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Characterisation of Polydimethyl Siloxane (PDMS)
by liquid-state NMR spectroscopy

Bachelor Thesis

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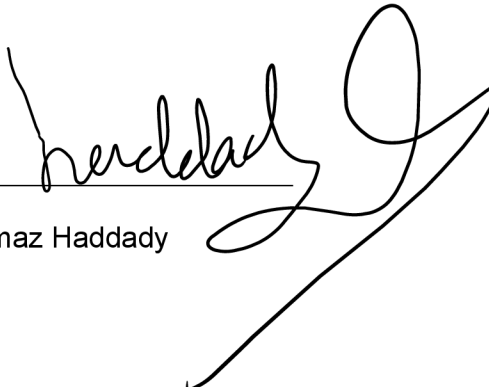
Annotation

This work analyzes how two liquid /viscose base materials (Base and Curing Agent by Ecoflex ®) [1], after putting together and polymerization, will produce silicones. We want to show how vinyl groups are consumed and how methyl attached groups increase during this process. And how Base and Curing Agent are different.

DECLARATION

I declare that I am the author of this qualification thesis and that in writing it I have used the sources and literature displayed in the list of used sources only.

Place, date
Linz, 2.10.2021



Solmaz Haddady

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Abstract

Silicone rubbers are promising materials that have extensively been used in many areas, including wearable electronic devices, actuator materials in soft robotics, and energy harvesters. Ecoflex, a commercially available polymer, is a group of silicone rubbers appearing with various Shore hardnesses that has become popular in recent years. High resolution NMR can be used for polymer characterization both in solution and in the solid state. The power of NMR as a method arises from the observation of individual carbon and proton atoms along the main chain and side chains of polymers. This makes it possible to characterize in detail the microstructure, the conformation, and the molecular organization in the solid and liquid. NMR experiments with more than one frequency dimension (2D and 3D NMR) have revolutionized materials characterization, mainly owing to the increase in resolution and the ability to visualize interactions that were previously obscured by peak overlap. It is possible not only to assign many peaks in the spectra, but also to explore interactions between polymer chains to understand at a molecular level the formation of compatible blends. NMR experiments in two and three dimensions can be combined to determine polymer chain conformation and chain packing. The goal of these studies is to understand the relationship between the polymer properties on a molecular level and the behavior of materials. And to show how base material changed during polymerization.

Aim of the thesis

This work analyzes how two liquid /viscose base materials (Base and Curing Agent by Ecoflex ®) [1], after putting together and polymerization, will produce silicones. We want to show how vinyl groups are consumed and how methyl attached groups increase during this process. And how Base and Curing Agent are different.

Structure of thesis

This thesis is dedicated to the subject of characterization of Polydimethylsiloxane (PDMS) by liquid-state NMR spectroscopy. After short introduction in chapter 1, the second chapter provides some basic information about polydimethylsiloxane (PDMS), their structure, general properties and their medical application. Chapter 3 provides short introduction about Nuclear Magnetic Resonance (NMR) and details in proton NMR (chapter 3.1), carbon NMR (chapter 3.2), silicone NMR (chapter 3.3) and (chapter 3.4) explain about diffusion ordered spectroscopy (DOSY NMR).

Chapter 4 provides some basic information in machine learning method. Chapter 5 provides experimental data, introduce experimental sources (chapter 5.1), experimental method (chapter 5.2). While experimental results are shown in chapter 6 and 7. Conclusion and discussion is provided in chapter 8.

1. Introduction

Currently, elastomers (rubbers) have been the object of study of many researchers due to some of their interesting biomechanical characteristics, such as: flexibility, chemical stability, and resistance to corrosion. Among the various elastomers in the market, there is one that has come to stand out in recent years, which is the polydimethylsiloxane, also known as PDMS. This material has been applied in several industrial areas ranging from mechanics to electronics and including biomedicine. Some of the reasons for its extensive use relate to its ease in the manufacturing process, its optical transparency, biocompatibility, and its low cost. Thus, some of the most relevant PDMS applications are mechanical sensors, electronic components, electrochemical sensors, medical equipment, and biomedical research among others.

PDMS belongs to the group of siloxanes, however, in its advent, it was called silicoketones or silicones, but since there was no double bond of $\text{Si} = \text{O}$, its name was later replaced by a specific nomenclature and its basic unit has become known as siloxanes. The most known material of this group is PDMS, a synthetic polymer whose main axis is made from the repetition of silicon and oxygen bonds and methyl groups. Once the methyl groups may be substituted by other groups, for example, phenyl or vinyl, allowing the attachment of organic to inorganic groups, PDMS has a unique property and can be altered for different applications [2].

Here in this study, we focused on NMR studies of Ecoflex silicone [1], Because of its polymer structures, conventional chromatographic methods often fail for different reasons and the lack of suitable standards. Nuclear magnetic resonance (NMR) spectroscopy provides an alternative for qualitative and quantitative characterization, as these analytical drawbacks do not exist. Although NMR spectroscopy is often regarded to be an expensive technique, it must be noted that the high investment costs for NMR spectrometers are compensated by the possibility of fast and powerful analysis.

Polymer characterization by NMR provides detailed structural information for product development and quality control (QC) considerations [3]. The goal of these studies is to understand the relationship between the polymer properties on a molecular level and the behavior of bulk materials.

2. Polydimethylsiloxane (PDMS)

Polydimethylsiloxane (PDMS) is a polymer belonging to the group of silicone elastomers. It is a hyperplastic material that has a wide application in the biomedical industry, from contact lenses to medical devices, and in the area of research and behaviors of diseases [4], because of its biocompatible material and its biomechanical behavior is similar to biological tissues, with applications in the study of aneurysmal behavior and devices such as: Micro pumps, optical systems, microfluidic circuits. Thus, attracting the attention of many researchers who see PDMS as a more sophisticated material which can replace previous methods and obtain more accurate data. The synthesis of silicone was first obtained in 1950 by the Wacker Chemie company. One of the first uses of PDMS occurred in the encapsulation of electronic components in order to extend the lifespan of the chips. With the development of technology and of behavioral studies and their characteristics, PDMS has been gaining new applications in micro and nanotechnology, and in the study of the biophysical behavior of blood flow in micro vessels [5].

2-1 Structure of PDMS

Siloxane is a kind of organosilicon compounds which is composed of $-\text{Si}-\text{O}-\text{Si}-\text{O}-$ backbones with side chains R attached to the silicon atoms (R_2SiO), where R is a hydrogen atom or an organic radical possibly bearing functional groups. Polymers of siloxanes are referred as silicones, such as polydimethylsiloxane (PDMS), which is the dominant polymer in the silicone industry [6].

The PDMS empirical formula is $(\text{C}_2\text{H}_6\text{OSi})_n$ and its fragmented formula is $\text{CH}_3[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{Si}(\text{CH}_3)_3$, n being the number of monomers repetitions. (Figure 1).

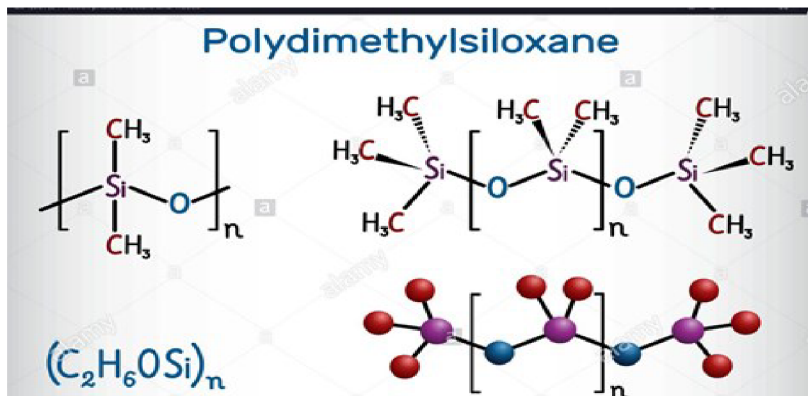


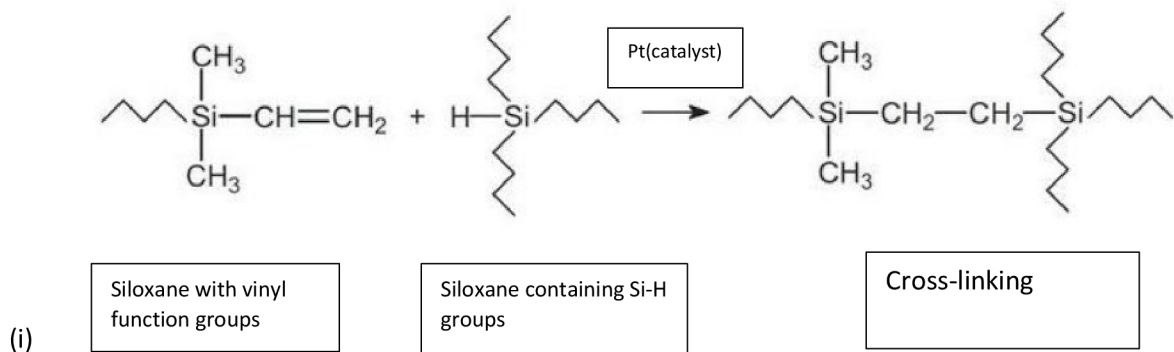
Figure 1. PDMS (polydimethylsiloxane) is the simplest member of the silicone polymer family.¹

Depending on the size of monomers chain, the non-cross-linked PDMS may be almost liquid (low n) or semi-solid (high n). The siloxane bonds result in a flexible polymer chain with a high level of viscoelasticity [7].

Siloxane polymers exist in forms of fluid, gel, elastomer, and resin. The polymerization of linear PDMS polymers into a cross-linked elastomer is done through an organo-metallic cross-linking reaction. (see scheme 1)

PDMS elastomer is formed through a cross-linking reaction of a two-part mixture consisting of long-chain PDMS polymer (base) with short-chain cross-linkers. The siloxane base oligomers (prepolymer) contain vinyl-terminated end groups ($CH_2=CH-$). The base solution also contains platinum-based catalyst and silica filler. The cross-linker typically contains oligomers such as dimethyl methyl hydrogen siloxane, tetrakis(dimethylsiloxy) silane (TDS) ($HSi(CH_3)_2O)_4Si$), and an inhibitor (tetramethyl tetra vinyl cyclotetrasiloxane). The platinum-based catalyst catalyzes the addition of the Si-H bond across the vinyl groups, forming Si- CH_2-CH_2 -Si linkages (i). Multiple reaction sites on both the monomer and cross-linking chain enhance 3D cross-linking that can also be accelerated through heat application. No waste product such as water is generated during such reactions. Increasing the ratio of the curing agent to the base will result in a higher rate of cross-linking and hence a harder elastomer [8].

¹ Adapted from [9]



Scheme1. Cross-Linking reaction of PDMS

2-2 General properties of PDMS

PDMS is a material that has good microstructural characteristics, good manufacturing ability and a low cost. In the study of the microfluidics, it has been verified that PDMS presents higher properties than the old techniques that used materials such as glass and silicon, once the use of PDMS makes the work simpler and cheaper. In addition, PDMS is thermally stable, optically transparent, works as a thermal and electrical insulation, has good chemical stability, and degrades quickly in the natural environment when compared to other polymers, and it presents no environmental problem [2].

Other important properties of PDMS are the permeability and elasticity. Permeability is the product of the solubility of a gas in a polymer and its diffusion. Siloxanes have greater permeability than most elastomers. The permeability of PDMS makes it advantageous for industrial applications in which it is necessary the separation of gases from the material, for example, in the development of artificial skins for burns [10].

The good elastic capacity of silicones comes from the Si-O structure being more flexible than other conventional polymers that have C-C carbon structures. However, the flexibility of the siloxanes should not be defined solely by their ease of twisting, but also by their possibility of folding so large that it can be reversed. The PDMS offers a good elasticity, due to the fact that it exists in a very compact shape. Thus, when subjected to a tensile force, the polymer is stretched releasing its tension and then returns to its initial state when the load is removed. The polymer has its elasticity determined by the ability of its regions, which are close, to slide on each other. This property is

influenced by the number of existing cross links, the more cross-linked the PDMS is, the less it will be elastic. As the PDMS is a soft material it is very sensitive to low loads. Furthermore, the PDMS is a visco-hyperelastic material, and the strain-rate effects are commonly observed [11].

2-3 Medical Application of PDMS

An important feature of PDMS is the biocompatibility, which is the ability of a material to be compatible with biological tissue. Any material, when implanted in the human body causes an inflammatory response due to the reaction of the immune system that begins to act, with the aim of removing the strange body [12], [13] which can lead to its encapsulation and, thus, damage the functioning of the implanted device [14]-[16]. Due to this effect, there was a need to look for materials that provide the least impact on the tissue [17], which is an aspect of PDMS because it reduces the impact and interferences of the tissue response.

The fact that PDMS is biocompatible and bio-stable makes it the most studied implantable polymer. The PDMS is one of the most successful polymers, because when implanted it only causes a brief inflammatory reaction in the organism, which explains its wide use in personal care and topical skin applications. A long history of its use in medical devices, including long-term implants, has made silicones widely recognized as biocompatible. Currently, PDMS has been used as a coating on devices to be implanted in both humans and animals [18], [19].

Due to its characteristics of biocompatibility, chemical stability, transparency, and mechanical elasticity, PDMS has been widely used in biomedical devices such as catheter and drainage tubing, dialysis membrane [20], micro pumps [21], micro valves [22], and are often found in fluidic circuits [23]-[25], and optical systems (adaptive lenses) [26]-[28]. It has also been used as research material, helping to understand the behavior of diseases, for instance, aneurysm and their respective treatments, [29] and in implants [30], [31].

3. Nuclear magnetic resonance (NMR)

High resolution NMR can be used for polymer characterization both in solution and in the solid state. The power of NMR as a method arises from the observation of individual carbon and proton atoms along the main chain and side chains of polymers. This makes it possible to characterize in detail the microstructure, the conformation, and the molecular organization in the solid. NMR experiments with more than one frequency dimension (2D and 3D NMR) have revolutionized materials characterization, mainly owing to the increase in resolution and the ability to visualize interactions that were previously obscured by peak overlap. It is possible not only to assign many peaks in the spectra, but also to explore interactions between polymer chains to understand at a molecular level the formation of compatible blends. NMR experiments in two and three dimensions can be combined to determine polymer chain conformation and chain packing. [32].

3-1 Proton NMR (^1H NMR)

All the protons of an organic compound can be identified by NMR because the natural abundance of ^1H is almost 100%.

In the ^1H NMR spectrum of a polymer, various features can be observed. When the molecular weight is large and the chain mobility is low, broadening of the ^1H NMR signals can be observed because of their short relaxation time. Particularly in the case of high molecular weight polymers, the protons attached to the main chain cannot be easily identified because of the broadening. Generally, ^1H NMR chemical shifts can be found in the 0–12 ppm range [32].

3-2 Carbon NMR: Carbon (^{13}C) NMR

Carbon has two stable isotopes: ^{12}C with a natural abundance of 99% and ^{13}C . ^{12}C cannot be detected by NMR ($I = 0$), whereas the natural abundance of ^{13}C that can be detected by NMR is about 1%, which is almost 1/100 of that of ^1H .

Generally, ^{13}C NMR signals are observed in the range of 0–200 ppm.

which is wider than those of ^1H NMR. Therefore, the ^{13}C NMR peak separation is better than the ^1H NMR, and the number of carbons can be predicted based on the ^{13}C NMR peak number. Besides, the interpretation of the ^1H NMR spectra is difficult because of the overlap of the signals in the narrow chemical shift range, which is not usually observed in ^{13}C NMR spectra because of the wider chemical shift range.

The integral intensity ratio of a conventional ^{13}C NMR spectrum is not quantitative, because of the different nuclear Over Hauser effect (NOE) that depends on the number of protons attached to the ^{13}C nuclei. Besides, the signal intensity of ^{13}C atoms bonded with more protons tends to be stronger. To obtain a quantitative integral intensity ratio of a ^{13}C NMR spectrum, it should be recorded in an inverse gated decoupling mode [32].

3-3 Siloxane NMR

Silicon is one of the most widespread elements in the natural world and, as such, this makes it a very interesting and useful element to study using NMR. Over the past few decades, a wide range of silicon-containing compounds have been investigated using both solid- and liquid-state NMR techniques. For example, siloxane polymers, which are extensively used in biomedical and cosmetic applications, have been extensively studied by NMR to understand their structure and individual building blocks. Similarly, the structure of silicates, zeolites and other materials have been studied by silicon NMR. Silicon NMR has been shown to be a powerful tool for the determination of active end groups, cross-linking moieties, and polymer sequencing of the isotopes of silicon, only ^{29}Si is NMR active. It has a natural abundance is 4.7% and the gyromagnetic ratio is 8.465 MHz/T, giving ^{29}Si an Larmor frequency of around 12.3 MHz.

Compounds containing the Si—O—Si linkage are important both in geochemistry and for commercially produced materials. They occur in a wide range of physical states; it is particularly common to find them as “pseudo-solids,” i.e., as glasses, gels, rubbers, and resins.

Unfortunately, it has not been easy to obtain detailed information about molecular structure and motion for silicones. This is partly due to the complexity of many of the systems [33].

3-4 DOSY NMR (Diffusion ordered spectroscopy)

Diffusion ordered spectroscopy (DOSY) can be used to observe the diffusion phenomena of molecules using pulsed field gradients (PFG) NMR measurement method. When the peak intensity of each NMR is plotted against the magnetic field gradient, the intensity decreases with increasing magnetic field gradient. A self-diffusion coefficient (D) corresponding to each NMR peak can be obtained by analyzing the decay profile. DOSY measurements can be performed using a special probe with a large magnetic field gradient.

In the case of 2D DOSY spectra, the X-axis represents the ^1H NMR chemical shifts, whereas the Y-axis represents the diffusion coefficient. Since the 2D DOSY signals in the same molecule have the same D value, they form a horizontal line. However, the signals with different D values are observed separately in the Y-axis direction. Namely, a mixture of various molecular species can be separated by using the difference in D of each molecular species.

Diffusion ordered spectroscopy (DOSY) is a well-established NMR method that reports diffusion coefficients for individual resonances in NMR spectra. DOSY is primarily used to analyse mixtures of small molecules and the oligomeric state of biomolecules. DOSY has also been used to analyse polymers and investigate micellization properties [34].

4. Data fitting by AI methods

Model fitting is a measure of how well a machine learning model generalizes to similar data to that on which it was trained. A model that is well-fitted produces more accurate outcomes.

A model that is overfitted matches the data too closely. A model that is underfitted doesn't match closely enough. Each machine learning algorithm has a basic set of parameters that can be changed to improve its accuracy. Model fitting is the essence of machine learning. If your model doesn't fit your data correctly, the outcomes it produces will not be accurate enough to be useful for practical decision-making. A properly fitted model has hyperparameters that capture the complex relationships between known variables and the target variable, allowing it to find relevant insights or make accurate predictions.

Fitting is an iterative process that makes sure your machine learning models have the individual parameters best suited to solve your specific real-world problem with a high level of accuracy [35].

This experiment used Biexponential fit to predict and generate data.

Bi-exponential decay function: $F(x) = A_1 \exp(-B_1 * t) + A_2 \exp(-B_2 * t)$

$A_1, B_1, A_2, B_2 =$ parameters

5. Experiment

5-1 Introduce experiment sources

5-1-1 Base

In terms of chemical structure, the base prepolymer is composed of repeating units of $-\text{OSi}(\text{CH}_3)_2$ terminating with a vinyl- $\text{CH}=\text{CH}_2$ group (Figure 2).

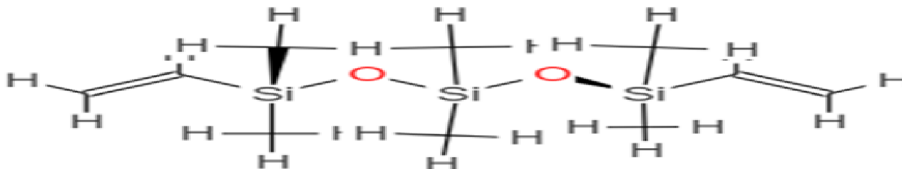


Figure 2. Chemical structure of minimal model for Base with vinyl groups (with H explodes)²

² Adapted from [36]

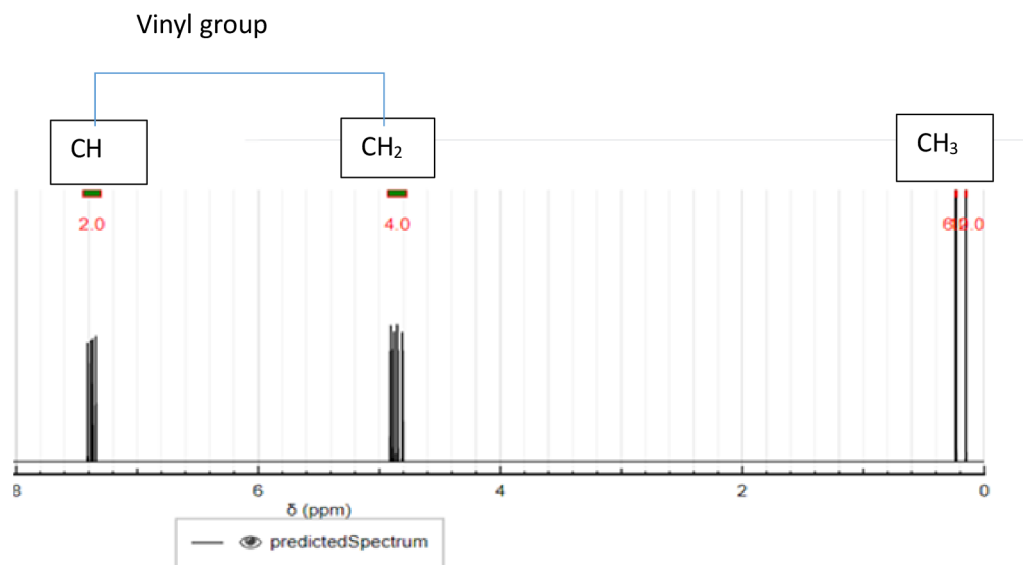


Figure 3. ¹H NMR spectra for minimal model of Base which is predicted in online software <https://www.nmrdb.org/> (Tools for NMR spectroscopists)

5-1-2 Curing Agent

The Curing Agent is similar but is much smaller and repeating units of $-\text{OSiHCH}_3-$ (Figure 4)

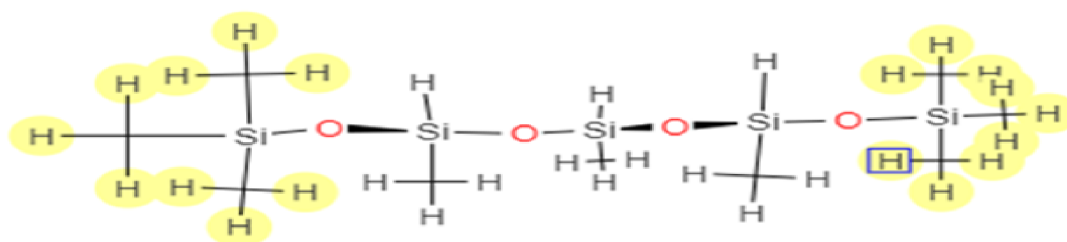


Figure 4. Chemical structure of minimal model for Curing Agent with Si-H groups (with H explodes)³

³ Adapted from [36]

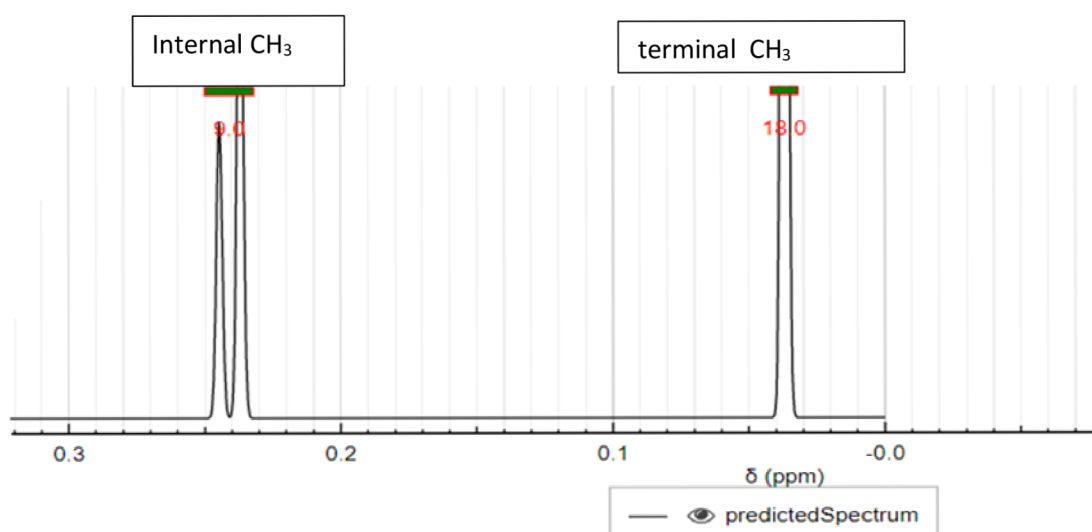
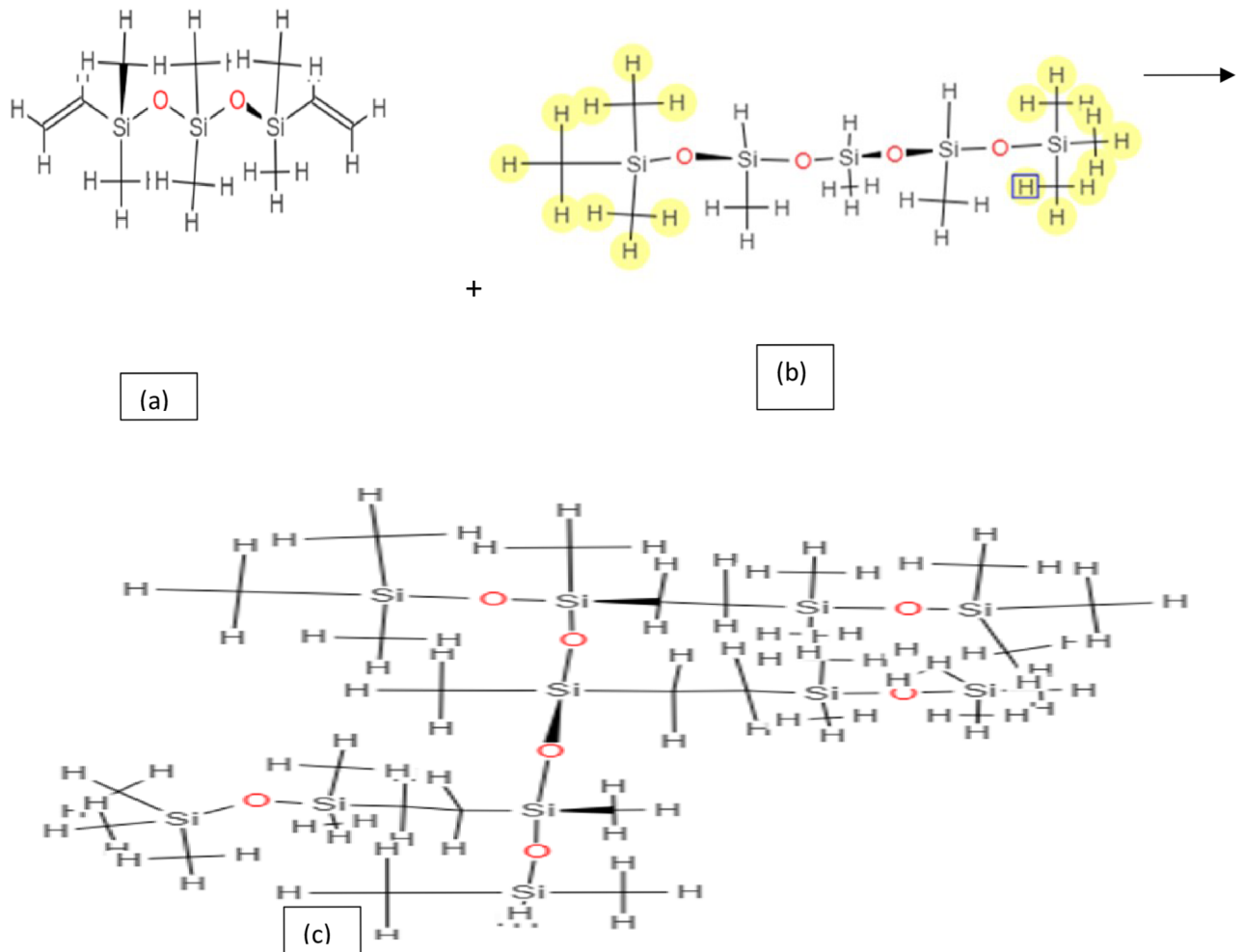


Figure 5. ¹H NMR spectra for minimal model of Curing Agent which is predicted in online software <https://www.nmrdb.org/> (Tools for NMR spectroscopists)

The Base and the Curing Agent crosslink by forming -Si-CH₂-CH₂-Si-.

This is illustrated in Scheme 2.



Scheme 2. Illustration of crosslink forming of (a) Base, (b) Curing Agent into (c) Cross-Linked PDMS⁴

The chemical structure of PDMS is shown in Scheme 2, the Si-O backbone is thermodynamically stronger than the C-C backbone, giving PDMS better thermal stability than hydrocarbon polymers.[36]

⁴ Adapted from [36]

5-1-3 Chloroform as solvent

Chloroform is an organic solvent very used in chemical and pharmaceutical industries. Chloroform is a colorless liquid with an ethereal odor. Its density is 1.489 g mL^{-1} and its melting point is $-63.5 \text{ }^\circ\text{C}$ and its boiling point is $61.15 \text{ }^\circ\text{C}$. It is slightly soluble in water and it is soluble in benzene, diethylether and carbon tetrachloride. Chloroform is today largely used as solvent in chemical processes [37].

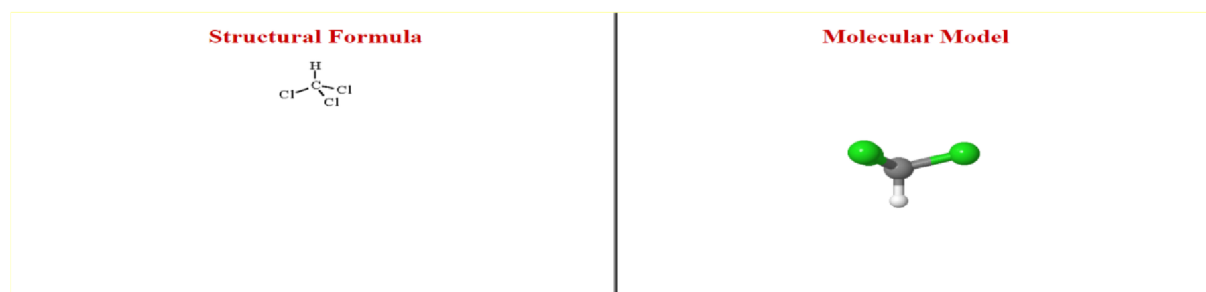


Figure 6. Chloroform is used for dissolving samples to do liquid NMR.⁵

5-2 Experimental method

Conventional PDMS was mixed in a 1:1 ratio (mixing ratio by weight) of base to curing agent from commercial Ecoflex, and stirred them for 5 min. For do liquid NMR we needed to add some solvent to dissolve the polymerized samples (to prepare the PDMS). Here used chloroform, then rested for 24 hours for polymerize. After setting parameters, initialization, amplitude, run proton spectra (^1H) and carbon spectra (^{13}C). Then data recorded [table 1].

Meanwhile all samples are predicted in software. (online software- <https://www.nmrdb.org/> (Tools for NMR spectroscopist) (Figures 2,3,4,5,7,8) to compare with real experiment (Figures 9 and 10).

⁵ Adapted from [37]


After polymerization happened, by looking at spectra, all signals are recorded and integrated for each signal. Measurements of each mixture were performed in the liquid phase.

A summary of the experimentally determined data is given in supplemental figures (see indexes-part D-figures: 19-25).

The measurement was recorded in ^1H NMR on Bruker AVANCE III, with frequency of 500.13 MHz.

Date, time	CHCl_3 [int]	Vinyl [int]	Si-H [int]	$(\text{CH}_2+\text{CH}_3)$ [int]
06-09-2019(12:35),	1	0.637	0.560	1000.25
06-09-2019(13:05),	1	0.673	0.555	1094.31
06-09-2019(13:35),	1	0.621	0.521	1081.20
07-09-2019(07:05),	1	0.333	0.501	1090.99
08-09-2019(00:05),	1	0.271	0.452	1177.56
08-09-2019(00:42),	1	0.252	0.449	1023.76
09-09-2019(8:54),	1	0.171	0.381	1017.57

Table 1. Shows recorded data for different experiment in several time from ^1H spectra for mixture of two samples: Base +Curing Agent (Ecoflex)

 CH_2 and CH_3 overlapped, therefore, it was not possible to separated signals, so calculated whole signal and assigned as sum of two groups (CH_2+CH_3).

- Formatting illustrated in figures below:

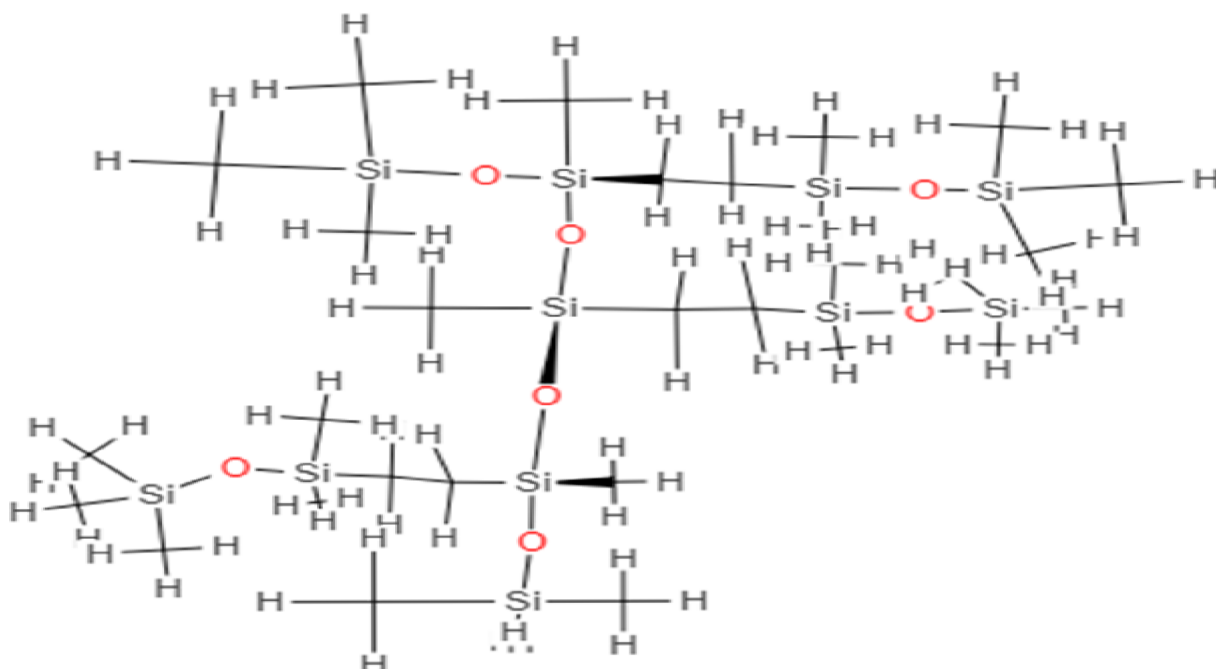


Figure 7. Chemical structure for minimal model of Base+Curing agent (Ecoflex). with H exploded⁶

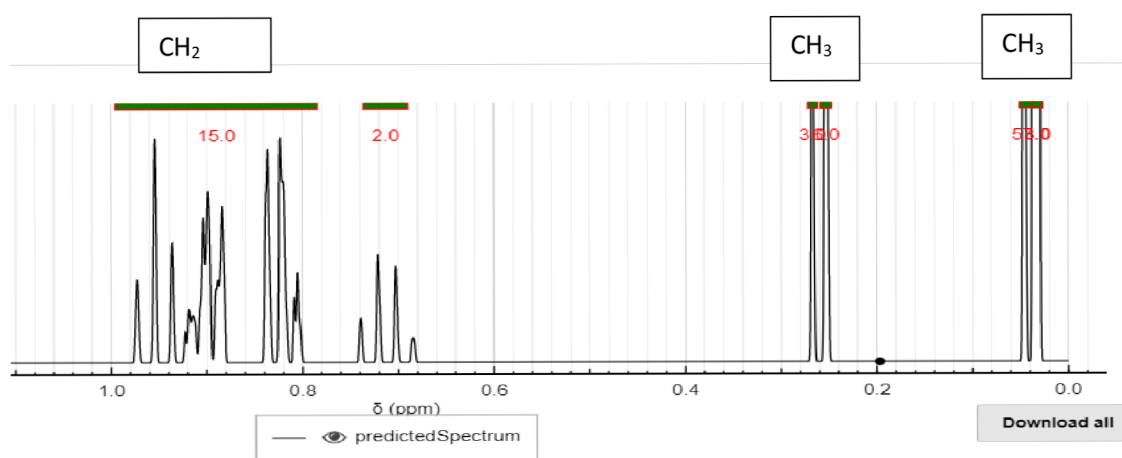


Figure 8. ¹H NMR spectra for minimal model of Ecoflex which is predicted in online software <https://www.nmrdb.org/> (Tools for NMR spectroscopist)

Figure 9 and 10 compares the spectra for the sample containing Base and Curing Agent.

⁶ Adapted from [36]

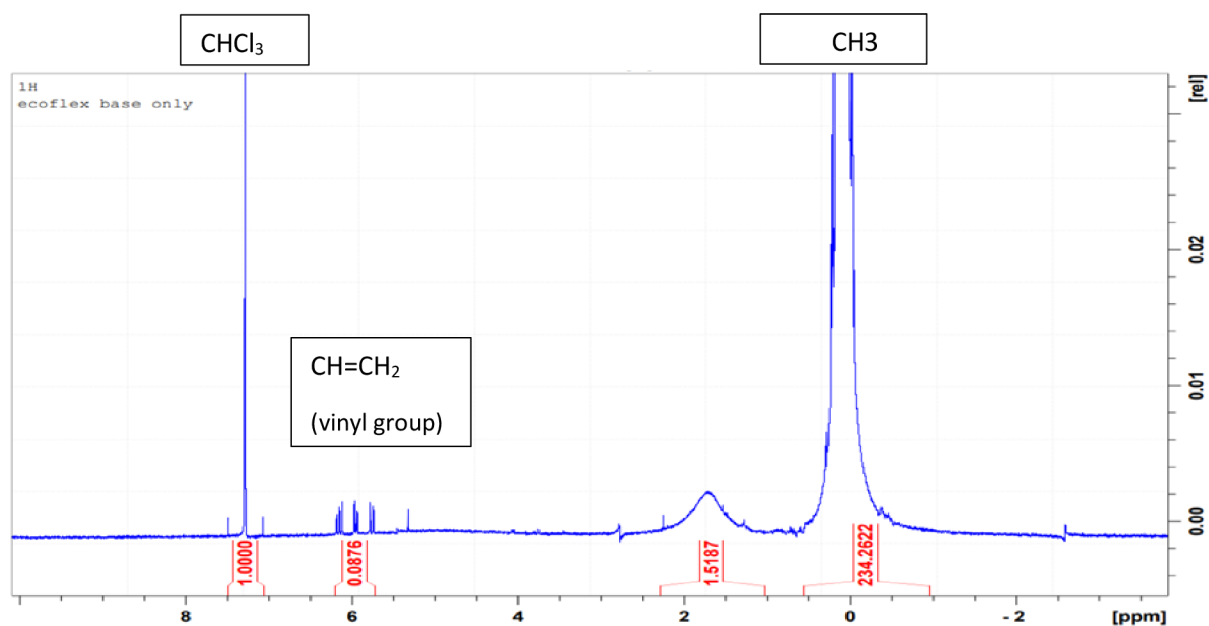


Figure 9. Experimental spectrum for Base done in ¹H NMR on Bruker Avance spectrometer with 500.13MHz

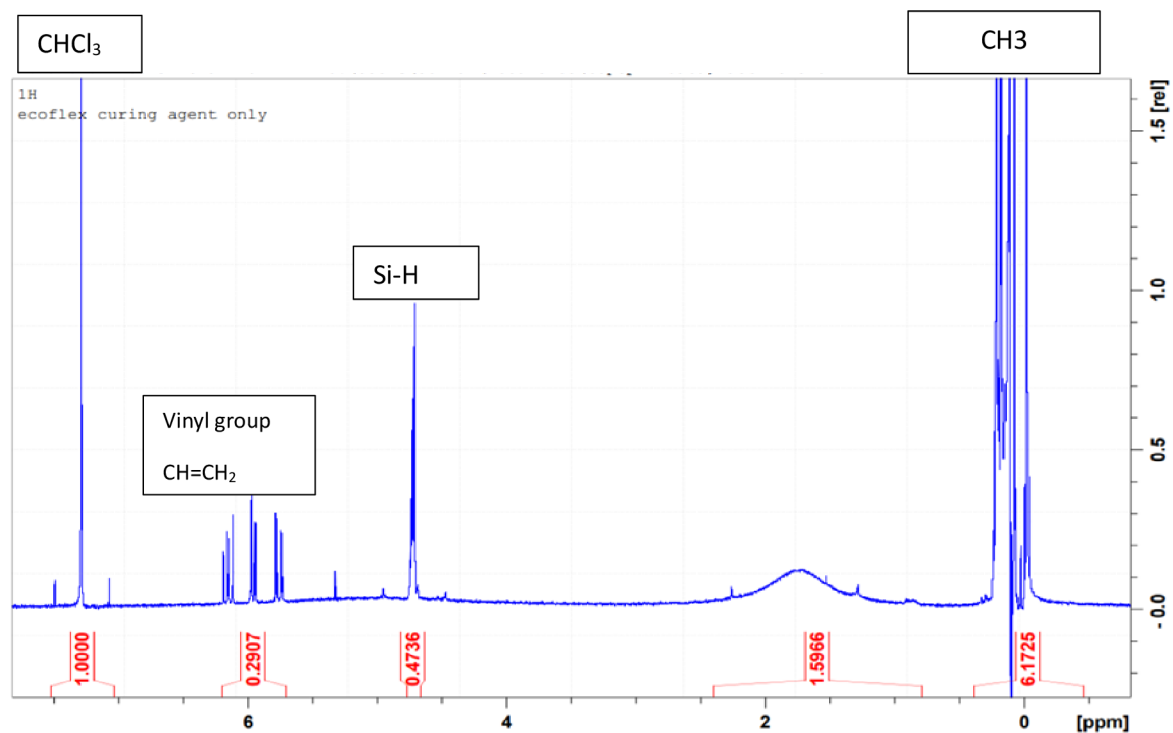


Figure 10. Experimental spectrum for Curing Agent done in ¹H NMR on Bruker Avance spectrometer with 500.13 MHz

6. Experimental result from Ecoflex (mixture of Base + Curing Agent)

After inserting the sample and a standard setup of the NMR spectrometer and the selection solvent, ^1H NMR is measured. This process is repeated several times. Integration of selected signals shows how the resonance changed during polymerization. [see supplemental figures (Appendices-part D)]. Then made graphs (Figures 11,12,13,14) to see behavior of experimental sources.

All graphs are done in notebook Jupyter [see appendices- E for more details].

```
A1 = 162.8821576095291
B1 = 0.025358322396272316
A2 = -162.24065844303107
B2 = 0.02535832204619816
```

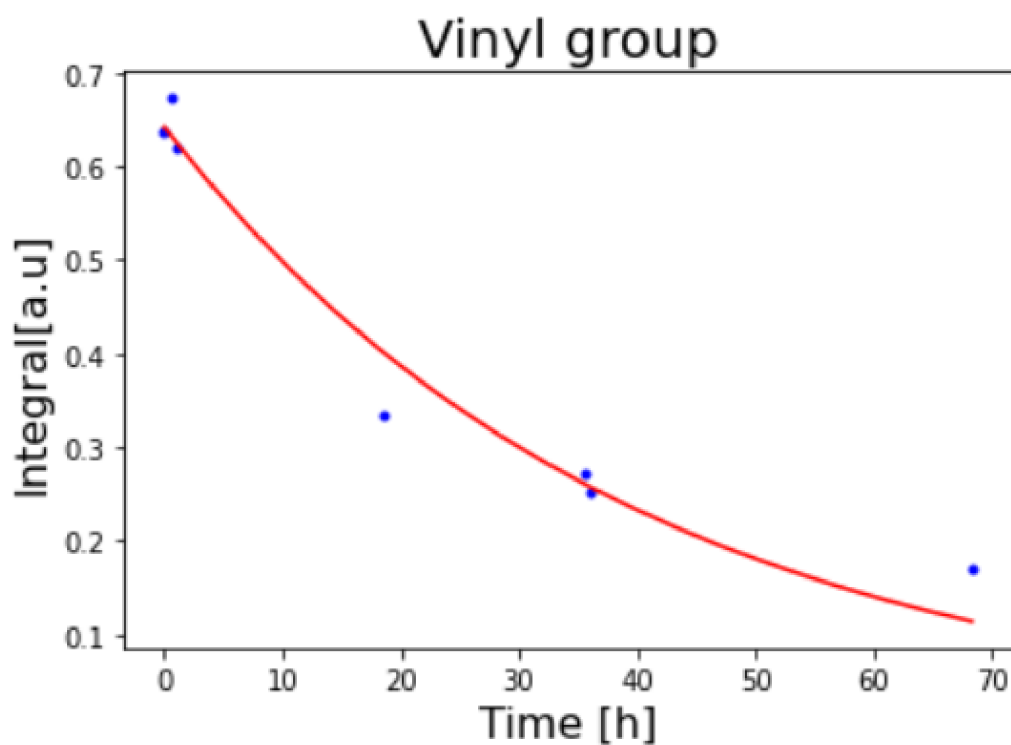


Figure 11. Behavior of vinyl groups in Ecoflex from start to end of experiment.

A1 = 64.45280318352573
B1 = 0.0053170898661265755
A2 = -63.905247535683614
B2 = 0.005316888105025254

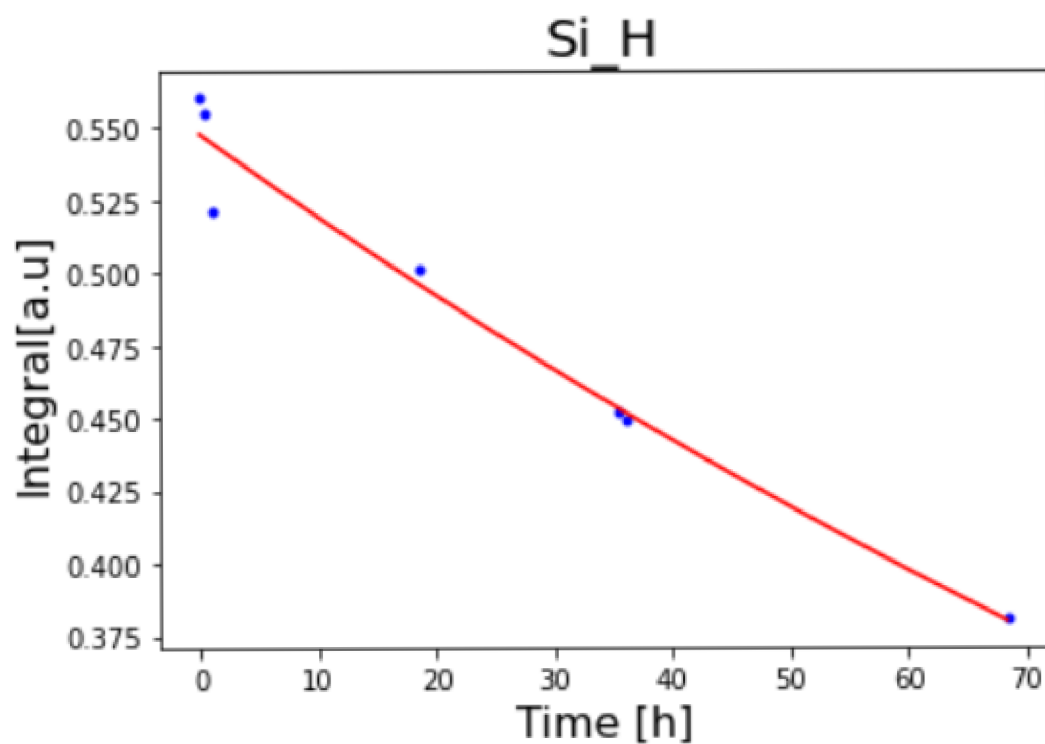


Figure 12. Behavior of Si-H groups in Ecoflex from start to end of experiment.

A1 = 26.693474377940344
B1 = 0.013567998228729297
A2 = -26.69236764932664
B2 = 0.01356799811006008

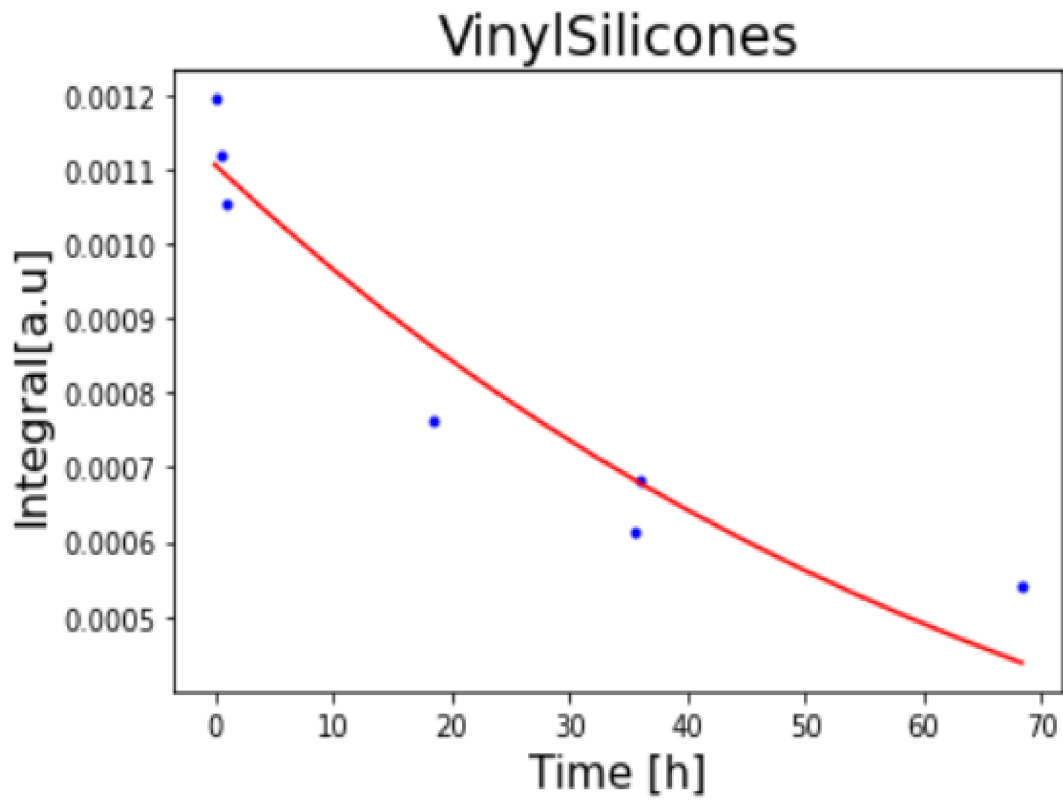


Figure 13. Behavior of combination of two resonance for (Vinyl + SiH) during experiment for Ecoflex.

A1 = -25.783698612395426
B1 = -0.0006029064889398439
A2 = 26.782570602567283
B2 = -0.0005811643240778852

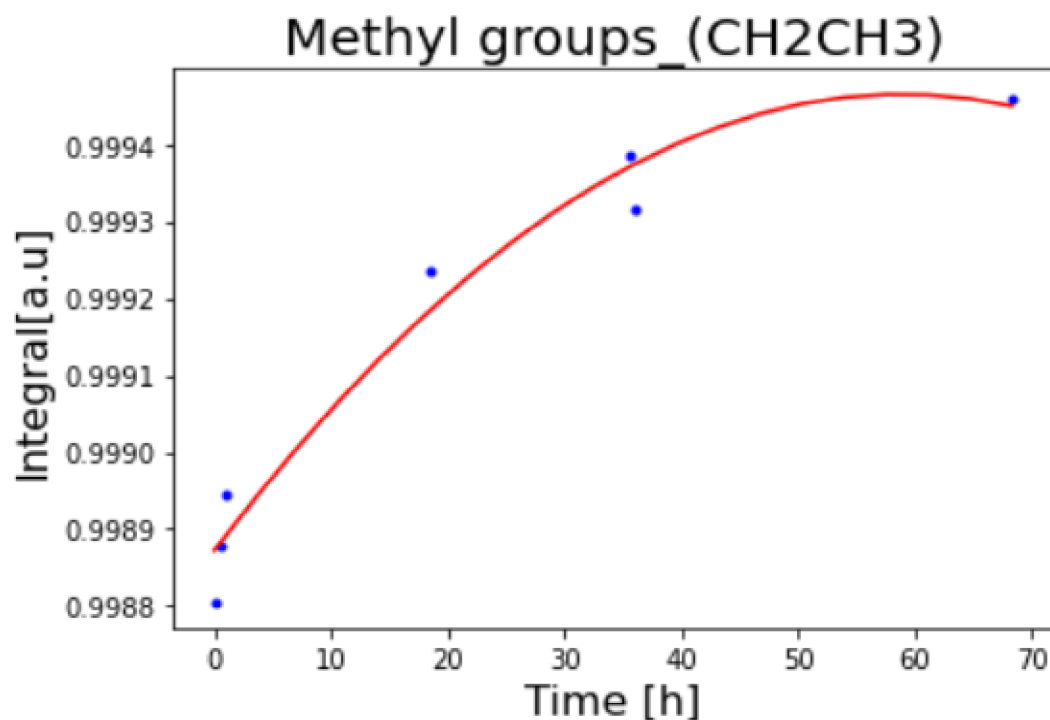


Figure 14. Behavior of (CH_2+CH_3) during experiment in time interval in Ecoflex.

7. Experimental result from DOSY NMR

Additional conclusions can be achieved by DOSY NMR. With this one can find out how many additional molecules are in the samples and how different these molecules are in size.

Since the 2D DOSY signals in the same molecule have the same D value, they form a horizontal line. However, the signals with different D values are observed separately in the Y-axis direction.

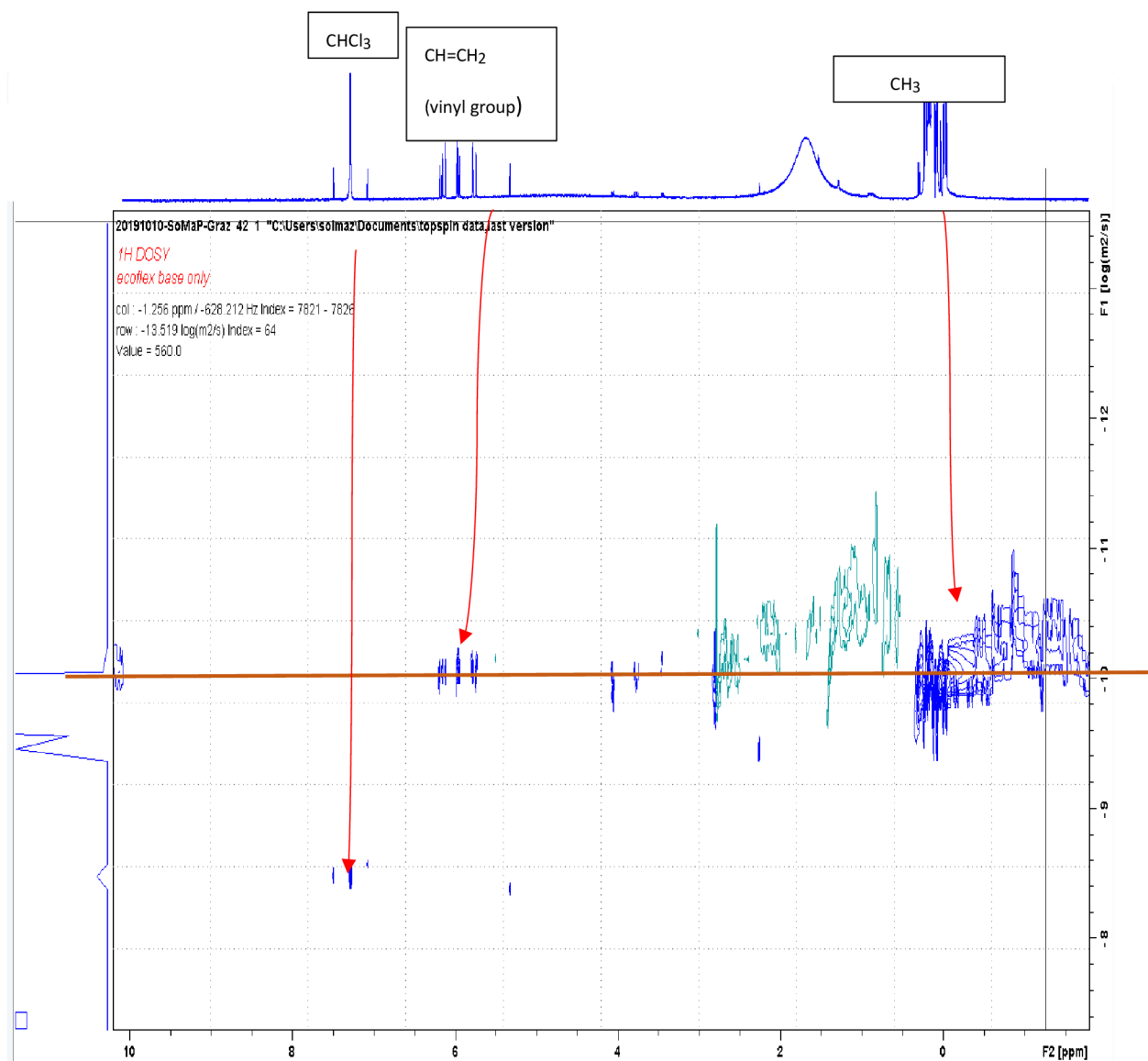


Figure 15. Experimental spectrum for Base -ecoflex done in DOSY NMR on Bruker Avance spectrometer with 500.13 MHz

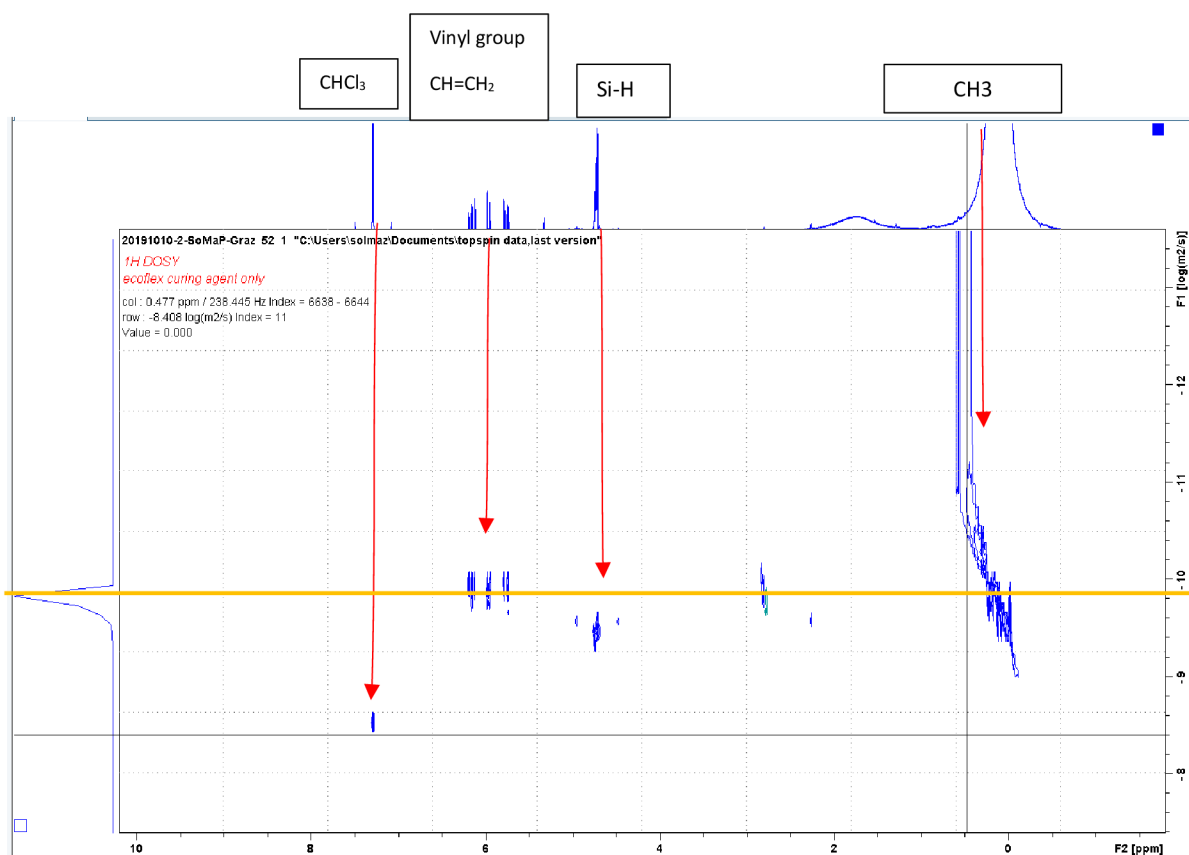


Figure 16. Experimental spectrum for Curing Agent-ecoflex done in DOSY NMR on Bruker Avance spectrometer with 500.13 MHz

8. Discussion and conclusion

The aim of this thesis was to: Investigate the behavior of original components in Ecoflex .

For that purpose, this experiment is designed and from the analysis and by comparing the experimental data obtained from NMR spectrometer and by visualizing the prediction graphs, it allows us to conclude that, during this process the vinyl groups that corresponds to the $\text{CH}=\text{CH}_2$, and the Si-H protonated silicone group decreased in intensity, that means they are consumed while the (CH_2) group increased.

The limitation in this experiment was to separate clearly CH₂ and CH₃ signals. In the start materials there was not any CH₂ but only CH₃ group. after polymerization CH₂ signals appeared but it was hard and needed farther job and more sensible software to separate their signals, therefore integrated for whole signals and assigned as (CH₂+CH₃), so could not calculated how many molecules are consumed in this reaction.

Appendices

A. Supplemental figures

Figures below demonstrates how the process can be repeated for different experiment in several time from ^1H NMR spectra for mixture of two samples (Base + Curing Agent) (Ecoflex):

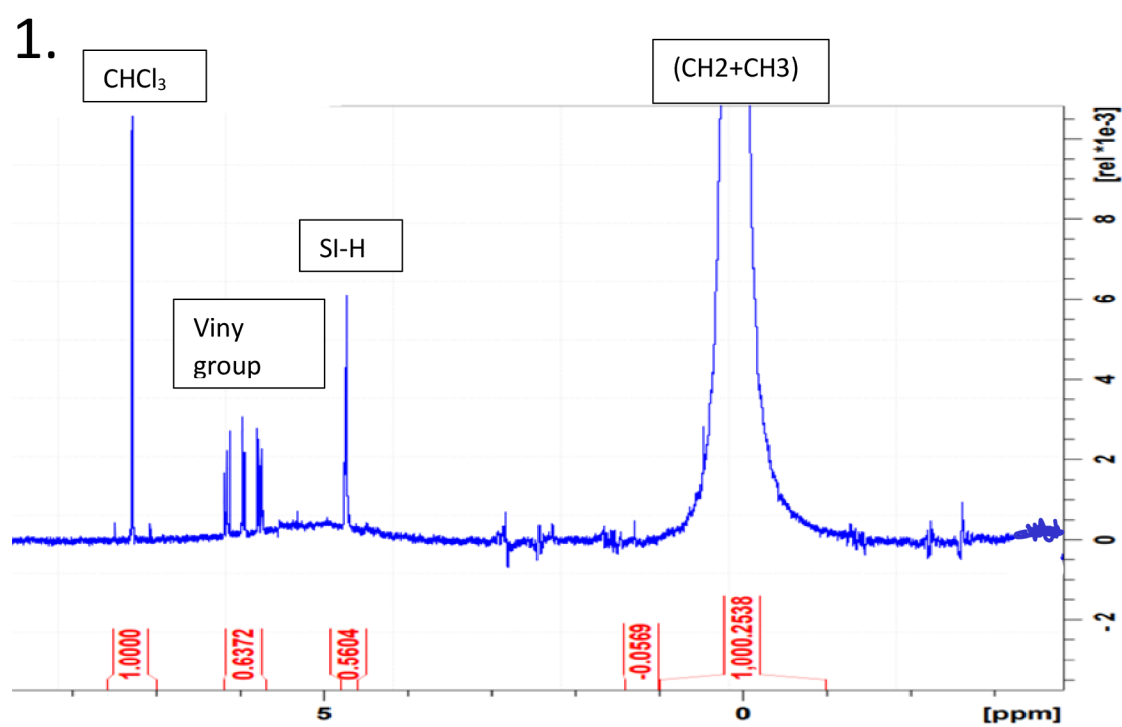


Figure 17. Experiment recorded in 06.09.2019 at 12:35 on ^1H NMR spectra and the signal for chloroform (CHCl_3) is normalized to 1 and just ignored, because the signal for solvent is not important in this experiment.

2.

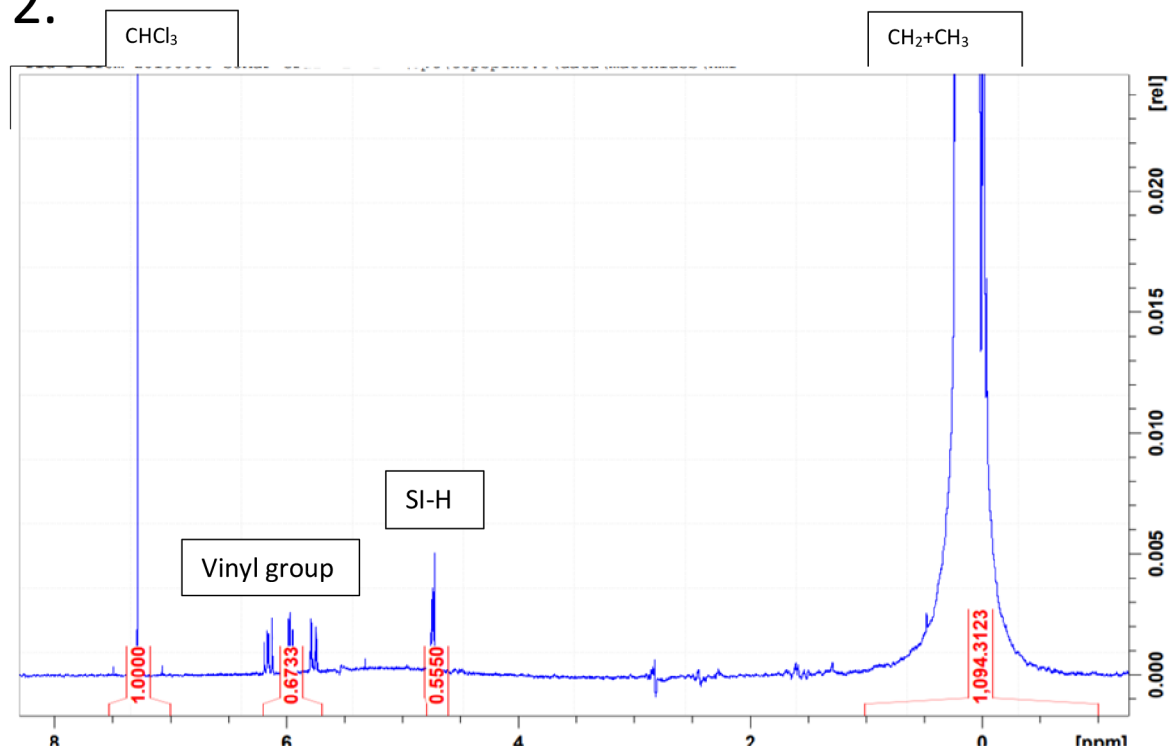


Figure 18. Experiment recorded in 06.09.2019 at 13:05 on ^1H NMR spectra

3.

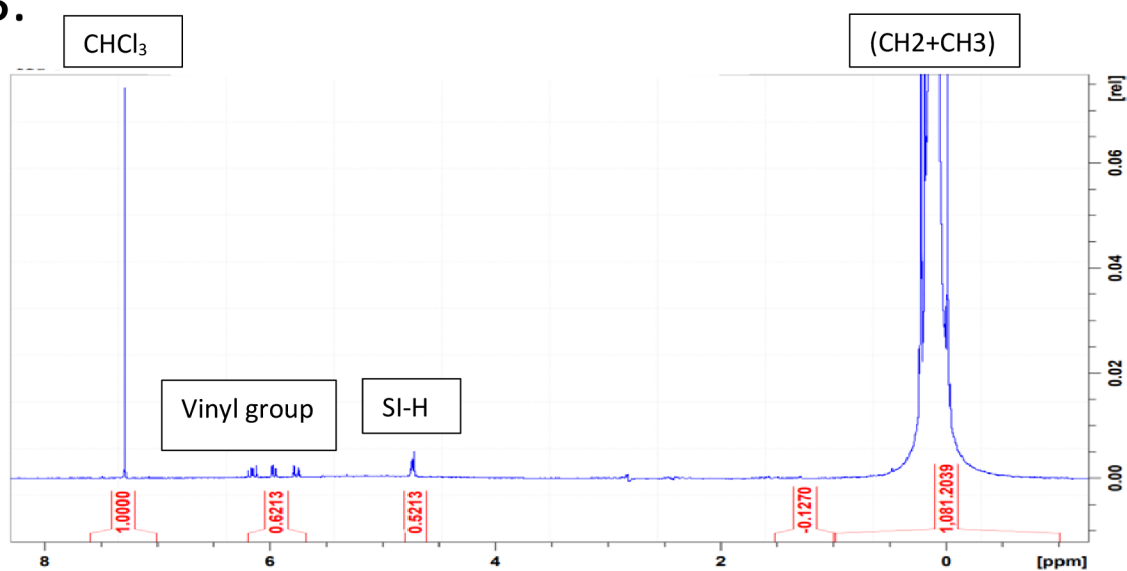


Figure 19. Experiment recorded in 06.09.2019 at 13:35 on ^1H NMR spectra

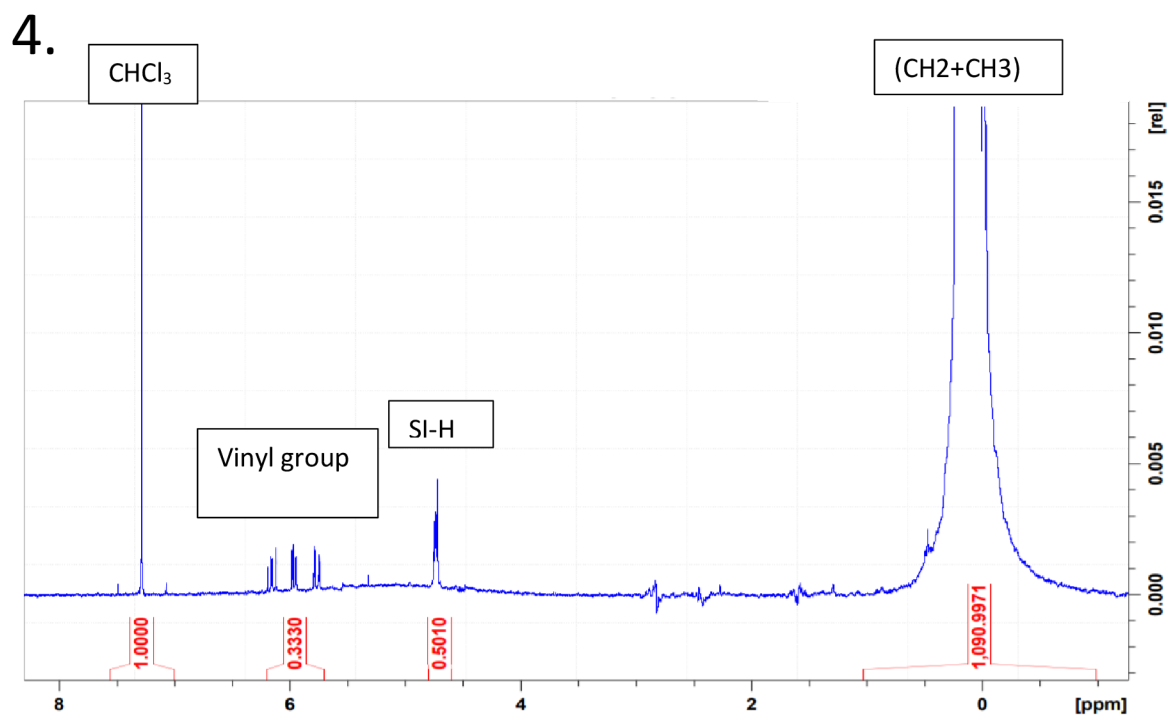


Figure 20. Experiment recorded in 07.09.2019 at 07:05 on ¹H NMR spectra

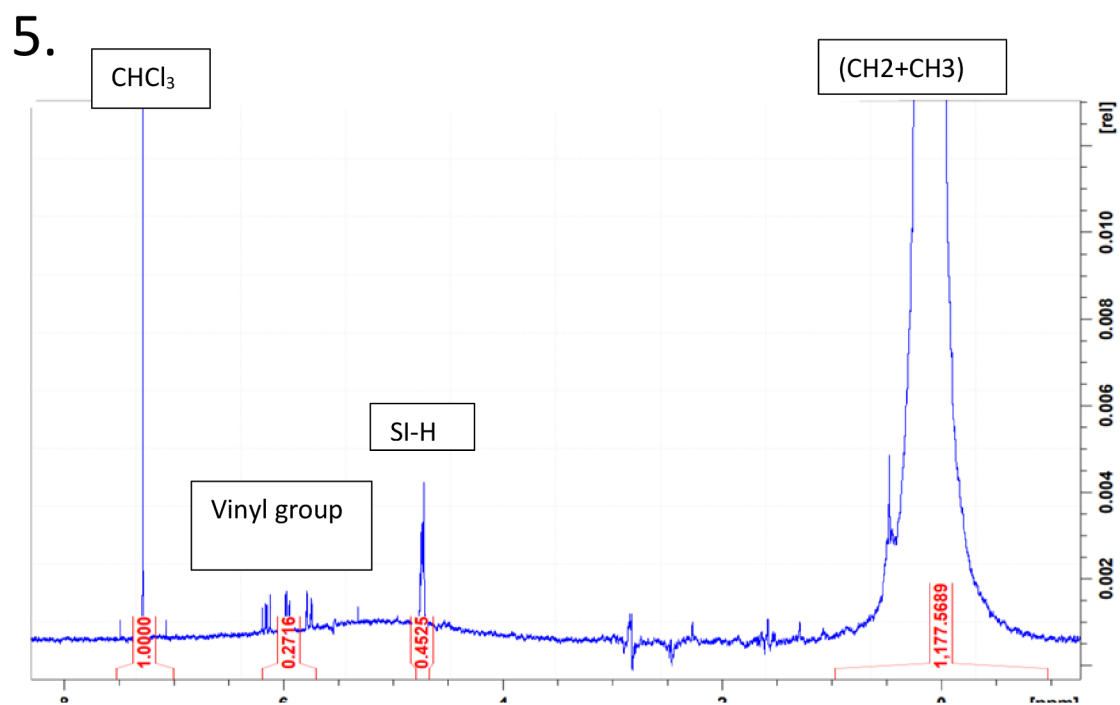


Figure 21. Experiment recorded in 08.09.2019 at 00:05 on ¹H NMR spectra

6.

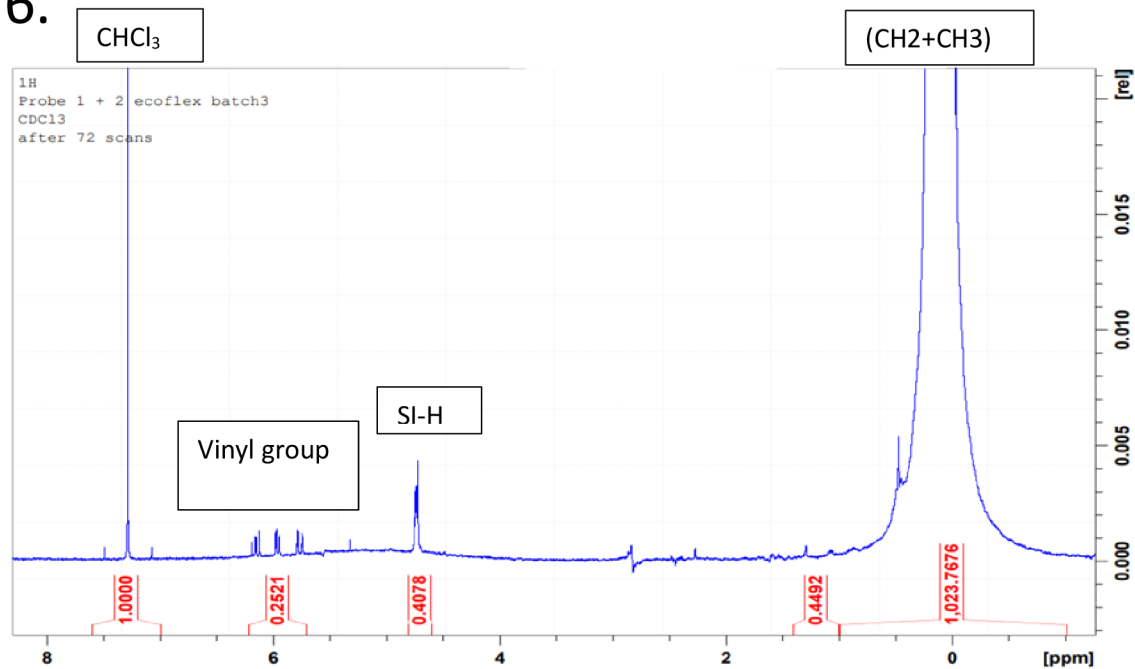


Figure 18. Experiment recorded in 08.09.2019 at 00:42 on ¹H NMR spectra

7.

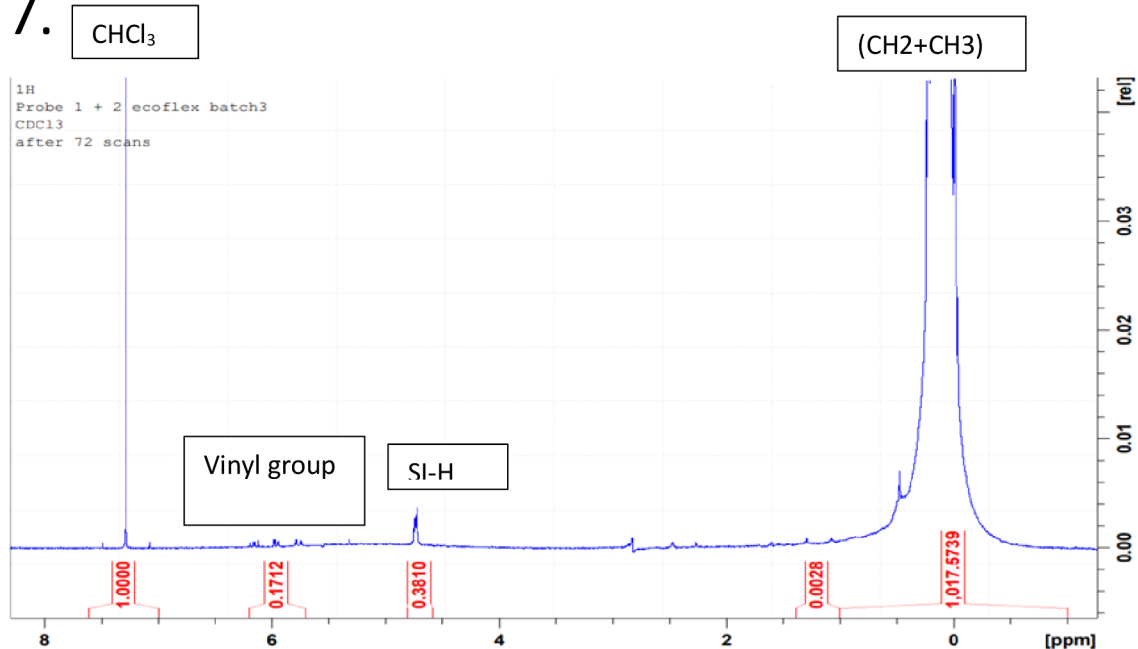


Figure 23. Experiment recorded in 09.09.2019 at 08:54 on ¹H NMR spectra

B. Jupyter Notebook

This program is done in Jupyter Notebook 6.1.4 (python3) platform by importing some useful package like:

- NumPy for providing mathematical operations and useful function,
- Seaborn for plotting and visualize random distribution
- Pandas as fast and powerful package for design and analyses labeled data
- Scipy optimize fit is a type of optimization that finds an optimal set of parameters for a defined function that best fits a given set of observations. This provides the flexibility and control to define the form of the curve, where an optimization process is used to find the specific optimal parameters of the function [42].

This program is used Biexponential function for fitting data, and all data points are equally and randomly in time interval from start to end of experiment distributed.

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