 415	1004	21455892	99,98
16	12,79	0,000	393 813	1342	21454888	99,98
17	12,81	0,000	347 825	1829	21453546	99,97
18	12,84	0,000	310 132	2442	21451718	99,96
19	12,86	0,000	277 302	3200	21449276	99,95
20	12,89	0,000	250 011	4468	21446077	99,93
21	12,91	0,000	225 925	6636	21441608	99,91
22	12,94	0,000	205 653	9581	21434973	99,88
23	12,96	0,000	187 554	13653	21425392	99,84
24	12,99	0,000	172 154	19413	21411739	99,77
25	13,01	0,000	158 263	27419	21392327	99,68
26	13,04	0,000	146 329	39388	21364908	99,56
27	13,06	0,000	135 465	56098	21325520	99,37
28	13,09	0,000	126 052	79703	21269421	99,11
29	13,11	0,000	117 413	108908	21189718	98,74
30	13,14	0,000	109 869	144652	21080810	98,23
31	13,16	0,000	102 895	190587	20936157	97,56
32	13,19	0,000	96 763	242134	20745571	96,67
33	13,21	0,000	91 057	290591	20503436	95,54

34	13,24	0,000	86 008	337933	20212846	94,19
35	13,26	0,000	81 282	385340	19874912	92,61
36	13,29	0,000	77 077	421813	19489572	90,82
37	13,31	0,000	73 119	442957	19067759	88,85
38	13,34	0,000	69 579	454796	18624802	86,79
39	13,36	0,000	66 231	452183	18170006	84,67
40	13,39	0,000	63 223	443784	17717823	82,56
41	13,41	0,000	60 365	429407	17274040	80,49
42	13,44	0,000	57 785	413432	16844633	78,49
43	13,46	0,000	55 324	397522	16431201	76,57
44	13,49	0,000	53 094	376593	16033679	74,71
45	13,51	0,000	50 959	361331	15657086	72,96
46	13,54	0,000	49 018	344977	15295755	71,27
47	13,56	0,000	47 152	328930	14950778	69,67
48	13,59	0,000	45 450	314043	14621849	68,13
49	13,61	0,000	43 809	301309	14307806	66,67
50	13,64	0,000	42 306	292649	14006497	65,27
51	13,66	0,000	40 854	289622	13713848	63,90
52	13,69	0,000	39 521	284613	13424226	62,55
53	13,71	0,000	38 228	278791	13139613	61,23
54	13,74	0,000	37 038	279618	12860823	59,93
55	13,76	0,000	35 882	282344	12581205	58,62
56	13,79	0,000	34 814	279317	12298861	57,31
57	13,81	0,000	33 774	276136	12019544	56,01
58	13,84	0,000	32 813	275918	11743408	54,72
59	13,86	0,000	31 873	279990	11467491	53,43
60	13,89	0,000	31 003	281594	11187501	52,13
61	13,91	0,000	30 151	283010	10905907	50,82
62	13,94	0,000	29 359	281214	10622896	49,50
63	13,96	0,000	28 583	277869	10341682	48,19
64	13,99	0,000	27 861	278391	10063814	46,89
65	14,01	0,000	27 152	278340	9785423	45,60
66	14,04	0,000	26 490	274371	9507084	44,30
67	14,06	0,000	25 839	269716	9232712	43,02
68	14,09	0,000	25 232	269449	8962996	41,76
69	14,11	0,000	24 632	268440	8693547	40,51
70	14,14	0,000	24 072	265412	8425107	39,26
71	14,16	0,000	23 519	261700	8159695	38,02
72	14,19	0,000	23 001	253427	7897995	36,80
73	14,21	0,000	22 489	245275	7644568	35,62
74	14,24	0,000	22 008	241418	7399293	34,48
75	14,26	0,000	21 533	234550	7157875	33,35
76	14,29	0,000	21 086	229584	6923325	32,26
77	14,31	0,000	20 643	222454	6693741	31,19
78	14,34	0,000	20 226	216585	6471287	30,15
79	14,36	0,000	19 813	209182	6254702	29,14
80	14,39	0,000	19 424	202180	6045521	28,17
81	14,41	0,000	19 037	193378	5843340	27,23
82	14,44	0,000	18 673	187052	5649963	26,32
83	14,46	0,000	18 310	180688	5462911	25,45
84	14,49	0,000	17 968	173618	5282223	24,61
85	14,51	0,000	17 628	168752	5108605	23,80
86	14,54	0,000	17 306	164626	4939853	23,01
87	14,56	0,000	16 986	160448	4775227	22,25
88	14,59	0,000	16 683	154884	4614779	21,50
89	14,61	0,000	16 380	149278	4459895	20,78
90	14,64	0,000	16 094	144183	4310618	20,08
91	14,66	0,000	15 809	140394	4166435	19,41
92	14,69	0,000	15 538	134849	4026041	18,76
93	14,71	0,000	15 268	130006	3891192	18,13
94	14,74	0,000	15 012	125816	3761186	17,52
95	14,76	0,000	14 755	120790	3635370	16,94

APPENDIX E. GPC Report

96	14,79	0,000	14 512	116075	3514580	16,37
97	14,81	0,000	14 269	110905	3398505	15,83
98	14,84	0,000	14 038	107257	3287600	15,32
99	14,86	0,000	13 807	105260	3180343	14,82
100	14,89	0,000	13 588	100865	3075083	14,33
101	14,91	0,000	13 368	97994	2974218	13,86
102	14,94	0,000	13 159	93375	2876224	13,40
103	14,96	0,000	12 949	90735	2782850	12,96
104	14,99	0,000	12 749	87471	2692114	12,54
105	15,01	0,000	12 549	84021	2604643	12,13
106	15,04	0,000	12 359	80825	2520622	11,74
107	15,06	0,000	12 168	78589	2439797	11,36
108	15,09	0,000	11 986	77313	2361207	11,00
109	15,11	0,000	11 803	74702	2283894	10,64
110	15,14	0,000	11 629	72556	2209192	10,29
111	15,16	0,000	11 454	70153	2136637	9,95
112	15,19	0,000	11 287	67887	2066483	9,62
113	15,21	0,000	11 119	65453	1998596	9,31
114	15,24	0,000	10 959	62605	1933143	9,00
115	15,26	0,000	10 798	60017	1870539	8,71
116	15,29	0,000	10 645	57390	1810522	8,43
117	15,31	0,000	10 490	56074	1753132	8,16
118	15,34	0,000	10 343	55937	1697058	7,90
119	15,36	0,000	10 194	54557	1641121	7,64
120	15,39	0,000	10 053	52308	1586564	7,39
121	15,41	0,000	9 910	49718	1534257	7,14
122	15,44	0,000	9 773	47612	1484539	6,91
123	15,46	0,000	9 636	46236	1436927	6,69
124	15,49	0,000	9 505	45691	1390692	6,48
125	15,51	0,000	9 372	44347	1345000	6,26
126	15,54	0,000	9 246	41772	1300653	6,06
127	15,56	0,000	9 118	40359	1258882	5,86
128	15,59	0,000	8 996	38710	1218522	5,67
129	15,61	0,000	8 873	37268	1179812	5,49
130	15,64	0,000	8 756	36248	1142545	5,32
131	15,66	0,000	8 637	35618	1106297	5,15
132	15,69	0,000	8 523	34630	1070679	4,98
133	15,71	0,000	8 409	33676	1036049	4,82
134	15,74	0,000	8 299	32076	1002373	4,67
135	15,76	0,000	8 188	31207	970297	4,52
136	15,79	0,000	8 082	29961	939090	4,37
137	15,81	0,000	7 975	28875	909128	4,23
138	15,84	0,000	7 872	27397	880253	4,10
139	15,86	0,000	7 769	26914	852856	3,97
140	15,89	0,000	7 669	25813	825942	3,84
141	15,91	0,000	7 569	24780	800129	3,72
142	15,94	0,000	7 473	23844	775349	3,61
143	15,96	0,000	7 376	23152	751505	3,50
144	15,99	0,000	7 283	22794	728353	3,39
145	16,01	0,000	7 189	22104	705559	3,28
146	16,04	0,000	7 099	20934	683455	3,18
147	16,06	0,000	7 008	20347	662522	3,08
148	16,09	0,000	6 920	20089	642174	2,99
149	16,11	0,000	6 832	19423	622086	2,89
150	16,14	0,000	6 747	18628	602663	2,80
151	16,16	0,000	6 662	18391	584035	2,72
152	16,19	0,000	6 579	17601	565644	2,63
153	16,21	0,000	6 496	16611	548043	2,55
154	16,24	0,000	6 417	16023	531433	2,47
155	16,26	0,000	6 336	15837	515410	2,40
156	16,29	0,000	6 259	15282	499573	2,32
157	16,31	0,000	6 180	14787	484290	2,25

APPENDIX E. GPC Report

158	16,34	0,000	6 105	14058	469504	2,18
159	16,36	0,000	6 029	13649	455445	2,12
160	16,39	0,000	5 956	13397	441797	2,05
161	16,41	0,000	5 882	12786	428399	1,99
162	16,44	0,000	5 811	12481	415614	1,93
163	16,46	0,000	5 739	12208	403133	1,87
164	16,49	0,000	5 670	11833	390925	1,82
165	16,51	0,000	5 600	11299	379092	1,76
166	16,54	0,000	5 533	10976	367793	1,71
167	16,56	0,000	5 466	10649	356818	1,66
168	16,59	0,000	5 400	10416	346168	1,61
169	16,61	0,000	5 334	10182	335753	1,56
170	16,64	0,000	5 271	9806	325571	1,51
171	16,66	0,000	5 207	9477	315765	1,47
172	16,69	0,000	5 145	9365	306288	1,42
173	16,71	0,000	5 082	9149	296922	1,38
174	16,74	0,000	5 022	8694	287773	1,34
175	16,76	0,000	4 962	8314	279079	1,30
176	16,79	0,000	4 903	8113	270765	1,26
177	16,81	0,000	4 844	7988	262651	1,22
178	16,84	0,000	4 787	7649	254663	1,18
179	16,86	0,000	4 729	7423	247014	1,15
180	16,89	0,000	4 674	7297	239591	1,11
181	16,91	0,000	4 618	6993	232294	1,08
182	16,94	0,000	4 564	6861	225302	1,04
183	16,96	0,000	4 509	6623	218440	1,01
184	16,99	0,000	4 456	6365	211817	0,98
185	17,01	0,000	4 403	6412	205452	0,95
186	17,04	0,000	4 352	6174	199040	0,92
187	17,06	0,000	4 300	6027	192866	0,89
188	17,09	0,000	4 250	5627	186839	0,87
189	17,11	0,000	4 199	5374	181212	0,84
190	17,14	0,000	4 151	5262	175837	0,81
191	17,16	0,000	4 101	5291	170575	0,79
192	17,19	0,000	4 054	5052	165285	0,77
193	17,21	0,000	4 006	4963	160233	0,74
194	17,24	0,000	3 960	4858	155270	0,72
195	17,26	0,000	3 913	4565	150412	0,70
196	17,29	0,000	3 868	4453	145847	0,67
197	17,31	0,000	3 822	4387	141393	0,65
198	17,34	0,000	3 778	4493	137007	0,63
199	17,36	0,000	3 733	4268	132514	0,61
200	17,39	0,000	3 690	4038	128246	0,59
201	17,41	0,000	3 647	4038	124208	0,57
202	17,44	0,000	3 605	4037	120170	0,56
203	17,46	0,000	3 562	3888	116133	0,54
204	17,49	0,000	3 522	3764	112245	0,52
205	17,51	0,000	3 480	3639	108481	0,50
206	17,54	0,000	3 440	3521	104842	0,48
207	17,56	0,000	3 400	3388	101321	0,47
208	17,59	0,000	3 361	3399	97933	0,45
209	17,61	0,000	3 322	3170	94534	0,44
210	17,64	0,000	3 284	3113	91364	0,42
211	17,66	0,000	3 245	3066	88251	0,41
212	17,69	0,000	3 208	2978	85185	0,39
213	17,71	0,000	3 171	2985	82207	0,38
214	17,74	0,000	3 134	2889	79222	0,36
215	17,76	0,000	3 098	2859	76333	0,35
216	17,79	0,000	3 063	2809	73474	0,34
217	17,81	0,000	3 027	2800	70665	0,32
218	17,84	0,000	2 992	2731	67865	0,31
219	17,86	0,000	2 957	2729	65135	0,30

APPENDIX E. GPC Report

220	17,89	0,000	2 924	2717	62406	0,29
221	17,91	0,000	2 890	2590	59690	0,27
222	17,94	0,000	2 857	2543	57100	0,26
223	17,96	0,000	2 823	2351	54557	0,25
224	17,99	0,000	2 791	2269	52206	0,24
225	18,01	0,000	2 759	2214	49938	0,23
226	18,04	0,000	2 727	2170	47724	0,22
227	18,06	0,000	2 696	2179	45554	0,21
228	18,09	0,000	2 665	2135	43375	0,20
229	18,11	0,000	2 634	1999	41239	0,19
230	18,14	0,000	2 604	1915	39241	0,18
231	18,16	0,000	2 574	1883	37326	0,17
232	18,19	0,000	2 545	1861	35443	0,16
233	18,21	0,000	2 515	1787	33582	0,15
234	18,24	0,000	2 487	1693	31795	0,14
235	18,26	0,000	2 458	1680	30101	0,14
236	18,29	0,000	2 430	1589	28421	0,13
237	18,31	0,000	2 402	1591	26832	0,12
238	18,34	0,000	2 374	1543	25241	0,11
239	18,36	0,000	2 347	1486	23698	0,11
240	18,39	0,000	2 320	1402	22213	0,10
241	18,41	0,000	2 293	1364	20811	0,09
242	18,44	0,000	2 267	1344	19447	0,09
243	18,46	0,000	2 241	1252	18103	0,08
244	18,49	0,000	2 216	1178	16851	0,07
245	18,51	0,000	2 190	1114	15673	0,07
246	18,54	0,000	2 165	1070	14559	0,06
247	18,56	0,000	2 140	1050	13489	0,06
248	18,59	0,000	2 116	985	12439	0,05
249	18,61	0,000	2 091	880	11454	0,05
250	18,64	0,000	2 067	900	10574	0,04
251	18,66	0,000	2 043	872	9675	0,04
252	18,69	0,000	2 020	803	8803	0,04
253	18,71	0,000	1 997	782	8000	0,03
254	18,74	0,000	1 974	751	7218	0,03
255	18,76	0,000	1 951	645	6467	0,03
256	18,79	0,000	1 929	598	5822	0,02
257	18,81	0,000	1 907	547	5224	0,02
258	18,84	0,000	1 885	538	4677	0,02
259	18,86	0,000	1 863	502	4139	0,01
260	18,89	0,000	1 842	502	3637	0,01
261	18,91	0,000	1 821	496	3135	0,01
262	18,94	0,000	1 800	386	2639	0,01
263	18,96	0,000	1 779	321	2253	0,01
264	18,99	0,000	1 759	305	1932	0,00
265	19,01	0,000	1 739	256	1627	0,00
266	19,04	0,000	1 719	256	1371	0,00
267	19,06	0,000	1 699	238	1115	0,00
268	19,09	0,000	1 680	190	877	0,00
269	19,11	0,000	1 660	207	687	0,00
270	19,14	0,000	1 641	142	480	0,00
271	19,16	0,000	1 622	128	339	0,00
272	19,19	0,000	1 604	75	210	0,00
273	19,21	0,000	1 585	66	136	0,00
274	19,24	0,000	1 567	69	69	0,00
275	19,26	0,000	1 549	0	0	0,00

*** Ave. Molecular(RT/MW range) ***

APPENDIX E. GPC Report

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[ No.1 ]
     Time(min) : 12,000 - 26,000
     Molecular : * - 58
     Area      :    32188553,0 (100,00%)
     Number-A.M.W.(Mn)  :      22 395
     Weight-A.M.W.(Mw)  :      39 106
     Z-A.M.W.(Mz)       :      68 141
     (Z+1)-A.M.W.(Mz1)  :     630 524
     Mw/Mn              :           1,74616
     Mv/Mn              :           0,00000
     Mz/Mw              :           1,74248

*** Comment ***
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