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Synthesis and characterization of hydrophilic silicone copolymers

Master of Science Thesis in the Master Degree Program Materials and Nanotechnology

DARIJA SKAKIC

Department of Chemical and Biological Engineering
Division of Polymer Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
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Synthesis and characterization of hydrophilic silicone copolymers

Syntes och karakterisering av hydrofila silikon-copolymerer

In collaboration with Mölnlycke Health Care AB

Conducted by:
Darija Skakic

Supervisors:
Dennis Hansson
Lars Lindgren

Examiner:
Mats Andersson

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percipitated copolymer

Abbreviations

AIBN	– Azobisisobutyronitrile
DMAEMA	– Dimethylaminoethyl Methacrylate
EtOAc	– Ethyl acetate
GF31	– 3-(Trimethoxysilyl)propyl methacrylate
HEAA	– N-Hydroxyethyl acrylamide
MAA	– Methacrylic acid
MeOH	– Methanol
NIPAM	– *N*-isopropylacrylamide
PSA	– Pressure sensitive adhesive
TRIS	– 3-[Tris(trimethylsiloxy)silyl] propyl metharcylate

Abstract

Wound dressings, scar dressings and other medical applications are all applications were pressure sensitive adhesives (PSA) may be used. There are different types of PSAs and one type is the silicone based, where vinyl and hydride-containing polydimethylsiloxane (PDMS) are blended and let to react. Silicone PSAs are used to securely attach medical devices to the body and since they are highly hydrophobic problems may arise under moist conditions. Problems may be loss of adhesion to the skin or risk of maceration. In this project, to improve wet adhesion of silicone PSAs, hydrophilic silicone compatible copolymers will be added to a standard silicone PSA.

Hydrophilic silicone copolymers of poly(tris(trimethylsiloxysilyl propyl) metharcylate-co-methacrylic acid) (TRIS/MAA), poly(tris(trimethylsiloxysilyl propyl) metharcylate-co-dimethylaminoethyl methacrylate) (TRIS/DMAEMA), poly(tris(trimethylsiloxysilyl propyl) metharcylate-co-*N*-hydroxyethyl acrylamide methacrylate) (TRIS/HEAA), poly(tris(trimethylsiloxysilyl propyl) metharcylate-co-*N*-hydroxyethyl acrylamide methacrylate) and poly(tris(trimethylsiloxysilyl propyl) metharcylate-co-*N*-isopropylacrylamide (TRIS/NIPAM) were synthesized by free radical polymerization in solution using azobisisobutyronitrile (AIBN) as initiator.

The effect of these copolymers as a component in silicone pressure sensitive adhesives was evaluated by moisture vapor transmission rate (MVTR) and contact angle measurements. Sole copolymer was characterized by size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR).

The addition of the copolymers resulted in an increased MVTR of up to 139 % for poly(TRIS-co-DMAEMA (5 mol %)) and poly(TRIS-co-NIPAM (5 mol %)) when added in a 5 wt % amount to a standard two component silicone formulation from Nusil. Contact angle did not differ significantly from reference. SEC confirmed large weight average molecular weight, $M_{W,}$ over 500 000 g/mol. NMR showed traces of monomer residue after purification of the copolymers, indicating that further purification is needed.

Keywords: silicones; pressure sensitive adhesives; copolymers; hydrophilic; vapor permeability.

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1. Introduction

Background

Silicone pressure sensitive adhesives (PSA) are commonly used in wound dressings, scar dressings and other medical applications. A PSA is an adhesive that, when pressure is applied, forms a bond with the adherend. These adhesives are generally a blend of vinyl and hydride-containing polydimethylsiloxane (PDMS), cured via addition curing. They are biocompatible and can securely attach medical devices to the body. The adhesives are also highly hydrophobic which can lead to problems under moist conditions (such as skin perspiration) – the adhesives lose their adhesion to skin. This is a problem as there is a risk of maceration (softening and whitening of skin when kept wet) and the adhesive may detach from the skin prematurely.

Traditionally, water absorbing fillers have been added to the PSAs. However, this often leads to swelling of the adhesive, loss in dry adhesion and leaking of the filler due to their affinity to water. [1]

To improve the wet adhesion properties hydrophilic silicone compatible copolymers may be added to the silicone pressure sensitive adhesives. The copolymers will introduce hydrophilic properties to the adhesive, improving wet adhesion, and since the copolymers are large molecules migration and leakage can be avoided. It would also allow better water vapor permeability and improve transportation of e.g. antimicrobial additives.

Aim

The aim of this project is to evaluate a patent application [2] from the health care company Convatec Technologies Inc., claiming the first time ever synthesis of a unique "amphiphilic silicone copolymer" used in a pressure sensitive adhesive. In this project synthesis of amphiphilic copolymers will be carried out and the copolymers will be evaluated to determine how they affect the properties of PSAs. The goal of the copolymers is to contribute to better "wet adhesion" and water vapor permeability, as claimed in the patent application.

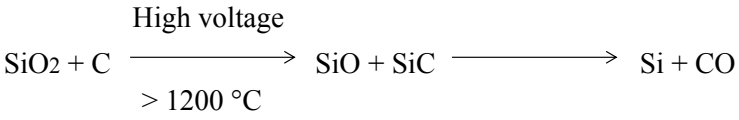
Delimitations

This master thesis is delimited to some of the monomers, solvents and the initiator presented in the patent application [2], see Chapter "Monomers in the project". The standard silicone PSA used in this project will be MED 6350, a commercial PDMS polymer from Nusil.

2. Theory

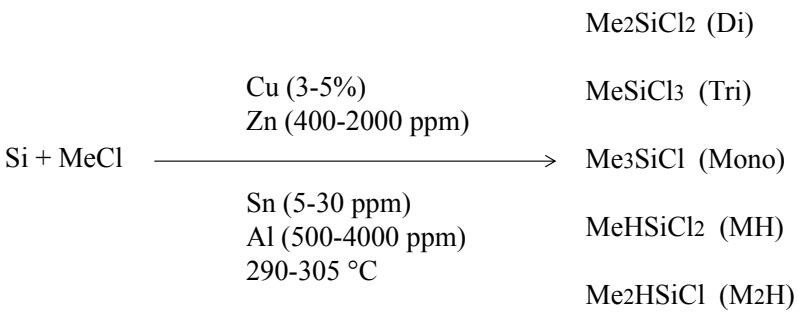
From sand to silicones

The term silicone originates from the word *sili*con and ket*one* and refers to polysiloxanes. Silicones belong to the category of synthetic polymers whose backbone constitutes of Si-O-Si linkages. The silicon atoms can also be bonded to organic groups, such as methyl groups (see Table 1). This basic repeating unit is known as *siloxane*. The most common silicone (and in largest volume produced) is polydimethylsiloxane, PDMS. The silicone industry became viable after Rochow's discovery, in 1940, of the direct process where elemental silicon reacts with methylene chloride (MeCl) to form methylchlorosilanes. [3-5] When silica (sand) is reduced, according to Scheme 1, in a carbo-electro reduction process chemical grade silicon is produced. The methyl chlorosilane (MCS) reaction is shown in Scheme 2. [3]



Scheme 1 Carbo-electro reduction process.

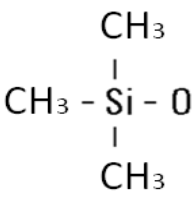
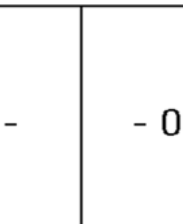
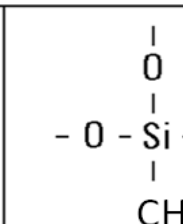
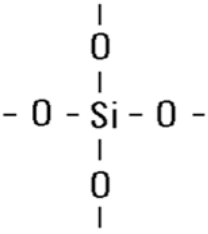
A critical factor in the MSC reaction is the selectivity for the dimethyldichlorosilane (Di), as PDMS is made from hydrolysis of Di. [3]



Scheme 2 MSC reaction.

Silicon is tetravalent and may thus have one, two or three organic substituents, where the methyl silicones have the most practical applications, see Table 1.

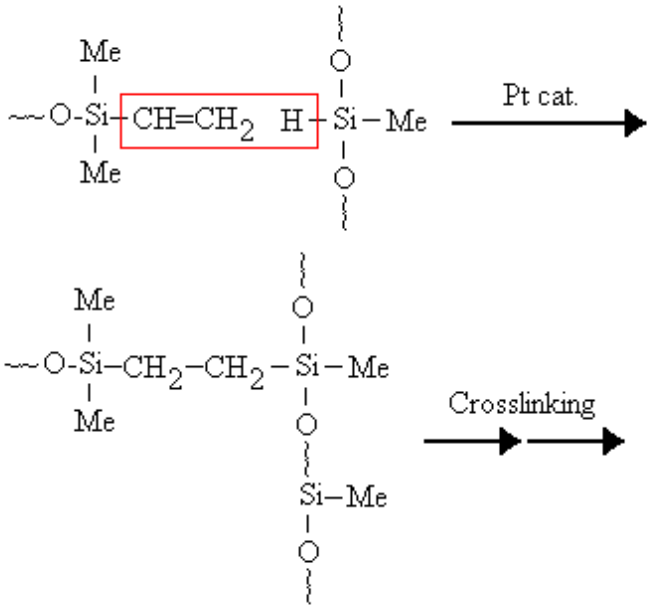
Table 1 Structural units of silicones

			
M monofunctional	**D** difunctional	**T** trifunctional	**Q** quadrifunctional

Silicone curing

The copolymers synthesized in this project will be formulated into a silicone based two component system. Blending of the two components (A and B) results in a hydrophobic cross-linked system, which is a PDMS crosslinked elastomer.

Addition curing, also known as hydrosilylation, are two component systems based on a Pt-catalyzed reaction that takes place between vinyl endblocked polymers and Si – H oligosiloxanes. Both components contain the vinyl endblocked polymer but one (component A) contains the catalyst (Pt) and the other (component B) contains the crosslinker. The crosslinking in this system is a spontaneous reaction at room temperature but the rate can be increased if the temperature is raised. This leads to a far more shortened curing time. The mechanism of the network formation through addition curing is showed in Scheme 3. [4]



Scheme 3 Network formation through addition curing. (Redrawn from [4])

Advantages using addition curing, instead of other methods such as cross-linking by condensation, are that this method eliminates shrinkage as there are no by-products formed. [5]

Silicone physicochemical properties

The element silicon is positioned just under carbon in the periodic table and this led to a belief that silicon could replace carbon. However, there are very few similarities between silicon and carbon. For instance, the Si-X bond is much larger than the C-X bond. Si also has a lower electronegativity than C $\left(\chi^{Si} \approx 1.80\,;\ \chi^{C} \approx 2.55\right)$ and has thus more polar bonds. The bond polarity contributes to strong silicon bonding. [5]

Silicones have the unusual combination of both high surface energy properties and low surface energy properties. The high surface energy comes from the inorganic chain similar to silicates whereas the methyl groups, which are organic, contribute to the low surface energy. Since the Si-O bonds are polar they would lead to strong intermolecular interactions had they not been shielded by the methyl groups. The shielding is made easy by the high flexibility of the silicone chain. There is

nearly free rotation around the Me_2Si-O bond. Despite the polar chain of silicones they have a low critical surface tension of wetting. [5]

Silicone biocompatibility

The definition of biocompatibility is *"the ability of a material to perform with an appropriate host response in a specific application". [6]*

It was discovered in the mid-1940's that silicones due to their hydrophobic property prevented blood from coagulating. Silicones are used in long term implantations as they are chemically stable and highly elastic, and the first report of silicone elastomers being implanted in humans was in 1946. Dr. Frank H. used silicone in a bile duct repair and reported that "*It is flexible, it will stretch, it will bounce like a rubber and it can be cast into any shape*". [5] In 1948 Dr. DeNicola implanted an artificial urethra tube and reported 14 months after the implantation that the artificial urethra "*had been retained with normal genito-urinary function ...*" [5] and that *"There is no evidence at this time that the tube is acting as a foreign body irritant* ..." [5]

Silicones are widely used in various medical applications due to properties such as *biocompatibility* and *biodurability* – which originate from silicones being hydrophobic, chemically and thermally stable materials with a low surface tension. [5]

Adhesion

When there is energy required to separate two bodies, the two bodies are said to adhere and the force necessary to break the bond between the two bodies is called *practical adhesion*. Adhesion is physical attraction between the surfaces of two materials and is dependent on the character of the physical forces holding the atoms and molecules together. [7, 8]

So, what is an adhesive? Basically it is a *material* which joins materials, when applied to their surfaces, and resist separation. There are two characteristic properties an adhesive must possess: [9]

1. An adhesive must spread on a surface, having a contact angle approaching zero – it must wet the surface. The adhesive will be liquid of low viscosity when applied.
2. The adhesive must harden and have high cohesive strength which is the strength of like molecules to stick together. The hardening can be achieved by loss of solvent, chemical reactions or by cooling if the adhesive is a hot melt. There is one exception to this second property and that is pressure-sensitive adhesives. These are permanently sticky.

There are six theories of adhesion which are; physical adsorption, chemical bonding, electrostatic attraction, mechanical interlocking, inter-diffusion and weak boundary layer theories. For this project, the most relevant adhesion theories are physical adsorption and mechanical interlocking. These will be further described below.

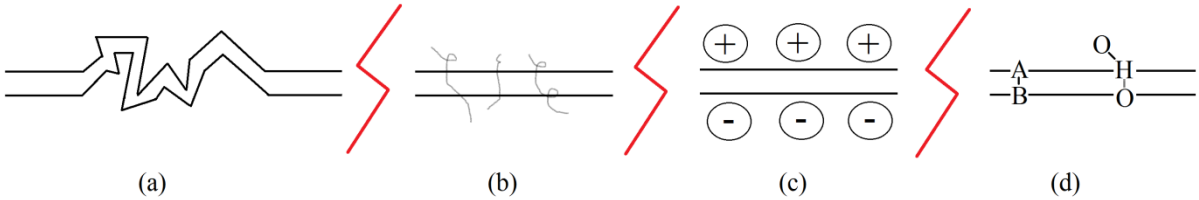


Figure 1 (a) mechanical interlocking; (b) interdiffusion of chains; (c) electrical interactions; (d) chemical interactions. (Redrawn from [10])

Physical adsorption

This theory involves van der Waals forces across the interface and attractions between permanent and induced dipoles. Since all materials have different polarities, resulting from their electron cloud, they also have different adhesion. An example is between metal and paper which are polar materials and polyethylene (PE) and silicone which are non-polar. Metal and paper easily adhere by any adhesive while PE and silicone are more difficult to bond. [9, 11]

There are three types of forces of attraction between dipoles; E_{PP} (permanent dipoles), E_{pi} (permanent dipole and corresponding induced dipole) and E_{ii} (instantaneously induced dipoles).

Between a pair of *permanent* dipoles, distance *r* at their centers, there is a potential energy E_{PP} given by equation (1),

$$E_{pp} = \frac{-2\mu_1^2\mu_2^2}{3kT(4\pi\varepsilon_o)^2 r^6} \quad (1)$$

where μ_1 and μ_2 are the dipole moments, and ε_0 is the permittivity in vacuum, k the Boltzmann's constant and T the absolute temperature.

If there is a non-polar molecule close to a polar molecule then the latter will *induce* a dipole in the former. Equation (2) gives the induced dipole moment, where E is the electric field and α is the polarizability of the non-polar molecule.

$$\mu_i = \alpha E \quad (2)$$

The potential energy in this case is E_{pi} and given in equation (3), where μ_1 is the dipole moment of the permanent dipole.

$$E_{pi} = \frac{-\mu_1^2\alpha}{4\pi\varepsilon_0 r^6} \quad (3)$$

The third type of physical adsorption interaction is between two *instantaneous* dipoles. These types of dipoles exist in non-polar molecule as a result of fluctuating distribution of electrons. The potential energy is given by equation (4),

$$E_{ii} = \frac{-3(\alpha_1\alpha_2)^2 I_1 I_2}{2(I_1+I_2)r^6} \quad (4)$$

where α_1 and α_2 are the molecules polarizabilities and I_1 and I_2 are their ionization potentials. [9]

Mechanical interlocking

A soft tacky adhesive can enter irregularities found in substrates with irregular surface, see Figure 1 (a). This is called mechanical interlocking and it occurs when an adhesive can wet a surface, creating a bonding force. Silicone pressure sensitive adhesives, as silicones flow readily, can penetrate into a porous or rough substrate (such as skin) and create a mechanical "bond". [9, 11]

Monomers used in the project

TRIS

3-[Tris(trimethylsiloxy)silyl]propyl methacrylate (TRIS) is a silicone based monomer with the chemical formula $C_{16}H_{38}O_5Si_4$, Figure 2 illustrates the chemical structure. TRIS is used as the basemonomer and constitutes the largest part in the copolymers. This is because TRIS has TMS groups, short for trimethylsilyl -$Si(CH_3)_3$, which makes it similar to PDMS and thus contributes to the good miscibility with the PDMS. [12]

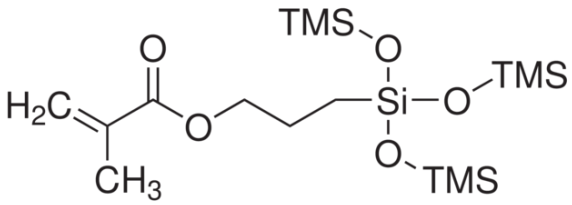


Figure 2 TRIS monomer

TRIS belongs to the acrylate family and contains a vinyl group which is crucial for free radical polymerization (see Chapter 2 "Free radical polymerization in solution").

MAA

Metharcylic acid (MAA) is also a member of the acrylate family and has the chemical formula $C_4H_6O_2$. Figure 3 illustrates the chemical structure of MAA. [13]

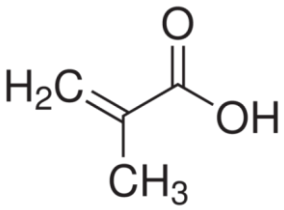


Figure 3 MAA monomer

HEAA

N-Hydroxyethyl acrylamide (HEAA) with the chemical formula $C_5H_9NO_2$ is an acrylamide having one nitrogen replacing the oxygen seen in acrylates. The chemical structure of HEAA is seen in Figure 4. [14]

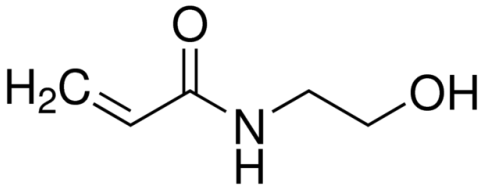


Figure 4 HEAA monomer

NIPAM

N-Isopropylacrylamide (NIPAM), chemical formula $C_6H_{11}NO$ and chemical structure illustrated in Figure 5. [15]

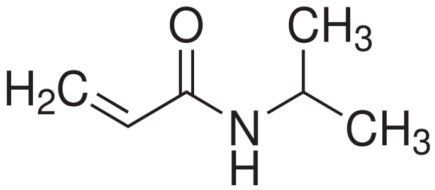


Figure 5 NIPAM monomer

DMAEMA

2-(Dimethylamino)ethyl methacrylate (DMAEMA), $C_8H_{15}NO_2$. This acrylate has the chemical structure shown in Figure 6. [16]

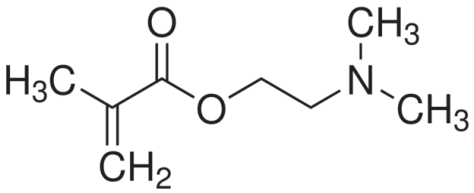


Figure 6 DMAEMA monomer

Initiator AIBN

Azobisisobutyronitrile (AIBN) is a common initiator used in free radical polymerization. Chemical structure can be seen in Figure 7. [17]

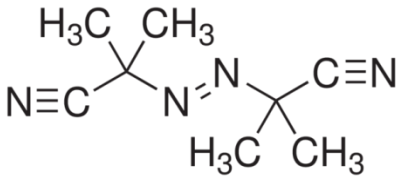


Figure 7 AIBN initiator

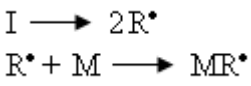
Free radical polymerization in solution

In free radical polymerization polymers are formed by the addition of free radical building blocks, in this project it is vinyl monomers added onto a growing chain. When the polymerization is in a solution the solvent facilitates heat transfer and also reduces viscosity of the medium. However, complications of chain transfer may arise and thus selection of solvent must be carefully made.

The polymerization proceeds in three stages: (1) *initiation,* an active center which acts as a chain carrier is formed; (2) *propagation,* growth of the macromolecule by a kinetic chain mechanism where monomers are added to the growing chain; (3) *termination,* the active center is transferred or neutralized which stops the progress of the kinetic chain. [18]

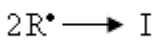
Initiation

The initiation step begins with an *initiator* that decomposes into free radicals, R*, when subjected to heat, electromagnetic radiation or a chemical process, see reaction (1). The free radical will have an *active center* which is the location of the unpaired electrons. The instability of the carbon double bond of the monomer, M, makes it susceptive to reaction with the free radical's unpaired electrons; hence the active center of the free radical can "grab" one electron from the double bond of the monomer creating a new active center at the end of the chain as it leaves an unpaired electron. [19]



(1)

The amount of generated radicals effective in the creation of a kinetic chain can be expressed as the efficiency factor, *f* (0-1). A low efficiency factor will lead to inefficient chain propagation and can be due to several factors, where one is *primary recombination* which is a result of to radicals combining, see reaction (2).

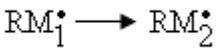


(2)

This can occur if the solution impedes the radical fragments, leading to a cage effect. The solvent plays an important part in solution free-radical polymerization as the extent of decomposition of the initiator varies with the solvent. An example is the decomposition of benzoyl peroxide where in tetrachloroethylene it only decomposes up to 35 % while it is 85 % in ethyl acetate. [18]

Propagation

When the synthesis has been initiated it is followed by the propagation reaction. In free radical polymerization the propagation process usually takes place within a fraction of a second. The propagation steps are similar to the initiation where electrons are transferred and the active center is moved down the chain, see reaction (3).



(3)

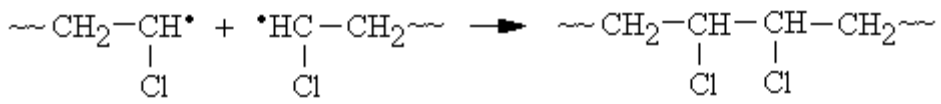
The propagation comes to an end when the termination occurs. [18]

Termination

The termination is the step where the active center is either transferred to another chain or neutralized. There are two ways in which the termination can take place; by *combination* or *disproportionation*.

Combination

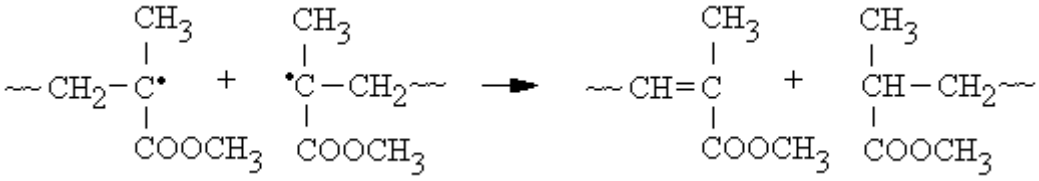
The termination reaction combination is between two end chains, where they couple together to form one long chain as seen in Scheme 4.



Scheme 4 Combination of two growing chains into one polymer.

Disproportionation

This occurs when hydrogen abstractions takes place in one end forming a carbon double bond and resulting in two dead polymer chains, see Scheme 5. [18]



Scheme 5 Disproportionation of two growing chains into two dead polymer chains.

Chain transfer

Chain transfer occurs when the active center of a growing polymer is transferred to another species through a collision. There are several types of chain transfer. In general; hydrogen abstraction from monomer, initiator, polymer solvent and modifier. There are five concepts of chain transfer; transfer to monomer, transfer to initiator, transfer to polymer, transfer to modifier and transfer to solvent. [18]

Copolymer equation

When using two or more monomers in a free radical polymerization the term is known as copolymerization. By copolymerizing two monomers the properties of the resulting polymer are often better than the properties for the parent homopolymers. The simplest case of copolymerization involves two monomers (e.g. M_1 and M_2) but can be presented in several different structures within the copolymer such as: *Statistical copolymer; Alternating copolymers; Block copolymers; Graft copolymers* and *Stereoblock copolymer.* [18]

The copolymerization between two monomers, M_1 and M_2, is presented in equations (5.1)-(5.4): where k_{11}/k_{22} and k_{12}/k_{21} correspond to *self-propagating* and *cross-propagating* rate constants, respectively. [18]

$$\sim\sim M_1^{\bullet} + M_1 \xrightarrow{k_{11}} \sim\sim M_1^{\bullet} \quad (5.1)$$

$$\sim\sim M_1^{\bullet} + M_2 \xrightarrow{k_{12}} \sim\sim M_2^{\bullet} \quad (5.2)$$

$$\sim\sim M_2^{\bullet} + M_2 \xrightarrow{k_{22}} \sim\sim M_2^{\bullet} \quad (5.3)$$

$$\sim\sim M_2^{\bullet} + M_1 \xrightarrow{k_{21}} \sim\sim M_1^{\bullet} \quad (5.4)$$

The rate of consumption of M_1 can be determined according to equation (6) if steady state conditions prevail and the radical activity only depends on the nature of the terminal unit. [18]

$$-d[M_1]/dt = k_{11}[M_1][M_1^{\bullet}] + k_{21}[M_1][M_2^{\bullet}] \quad (6)$$

The rate of consumption for M_2 is then

$$-d[M_2]/dt = k_{22}[M_2][M_2^{\bullet}] + k_{12}[M_2][M_1^{\bullet}] \quad (7)$$

By assuming that $k_{21}[M_1][M_2^{\bullet}] = k_{12}[M_2][M_1^{\bullet}]$ the *copolymer equation* is obtained by dividing equation (6) by equation (7), so that

$$d[M_1]/d[M_2] = ([M_1]/[M_2])\{(r_1[M_1] + [M_2])/([M_1] + r_2[M_2])\} \quad (8)$$

where r_1 and r_2 represent relative reactivity ratios from $k_{11}/k_{12} = r_1$ and $k_{22}/k_{21} = r_2$.

Several limiting cases of *r* can be derived:

- $r_1 = r_2 > 1$: block copolymerization, since both reactivity ratios are larger than unity the propagating monomers prefer to react with themselves, forming blocks of M1 and M2.
- $r_1 = r_2 \gg 1$: block copolymerization, since the reactivity ratios are much higher than unity there is no inclination for the monomers to react with each other leading to two homopolymers.
- $r_1 = r_2 \approx 1$: ideal copolymerization, the propagating species M1* and M2* have the same preference for adding one or the other, resulting in a random copolymer.
- $r_1 = r_2 \approx 0$: alternating copolymerization, each of the two propagating species prefers adding the other monomer.
- $r_1 \gg 1 \gg r_2$: M1* is more reactive toward both propagating species and the copolymer will contain more of the reactive monomer in statistical placement. [20]

Characterization methods

Contact angle

The spreading or deformation of a water droplet on a solid surface is determined by the surface and interfacial energies. The contact angle, θ, is the angle under which the droplet meets the surface and may be evaluated by taking into account the three interfacial tensions in Figure 8:

γ_{SL} – between surface and liquid
γ_{SG} – between surface and gas
γ_{LG} – between liquid and gas

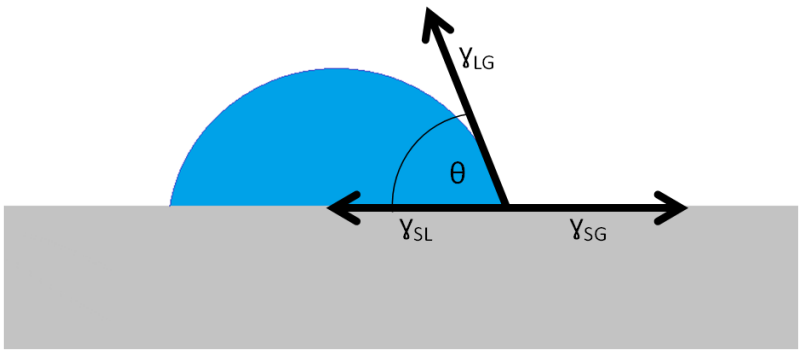


Figure 8 Different contact angles of a water droplet on a solid surface

The contact angle is also a quantification of the wetting of the solid by the liquid and is determined by Young's equation:

$$\cos\theta = \frac{\gamma_{SG}-\gamma_{SL}}{\gamma_{LG}}\gamma_{LG} \quad (9)$$

The lower θ the better the wetting. Poorly wetting systems may e.g. be water on Teflon where the water droplet rolls off the surface, hence θ approaches 180°. The other opposite is when the liquid spreads and covers the surface, complete wetting is achieved and θ approaches 0°. [21, 22]

Moisture vapor transmission rate (MVTR)

The definition of moisture vapor transmission rate (also water vapor transmission rate) is as follows:

"The rate of water vapor flow, under steady specified conditions, through a unit area of a material, between its two parallel surfaces and normal to the surfaces." [23]

And the metric unit of measurements is $1\frac{g}{24h*m^2}$.

3. Experimental

Chemicals

Table 2 Chemicals used in this project

Monomers	Solvents	Initiator	Silicone PSA
TRIS (from Sigma-Aldrich)	EtOAc (from Sigma-Aldrich)	AIBN (from Chalmers)	MED 6350 (from Nusil)
NIPAM (from Sigma-Aldrich)	MeOH (from Sigma-Aldrich)		
DMAEMA (from Sigma-Aldrich)			
MAA (from Sigma-Aldrich)			
HEAA (from Sigma-Aldrich)			

Methodology

Synthesis and purification of copolymer

In the synthesis of the copolymer monomer weight was kept at 50 g for all the experiments. Amount of initiator was kept at approximately 0.087 g and the solvent was kept at 120 g, generating a 30 wt % solution.

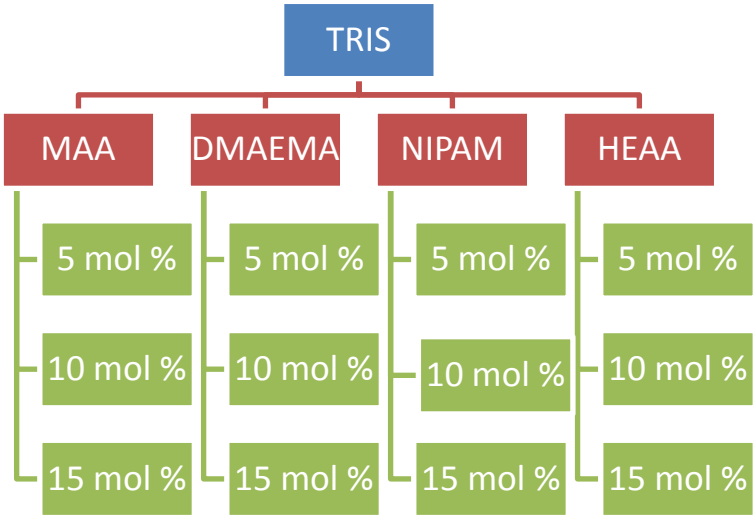
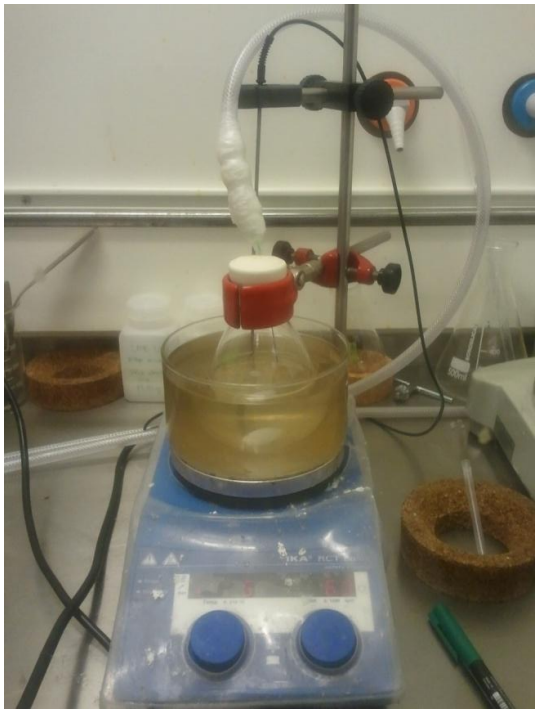


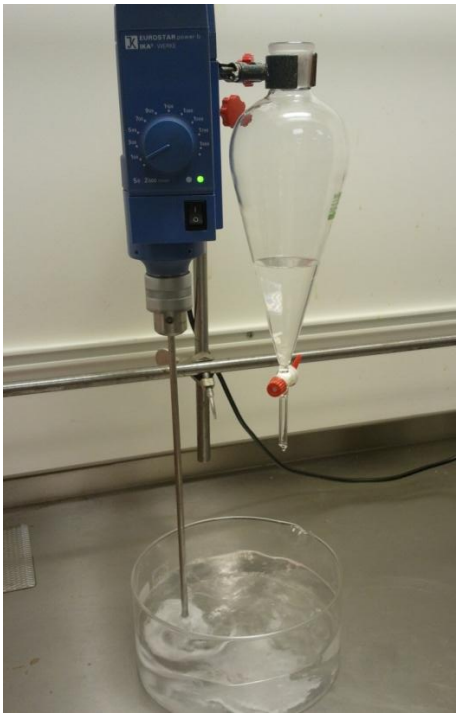
Figure 9 A scheme of poly[TRIS]-combinations and molar percentages of MAA/DMAEMA/NIPAM/HEAA.

The synthesis was carried out in a round bottom flask, see Picture 1, placed in an oil bath holding 65 °C. The two monomers (TRIS and MAA/DMAEMA/NIPAM/HEAA), see Figure 9, were added to the flask with solvent and initiator. Stirring was important throughout the entire synthesis to promote good mixing. The synthesis for each copolymer lasted for six hours. For more detailed description see Appendix I.

The copolymer solution was purified by precipitation in methanol, see Picture 2. This is because the copolymer is not soluble in methanol while the pure monomers are. In Picture 3 the precipitated copolymer is shown.



Picture 1 Synthesis reaction set-up



Picture 2 Copolymer purification set-up

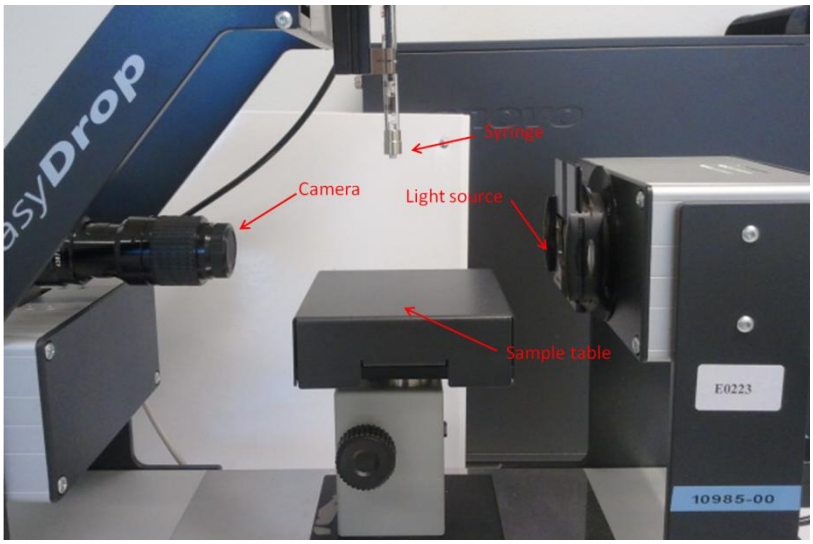
Picture 3 A close-up of the precipitated copolymer

Formulation of copolymer and two component system

Each copolymer was blended with MED 6350 (a commercial PDMS polymer) in a 1:20 ratio of copolymer to MED 6350. The blends were cast onto PUR-films and then cured on a heating plate to generate the final PSA. For more details see Appendix II.

Contact angle measurements

The contact angle measurements were performed on the formulations above and not on the pure copolymers. Each formulated film was measured with the EASYDROP Contact angle Measurement System, see Picture 4, using deionized water. Three positions were measured for every formulated film during 60 seconds to ensure a correct average contact angle. More details in Appendix II.



Picture 4 Contact angle measurement equipment

Moisture vapor transmission rate (ID: T-1070)

A cylinder was filled with deionized water up to a level leaving a 5 mm air gap. The produced films, from the formulations, three specimens of each, were punched out in a circular shape larger than the opening of the cylinders. The cylinder was covered with the specimen, weighed, and placed in an oven (37°C) for 24 hours. After 24 hours the cylinder with the specimen was weighed again and moisture vapor transmission rate could be obtained by calculating the loss of water.

NMR and SEC

^{1}H NMR spectrum was recorded on a Varian 400 spectrometer. The samples were dissolved in $CDCl_3$ and the ^{1}H NMR spectra were obtained at 298 K with $CDCl_3$ as internal standard. Size-exclusion chromatography (SEC) was performed on a Waters Alliance 2000 GPCV at 135°C with 1,2,4-trichlorobenzene as eluent at 1 mL/min using an RI-detector. It was calibrated using polystyrene standards.

Failed method

GF31 is a chemical similar to TRIS but much cheaper, see Figure 10 and 11. The first synthesis was therefore done with GF31 instead of TRIS. The first polymerization was between GF31 and MAA, Table 3.

Table 3 First synthesis between GF31 and MAA

Chemical	Amount
GF31	111.95 (g)
MAA	37.54 (g)
EtOAc	350 (g) (+ 400 mL)
AIBN	0.95 (g)

This first synthesis was done in a batch size of 500 g. A reactor with a built in heat controlled oil circulation was used with a SVL multi-joint lid 5-NECK on top. Through the center neck a mechanical stirrer passed and through the others nitrogen gas was connected and in-let of chemicals occurred,

the rest were sealed. The synthesis progressed in the same manner as described in Chapter 3 – *Synthesis and purification of copolymer.* Problems faced here were leakage of solvent and GF31 interaction with MAA. As seen in Table 3 an extra amount (400 mL) of EtOAc was added during the synthesis due to fact that 80 % of the solvent (EtOAc) had evaporated within six hours. GF31 (since it is different from TRIS) formed a type of hard, brittle, white copolymer instead of the expected clear, tough and rubbery copolymer. The –Si-O-Me groups of GF31 are probably more reactive than the TMS groups of TRIS, leading to the hard, brittle copolymer formed. However, the side group of monomer GF31 is not flexible enough to form a soft polymer and less MAA would improve the softness. Even though, later on, the leakage problem was solved (by sealing the center neck better) the reactor was disregarded as an optimal set-up and was replaced by round bottom flask (reactor with batch size 150 g) with a rubber septa using TRIS instead of GF31.

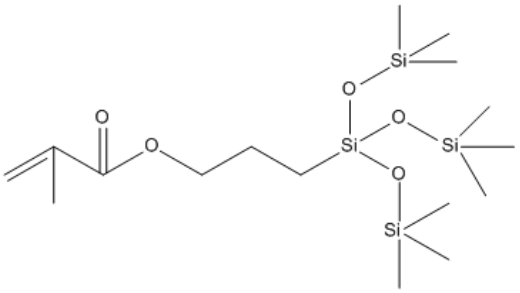


Figure 10 Chemical structure of TRIS.

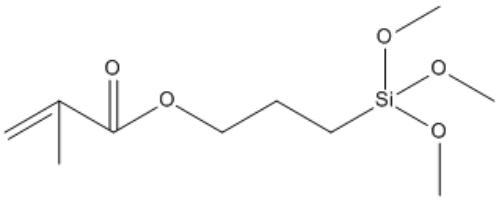


Figure 11 Chemical structure of GF31.

4. Results and discussion

Polymerization

Yield

The yield does not take into consideration amount of monomer left in the copolymer. In Chapter 4 – *NMR* calculations of copolymer composition and percentage of monomer left are made. For some copolymers, e.g. sample 1, the yield is much lower than for the rest, as seen in Table 4. This may be due to loss of copolymer in the first purification method, see Appendix I. Sample 1 (15 % MAA) showed some solubility in MeOH, which means that when excess MeOH/EtOAc was poured off some polymer residue may also have been poured off, hence the lower yield. Also, in the precipitation method the solution started to become turbid when all copolymer solution had been blended with the MeOH, this was a fact for all copolymers. The EtOAc to MeOH ratio was probably too small and the copolymer started to dissolve. There was most likely some loss of copolymer in this step too. It would probably have been better to use a larger quantity MeOH to avoid dissolution of the copolymer.

The best yield was expected for sample 8-9 as they had not been purified by the first method first, and hence the loss of polymer was strictly restricted to the new method. But as seen the yield is 63 % for Sample 8 and 70 % for sample 9.

Sample 7-9 are the poly[TRIS-co-HEAA] copolymers. Amount of HEAA increases from sample 7 to sample 9, and hence increased hydrophilicity. The reason to why there is a loss of polymer in the purification step could be that the copolymer (as the HEAA increases) became more soluble in MeOH. But as seen in Table 4 sample 7-9 are the copolymers containing the highest amount of TRIS. This speaks against the possibility of increasing HEAA contributing to increased hydrophilicity and thus making the copolymer soluble in MeOH. Also, sample 9 should be more soluble in MeOH than sample 8 as it contains more HEAA. The same behavior is seen in sample 4-6 (poly[TRIS-co-NIPAM]) where there is a larger loss of copolymer for sample 4 than for sample 6. It seems that the yield is somewhat circumstantial.

Table 4 Results from all evaluations

Copolymer	Sample	Expected comonomer (mol%)*	Comonomer comp. in polymer (mol%)	MVTR ($g/m^2/24h$) **	Contact angle (°)**	Mw (g/mol)	Mn (g/mol)	Monomer left in copolymer (mol%)	Yield (%)
poly[TRIS-co-MAA]	A	5	8.03	N/A	N/A	485 000	126 000	10.8	N/A
	B	10	11.45	N/A	N/A	508 000	88 000	8.50	N/A
	1	15	19.25	530	125	N/A	N/A	3.92	36
poly[TRIS-co-DMAEMA]	2	5	2.39	839	121	363 000	81 000	1.04	64
	C	10	13.45	N/A	N/A	443 000	106 000	13.7	N/A
	3	15	18.23	492	127	N/A	N/A	1.88	61
poly[TRIS-co-NIPAM]	4	5	10.60	1058	121	N/A	N/A	1.57	80
	5	10	16.01	468	128	N/A	N/A	1.35	84
	6	15	19.24	594	126	N/A	N/A	1.44	82
poly[TRIS-co-HEAA]	7	5	2.63	470	128	N/A	N/A	2.12	83
	8	10	5.01	505	124	N/A	N/A	0.77	63
	9	15	10.24	500	127	N/A	N/A	2.08	70
Reference (MED 6350)	R	N/A	N/A	441	128	N/A	N/A	N/A	N/A

*Comonomer is defined as MAA/DMAEMA/NIPAM or HEAA

** MVTR and contact angle measured on copolymer formulations with 1:20 ratio copolymer:MED 6350

SEC – molecular weight

According to the patent application it is stated that the molecular weight is larger than 10 000 g/mol. In Figure 12 and 13 and Appendix III Figure 16-17 all values show a M_W well above 10 000 g/mol at the lowest 360 000 g/mol and for the highest at 508 000 g/mol. SEC was only done on Sample A-C, see Table 4, and Sample 2 as the copolymers are TRIS-based it is assumed that the rest of the copolymers possess a similar molecular weight. The second peak in both figures represents some low molecular substance, probably monomer residue. Before H-NMR measurements Sample 2 was purified one more time, see Appendix I, First purification method.

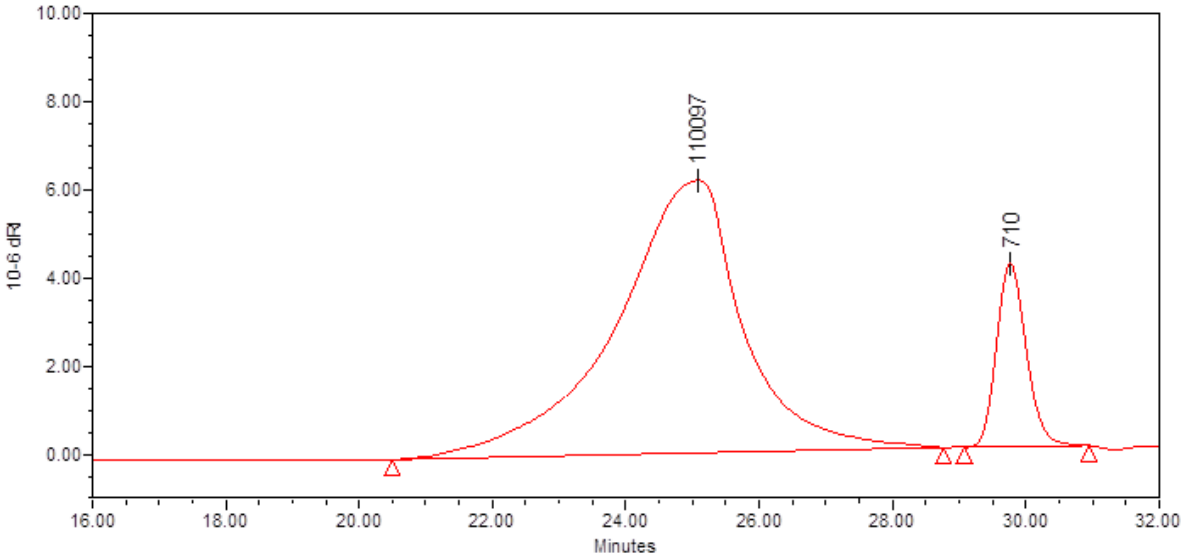


Figure 12 SEC of Sample 2, M_w = 360 000 g/mol

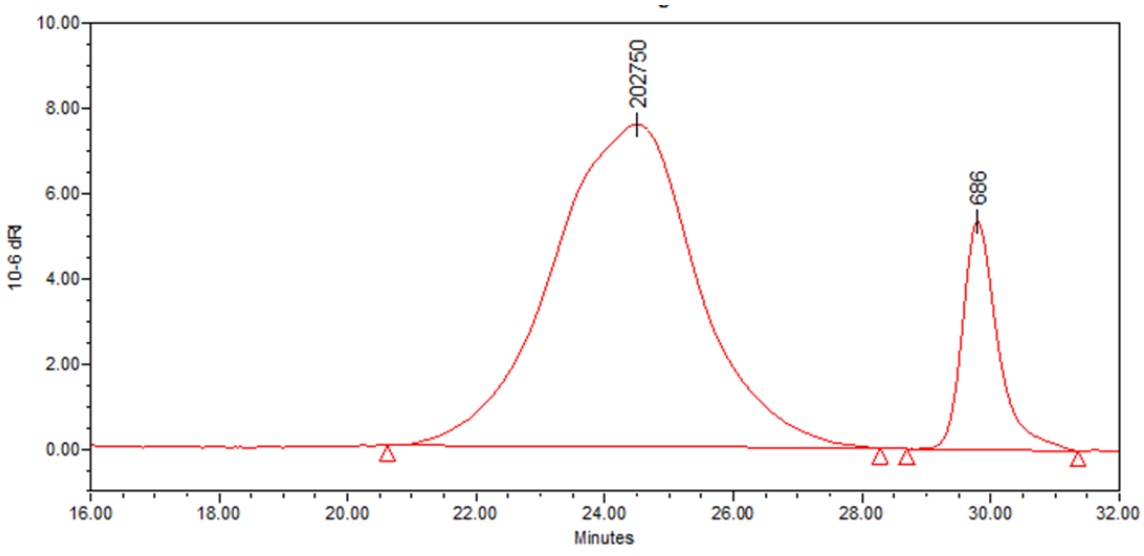


Figure 13 SEC of Sample A, M_W= 485 000 g/mol

^{1}H- NMR

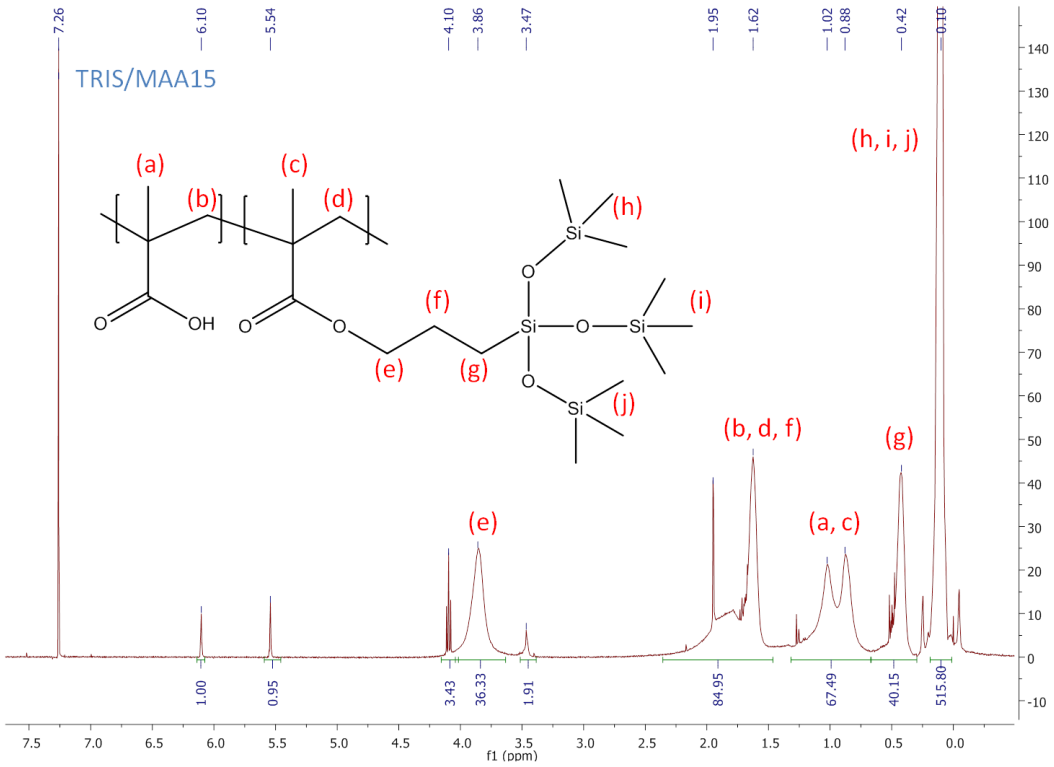


Figure 14 NMR of Sample 1

^{1}H- NMR was done to be able to calculate the composition in the copolymer. Calculations are shown below on Figure 14:

$$x_T + x_M = 1 = 100\% \quad (10)$$

where x_T and x_M are fractions of TRIS and MAA in the copolymer, respectively.

$$\frac{Integral\ (a,c)}{Integral\ (e)} = \frac{67.49}{36.33} = \frac{3x_M + 3x_T}{2x_T} \quad (11)$$

Applying equation (10) into equation (11) and

$x_T = 80.75\ \%$ (expected value is 85 %)

The two peaks at 6.10 ppm and 5.54 ppm are from the double bonds in the two monomers.

$$\frac{Integral\ (2x_{Mo})}{Integral\ (g)} = \frac{2x_{Mo}}{2x_T} = \frac{1.95}{40.15} \quad (12)$$

Where x_{Mo} is the fraction of monomer left in the copolymer.

$$x_{Mo} = 0.048567 x_T$$

Since x_T is 80.75 of the copolymer composition x_{Mo} is then

$$x_{Mo} = 0.048567 * 0.8075 = 0.0392188 = 3.92\ \%$$

According to the calculations above there is approximately 3.92 % monomer residue left in the copolymer. That is quite a large difference to 10.8 % left in sample A (calculated in the same manner as above) which was purified by the first purification method, see Appendix I, First purification method.

Table 4 presents the copolymer compositions for each copolymer. These data are not exact as the integrals were calculated by hand in MestreNova, an analytical chemistry software suite. This results in an inaccuracy that has to be taken into account and the data showed above has to be considered as approximate values. For all the copolymers there is a continuous increase of the comonomer which is consistent with the expected values.

One copolymer is standing out from the others and it is poly[TRIS-co-HEAA] (sample 7-9). The expected (the input) percentage of HEAA was 5 – 10 – 15 but the output was approximately 3 – 5 – 10, which means that TRIS has less affinity for HEAA than for the rest of the monomers. Hence, one can assume $r_{TRIS} \gg 1 \gg r_{HEAA}$ leading to TRIS being more reactive toward both propagating species and the copolymer will contain more of the reactive monomer (TRIS) in statistical placement. In comparison TRIS to the other monomers the r values were $r_{comonomer} > r_{TRIS}$ as can be seen in Table 4 where the output was larger than 5 – 10 – 15 for the comonomers (exception DMAEMA where 5 % was input and 2.39 % was output).

As seen in Table 4 the amount of monomer left in the copolymer varies between 0.77 – 3.92 % for the polymer purified by precipitation. For copolymers A-C the level of monomers left are much higher (8.5 – 13.7 %) and this proves that the first purification method was insufficient.

Contact angle measurements

All contact angle measurements were performed on the formulated films and not on the pure copolymers.

As seen in Table 4 the contact angle (°) of the copolymer formulations does not differ from the reference formulation (pure MED 6350) especially much. The contact angle was expected to be lower than the reference, but as seen it is higher for sample 7. The contact angle is in the interval 121° - 128° and is too narrow to say anything about whether the contact angle actually has been modified or not. One reason to why these measurements may not have been very accurate is the fact that the angle was measured on a droplet that was out in the open. Lights from the surroundings and air conditioning in the room could have affected the measurements. Observed during the measurement was that the droplet size steadily decreased, which either means that the droplet evaporates or that the surface has changed. Had these measurements been done in a closed environment of the droplet, then perhaps, there would have been different values.

Another fact to why there is such little change in the contact angle is that silicones are highly hydrophobic materials, and since there is a very small amount of hydrophilic material integrated in the silicone a large difference in the contact angle is really not expected. Had there been a large

difference in contact angle the possibility of migration, within the formulation, of the hydrophilic copolymer could be a reason. However, that was not the case and is very unlikely since the copolymers are large molecules and the probability of migration is therefore small.

Moisture vapor transmission rate

The higher MVTR the better vapor transmission. As seen in Table 4 all formulations show higher MVTR than the reference. This means that the formulations containing the hydrophilic copolymers actually "breathe" better and are more likely to let vapor through. Sample 4 [poly(TRIS-co-NIPAM(5 mol%))] has an MVTR that is 139 % better than the reference. The rest of the formulations show an improvement between 6 – 90 %. As only three tests on each formulation was done it is not statistically correct to say that there has been an improvement of the MVTR as there is no clear standard deviation to take into account. However, all formulations show higher MVTR than the reference.

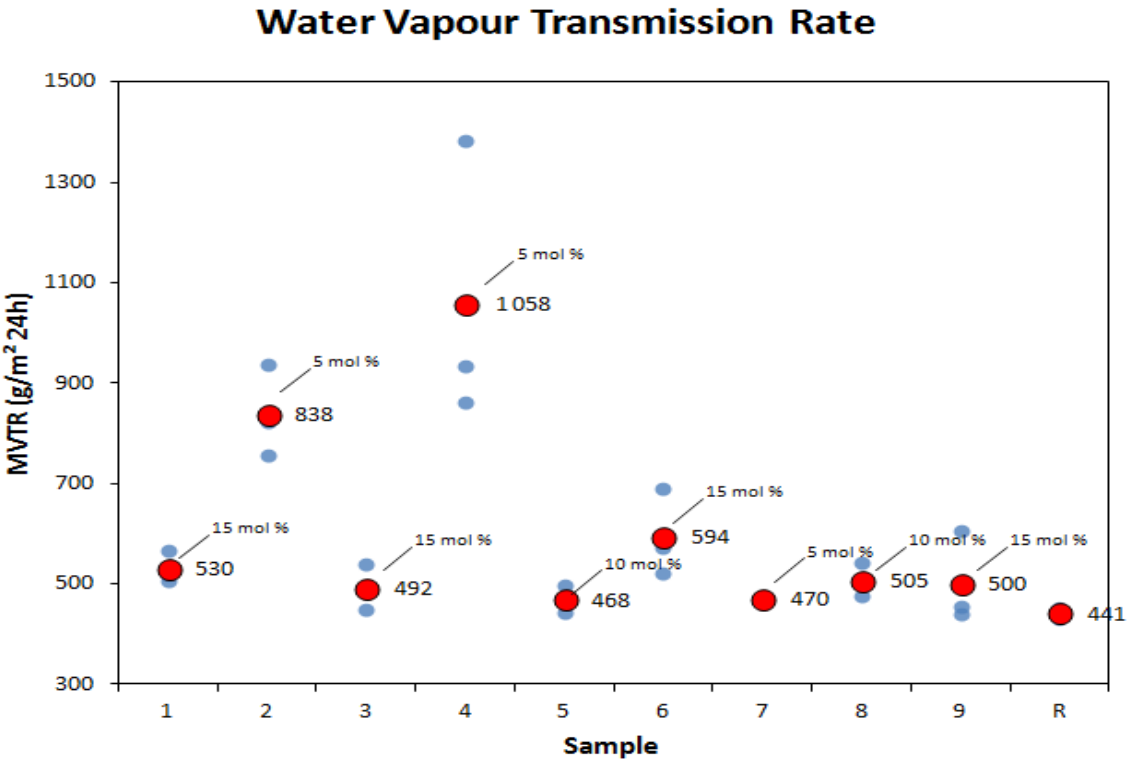


Figure 15 MVTR data for all samples. Blue = values for each test. Red = average.

In the investigated patent application there was no MVTR-testing done. However, testing of wet adhesion was done by taking a 1-inch by 1.5-inch strip of adhesive and attach it to the abdominal skin of a human subject and removing it after 40-60 min of aerobic activity. [2] According to their results good wet adhesion was achieved with the formulation containing 5 mol % NIPAM and weak wet adhesion was achieved with the formulation containing 5 mol % DMAEMA, sample 4 (MVTR = 1058) and 2 (MVTR = 838) respectively in this project. These two formulations showed best MVTR results and are in accordance with the patent application investigated. Why the formulations with lower amount of polar part showed the best MVTR values must be due to morphology. However, due to monomer residue, wet adhesion testing on humans was not possible.

There were some formulations with bubbles in the film, seen Picture 5 and 6. Especially sample 2, 4 and 8. This may have affected the MVTR and contributed to a higher value than expected. Formulation 8 had also a large amount of bubbles but a low MVTR. The bubbles may have been caused by solvent or monomer evaporating, or air that has been trapped during the speed mixing. As seen in Figure 15 there is one value for sample 4 that is well above the others. Since the value is almost 50 % larger than the second highest value it could be faulty, perhaps an increased amount of bubbles in the film or leakage of the cylinder.

Picture 5 From MVTR. Representing sample 9 - 7 from left to right.

Picture 6 From MVTR. Representing sample 2 - 4 from left to right.

5. Conclusions

This study showed that synthesis of "hydrophilic" silicone copolymers can be relatively easy performed, and the molecular weight achieved was high (M_w > 500 000 g/mol).

^{1}H- NMR showed that the composition in the copolymers was not as the feed monomer composition. For poly[TRIS-co-MAA] and poly[TRIS-co-NIPAM] there was a higher percentage of comonomer than assumed while the values varied for poly[TRIS-co-DMAEMA], and for poly[TRIS-co-HEAA] there was a lower percentage of comonomer. NMR also indicated monomer residue left in the copolymers, between 0.77 – 3.92 %, indicating that the purification step needs to be optimized or repeated more than once to remove monomers left in the copolymer.

According to contact angle measurements, wetting of the silicone surface was not greatly affected. As the addition of copolymer was only 5 wt % and of those 5 wt % only 5 – 15 mol % contained a hydrophilic part a large change in contact angle was not expected. The contact angle was evaluated as the patent application [2] stated large change in "wet adhesion".

The most relevant results for this project were the MVTR results as they portrayed the improvement of the silicone PSA (pure MED 6350). The MVTR values showed an large increase in water vapor permeability for sample 2 and 4, 5 mol % DMAEMA and 5 mol % NIPAM respectively. If there is a correlation between good "wet adhesion" and MVTR = 1058 (sample 4) contra weak "wet adhesion" and MVTR = 838 (sample 2), then it is possible to conclude that for the rest of the copolymer samples (MVTR << 800) no or little "wet adhesion" was achieved. Why there was no radical improvement for sample C and 3, and sample 5 and 6 (DMAEMA 10-15 mol % and NIPAM 10-15 mol % respectively) can be due to the results of sample 2 and 4 being faulty. The explanation could also be that the values are correct and that the addition of only 5 mol % was enough to change the morphology of the film in a way generating a higher MVTR, and increasing the mol % of comonomer did not change the morphology in the same way, thus not generating a higher MVTR.

Overall, it can be concluded that this method is not optimal for increasing hydrophilicity of PSAs as the method is somewhat complicated to perform and the purification of the copolymers is time consuming and unsatisfactory. However, silicone compatible copolymers were successfully synthesized and characterized. Taking the data retrieved in regard many questions about the quality of the patent application are raised.

6. Future work

For this project, future work would be to further purify the copolymers and then evaluate their adhesive properties directly on the skin. This would give more realistic values to whether or not the modified PSAs have achieved better wet adhesion or not. Also to redo the formulations without bubbles and once again measure MVTR. To add more analysis in form of morphology analysis to se whether or not there is a difference in structure between the different formulations.

Another project of future work is to evaluate the new patent application from Convatec Technlogies Inc. [24] where PSAs are modified by the addition of a low molecular weight, organic, hydroxy containing compound. This method is more straight on and does not involve any complicated synthesis or purification steps. It is simply addition of a hydroxy containing compound to a PSA prior to curing. This may be an interesting study for future work.

7. Acknowledgments

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Appendix I – Synthesis and purification

The synthesis was carried out by combining TRIS with the other monomers, see Figure 9. The combination resulted in four copolymers divided into three categories; variations of 95, 90 and 85 mol % of TRIS.

The procedure for the synthesis of poly[TRIS]-based copolymers by free radical polymerization, using poly[TRIS-co-MAA] as an example, is as follows:

1. 49.47 g of TRIS and 0.56 g of MAA was added to a 250 ml round bottomed flask containing a magnetic stirring bar.
2. To the flask was added 120 g of EtOAc to afford a 30 wt % solution.
3. The flask was sealed with a rubber septa and flushed with with nitrogen for 10 minutes.
4. The flask was then placed in an oil bath, as seen in Picture 1.
5. 0.087 g of AIBN, dissolved in EtOAc, was added to the flask when the temperature of the oil bath reached 65 °C.
6. The reaction was continued for 6 hours and stirred at 65 °C under N_2 atmosphere.
7. The solution was poured into a plastic jar, sealed and let to cool down to room temperature.

Calculations of amount of TRIS and MAA needed for the poly(TRIS-co-MAA), sample 1, see below.

$$X + Y = total\ 50\ g\ monomer \quad (1)$$
$$X = TRIS\ [g\ ];\ Y = MAA\ [g\ ]$$

M_{TRIS} = 422.81 g/mol
M_{DMAEMA} = 157.21 g/mol
M_{NIPAM} = 113.16 g/mol
M_{MAA} = 86.06 g/mol
M_{HEAA} = 115.13 g/mol

$$X = M_{TRIS}\left[\frac{g}{mol}\right] * 0.95 * A[mol] = 401.6695A[g] \quad (2)$$
$$Y = M_{MAA}\left[\frac{g}{mol}\right] * 0.05 * A[mol] = 4.303A[g] \quad (3)$$
$$A = total\ amount\ mol$$

$$X + Y = 50 = 405.9725A \quad (4)$$
$$A=0.12316\ mol$$

$$X = 422.82 * 0.95 * 0.12316 = 49.47\ g$$
$$Y = 86.06 * 0.05 * 0.12316 = 0.53\ g$$

See Table 5-8 for detailed composition of all monomers.

Table 5 poly(TRIS-co-MAA)

Monomer	Sample A*	Sample B*	Sample 1
TRIS (g)	49.47	48.90	48.28
MAA (g)	0.56	1.11	1.78
AIBN (g)	0.087	0.088	0.087
EtOAc (g)	120	120	120
Molar fraction (TRIS/MAA)	0.947/0.053	0.899/0.101	0.847/0.153

Table 6 poly(TRIS-co-DMAEMA)

Monomer	Sample 2	Sample C*	Sample 3
TRIS (g)	49.04	48.02	46.92
DMAEMA (g)	0.96	2.00	3.08
AIBN (g)	0.087	0.087	0.087
EtOAc (g)	120	120	120
Molar fraction (TRIS/DMAEMA)	0.95/.05	0.89/0.11	0.85/0.15

Table 7 poly(TRIS-co-NIPAM)

Monomer	Sample 4	Sample 5	Sample 6
TRIS (g)	49.32	48.56	47.75
NIPAM (g)	0.70	1.44	2.25
AIBN (g)	0.087	0.087	0.088
EtOAc (g)	120	120	120
Molar fraction (TRIS/NIPAM)	0.95/0.05	0.90/0.10	0.85/.15

Table 8 poly(TRIS-co-HEAA)

Monomer	Sample 7	Sample 8	Sample 9
TRIS (g)	49.29	48.53	47.72
HEAA (g)	0.72	1.44	2.30
AIBN (g)	0.087	0.087	0.087
EtOAc (g)	120	120	120
Molar fraction (TRIS/HEAA)	0.95/0.05	0.90/0.10	0.85/0.15

* Sample A, B and C were not further evaluated.

Purification by precipitation

1. The weight of the crude polymer was adjusted to a 30 wt % solution and added to a 250 mL glass separation funnel.
2. 1500 mL of MeOH was added to a 2000 mL beaker.
3. The copolymer solution was drop wise precipitated into the MeOH while constant stirring, as seen in Picture 2.
4. The copolymer, seen in Picture 3, (a white, tacky, soft solid) was then retrieved, by pouring off the solution and picking up the polymer, and stored in a sealed cup.

Some observations made during the purification step are:

1. The copolymer precipitates as white threads.
2. The copolymer is quite firm and non-sticky.
3. The solution is clear until the end where it turns turbid and the copolymer is more tacky and sticky.

First purification method

Sample A, B and C were not further evaluated as they were purified by another method that proved to be insufficient to purify polymers. In the patent application the purification step was described as "washing the copolymer with MeOH", hence, in this project the procedure was interpreted into the following:

The copolymer was dried after the synthesis and then dissolved in 20 g EtOAc on that was added the double amount of MeOH (40 g). The solution was stirred manually with a spoon or such and left to sit for 24 hours. The excess MeOH/EtOAc was poured off after 24 hours and 40 g of MeOH was added again. In total the procedure was repeated three times. According to NMR spectra there was more than 10 % monomer left after this purification step and that is why the method was disregarded. Sample A, B, C and 2 were purified by this method but since there was no time left to purify sample A, B and C according to the purification described above they were not further evaluated.

As this method showed to be insufficient it was decided to proceed with a more commonly used method, see Chapter 3 - Synthesis and purification of copolymer.

Appendix II – Formulation and contact angle

Formulation

The copolymers were blended with a silicone adhesive (two component system) in ratio 1:20. The procedure is as follows (poly[TRIS-co-MAA] is set as an example):

1. 0.798 g of copolymer was blended with a conventional PDMS at 5 wt% (5.016 g of component A and 5.014 g of component B) prior to curing.
2. The blend was mixed in a SpeedMixer DAC 150 FVX-K for 30 seconds at speed of 3 500 rpm.
3. It was cast onto a PUR-coated film (thickness 20 µm); coating thickness of 300 µm.
4. The film was cured on a heating plate, 150 °C, for 15 minutes.

Since the copolymers (after purification) where not dried to a 100 % calculations of the percentage of solvent left had to be done before any formulations could be made.

Calculating percentage of solvent left in the wet copolymer was performed as follows (taking Sample 1 as example):

1. 3.43 g of copolymer was set to dry in an oven at 45°C
2. After one day the sample was weighted to 2.01 g
3. The weight difference is the amount of solvent in the wet copolymer

$$\frac{3.43 - 2.01}{3.43} * 100 = 41.39\ wt\ \%\ solvent\ in\ the\ wet\ copolymer$$

Table 9 Wt % solvent in copolymer after purification.

Sample	Wet weight (g)	Dry weight (g)	wt % solvent in wet copolymer	wt % solvent in wet copolymer after removal of *some* solvent [FINAL]
1	3.43	2.01	41.39	37.35
2	3.81	2.78	27.03	24.30
3	3.63	2.49	31.40	27.57
4	3.63	2.52	30.57	26.60
5	5.00	3.35	33.00	18.99
6	3.57	2.27	36.41	28.12
7	3.62	2.19	39.50	22.98
8	3.01	2.05	31.89	29.38
9	4.87	2.91	40.24	34.25

Table 10 (g) copolymer needed to acheive a 5 wt % in the formulation blend (based on Table 10 last column)

Formulation (sample)	Wet copolymer (g)	Component A (g)	Component B (g)	wt % copolymer in blend
1	0.798	5.016	5.014	4.75
2	0.655	5.036	5.057	4.68
3	0.692	5.018	5.037	4.75
4	0.678	5.013	5.024	4.72
5	0.615	5.028	5.020	4.72
6	0.698	5.029	5.023	4.75
7	0.699	5.027	5.034	5.07
8	0.716	5.018	5.050	4.78
9	0.761	4.968	4.934	4.82

Contact angle

Contact angle measurements were performed on a EASYDROP Contact Angle Measurement System from KRÜSS with DSA1 control and evaluating software.

1. A sample, size 2 cm x 5 cm, was taken from each formulation.
2. One sample at a time was put on the sample table, see Picture 4.
3. The sample was illuminated with a PC-controlled illumination.
4. The syringe was filled with deionized water and a droplet, size 3 µL, was produced at the tip of the needle and applied on the surface.
5. Pressing start in the computer software system the measurements started and proceeded for one minute.
6. Three positions were tested on each sample.

Appendix III – Results

MVTR

For the calculations of the MVTR values Equation (1) was applied

$$X = \frac{(W_1+W_2)*1000*24}{T} \quad (1)$$

where

$X = MVTR\ (g * m^{-2} * 24h^{-1})$
$W_1 = mass\ of\ the\ cylider\ including\ belonging\ devices, sample\ and\ test\ liquid$
$W_2 = mass\ of\ the\ cylider\ including\ belonging\ devices, sample\ and\ test\ liquid\ after\ test\ period$
$T = test\ period\ in\ hours$

In this experimental setup deionized water was used as liquid and the test period was set to 24 hours.

Table 11 MVTR raw data (red-marked number is disregarded)

Formulation	W1 (g)	W2 (g)	W1-W2 (g)	Average (g)
1	211.9196	211.4015	0,5181	0.5299
	212.3917	211.8254	0,5663	
	213.0770	212.5716	0,5054	
2	212.0806	211.1452	0,9354	0.8383
	212.8864	212.1294	0,757	
	211.4589	210.6363	0,8226	
3	213.7987	213.3518	0,4469	0.4917
	211.9481	211.4588	0,4893	
	213.4925	212.9537	0,5388	
4	213.4925	212.1103	1,3822	1.058
	213.4836	212.5515	0,9321	
	193.8189	192.9592	0,8597	
5	214.0372	213.5713	0,4659	0.4681
	213.8197	213.3245	0,4952	
	212.4946	212.0513	0,4433	
6	212.7705	212.1994	0,5711	0.5937
	212.4817	211.7913	0,6904	
	214.7531	214.2335	0,5196	
7	211.6362	211.1662	0,4700	0.4701
	212.1055	211.6317	0,4738	
	212.6865	212.2200	0,4665	
8	213.8735	213.3730	0,5005	0.5050
	213.4656	212.9915	0,4741	
	210.7122	210.1718	0,5404	
9	212.1140	211.6611	0,4529	0.4998
	214.0479	213.4419	0,6060	
	213.5159	213.0754	0,4405	
R	212.7272	212.2760	0,4512	0.4412
	213.8336	213.4024	0,4312	

SEC

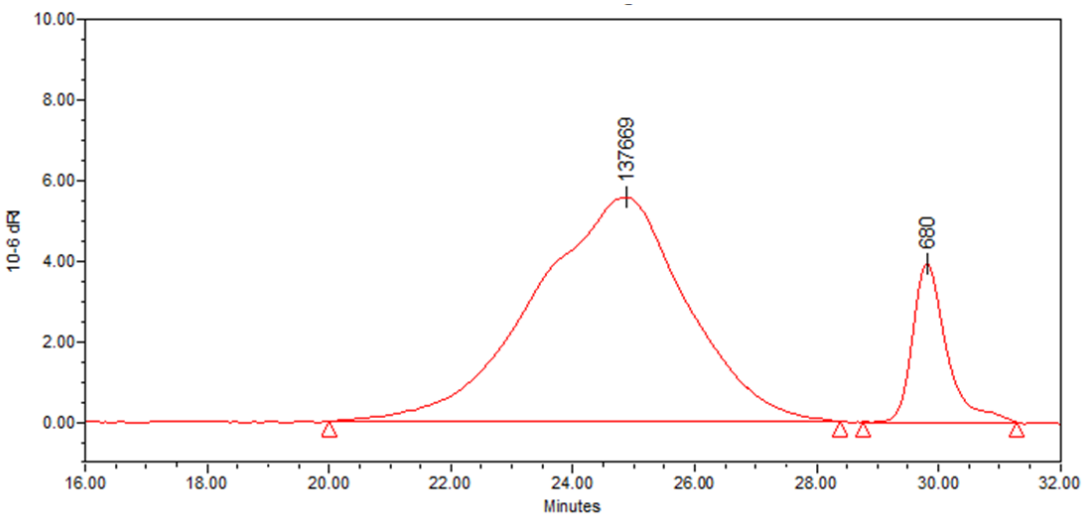

Figure 16 SEC of Sample B, M_W = 508 456 g/mol

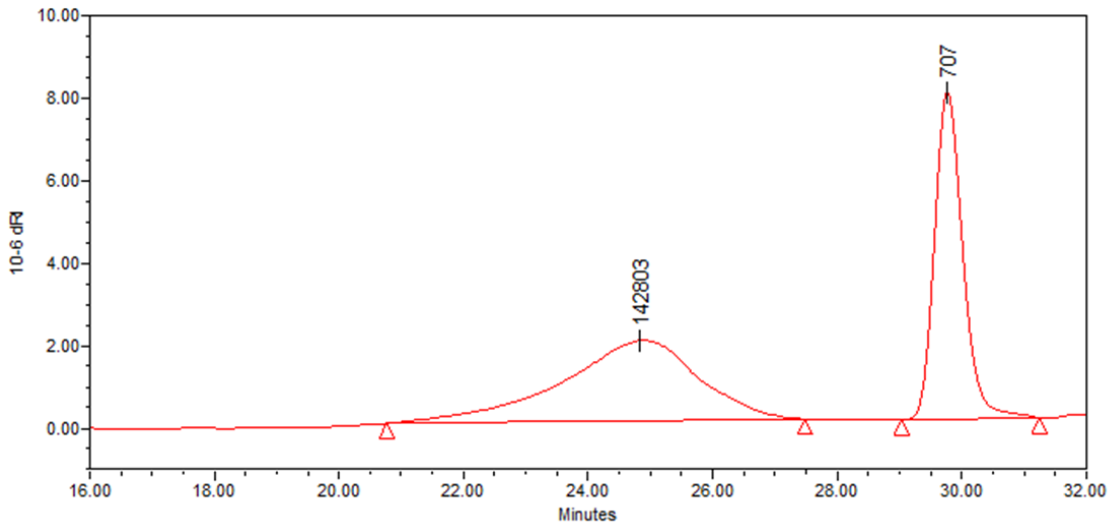

Figure 17 SEC of Sample C, M_W = 443 117 g/mol

^{1}H- NMR

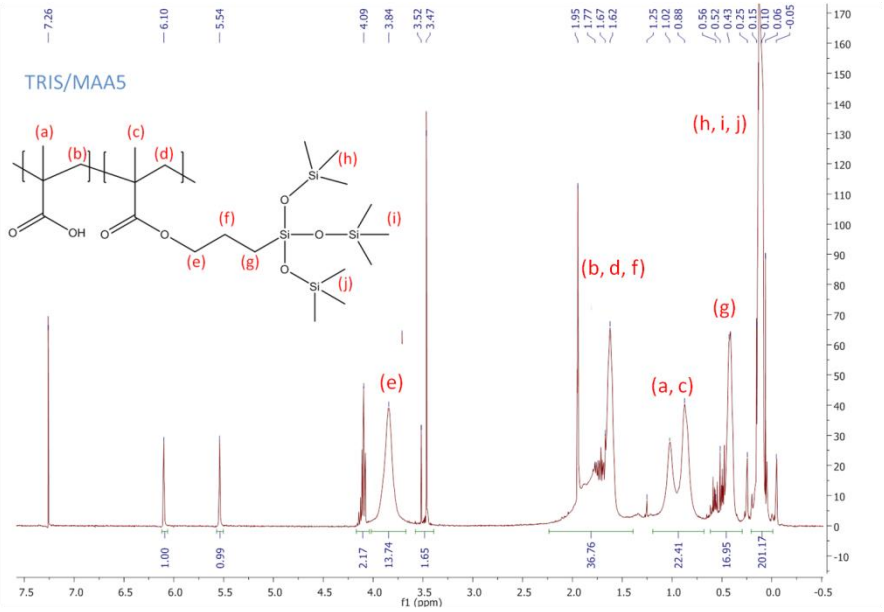

Figure 18 NMR of Sample A

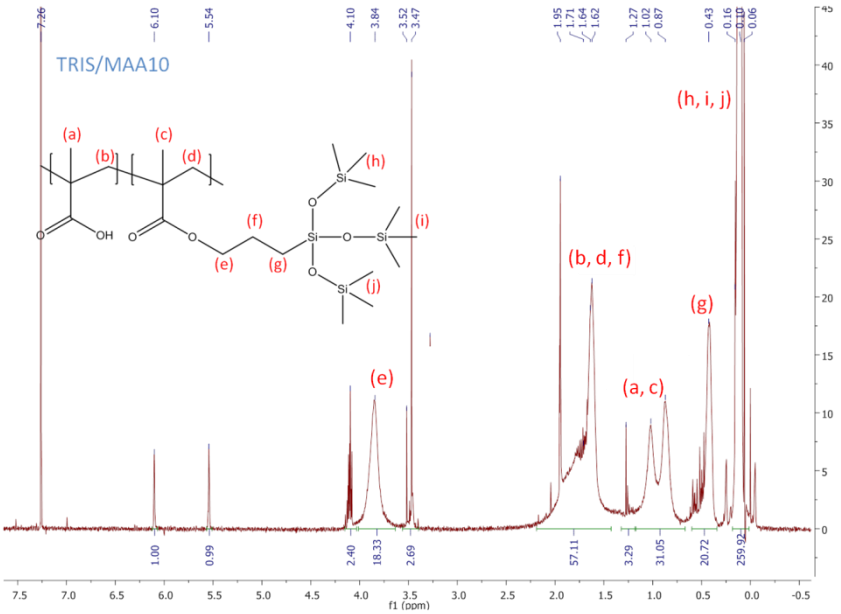

Figure 19 NMR of Sample B

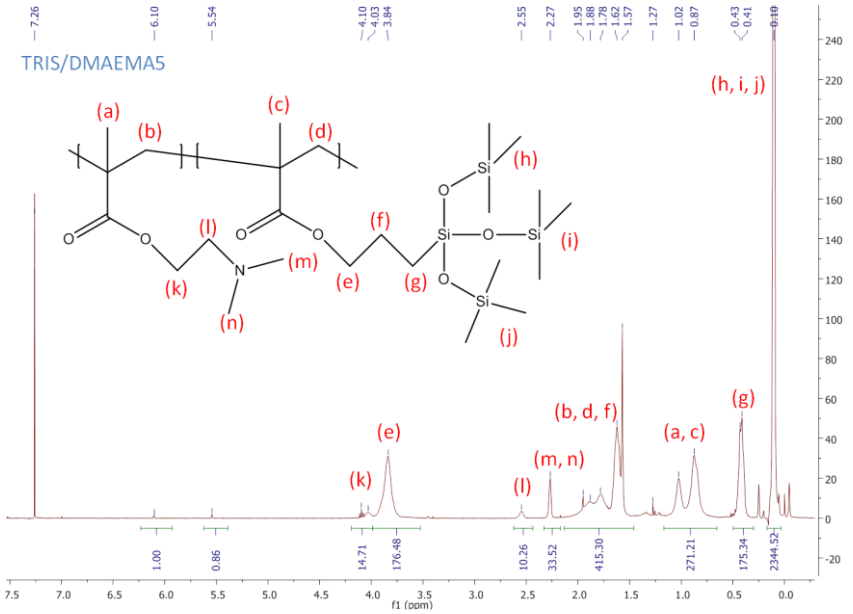

Figure 20 NMR of Sample 2

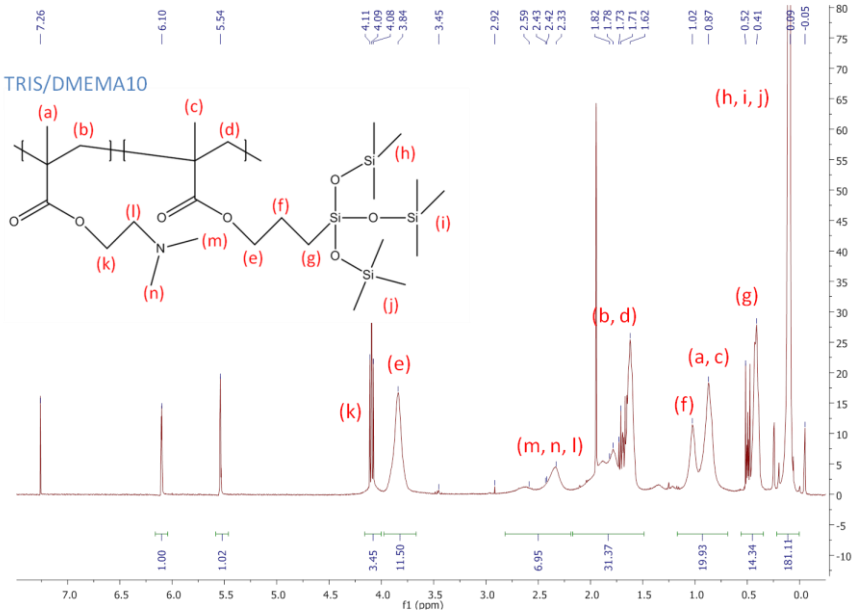

Figure 21 NMR of Sample C

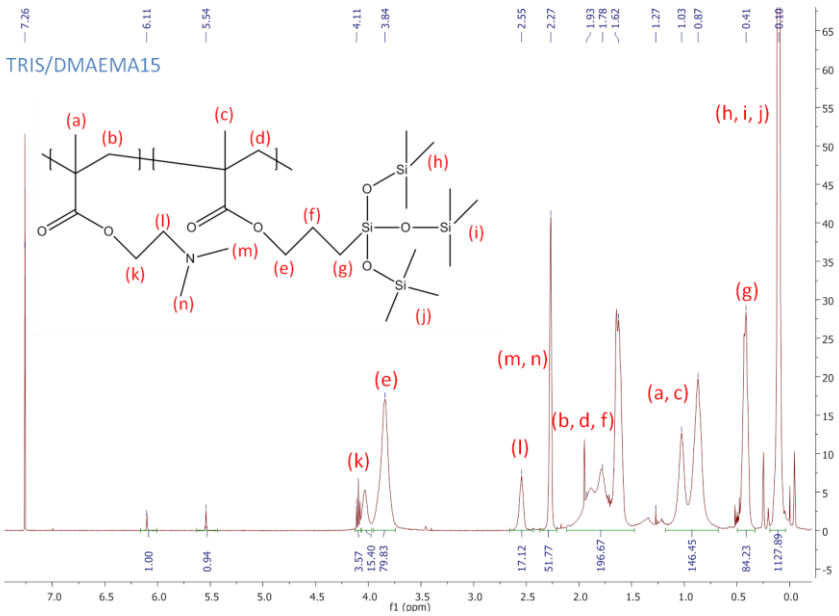

Figure 22 NMR of Sample 3

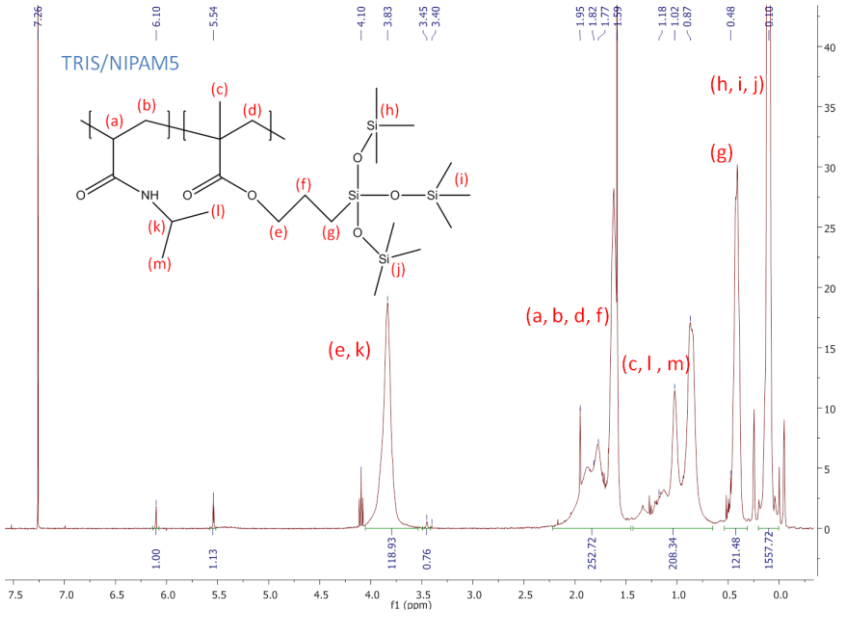

Figure 23 NMR of Sample 4

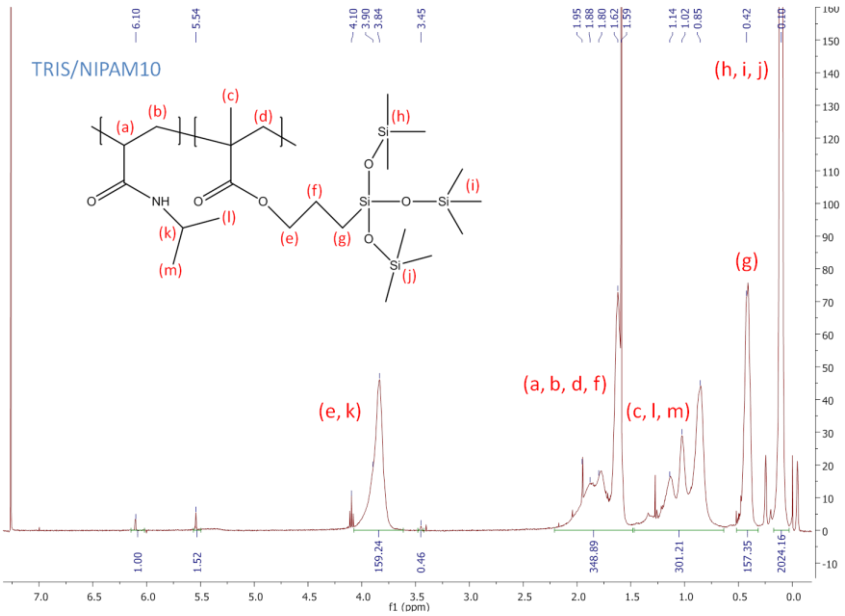

Figure 24 NMR of Sample 5

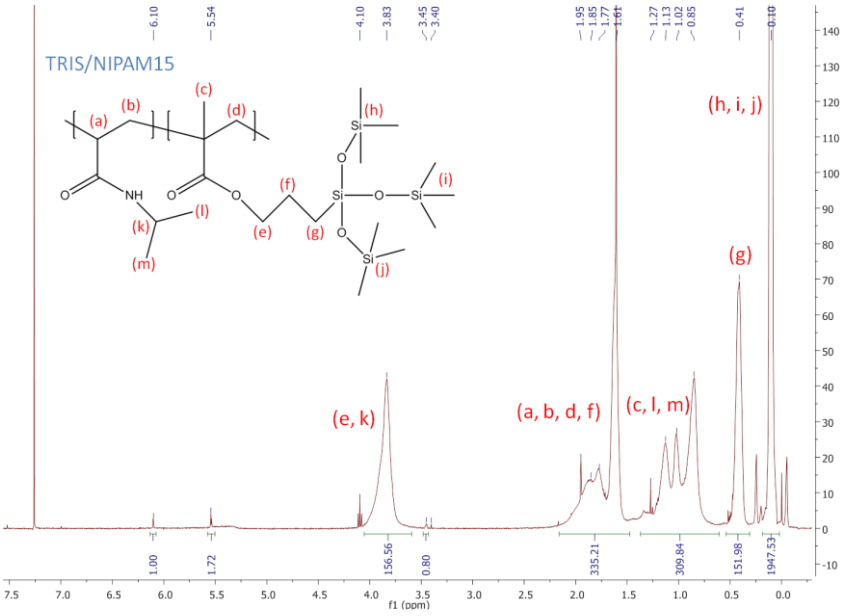

Figure 25 NMR of Sample 6

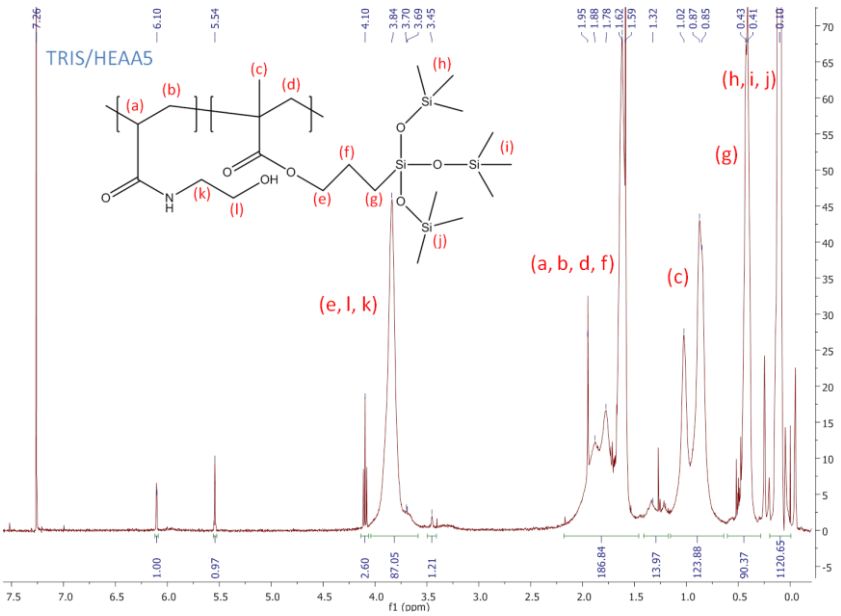

Figure 26 NMR of Sample 7

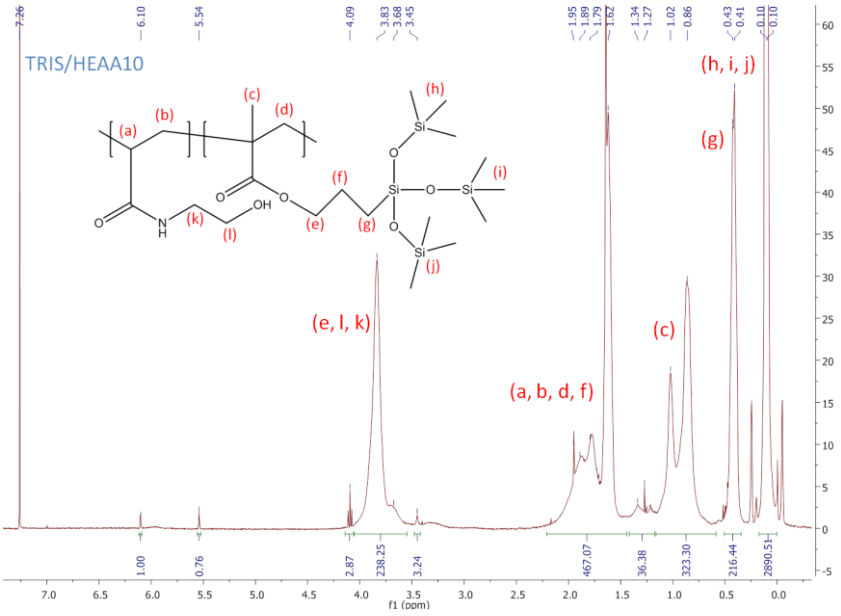

Figure 27 NMR of Sample 8

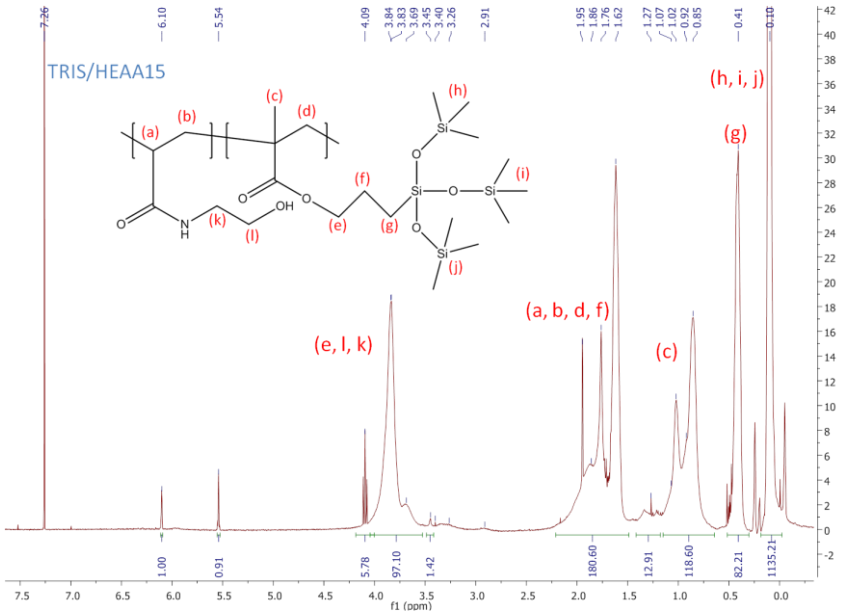

Figure 28 NMR of Sample 9