

# CHARACTERIZATION OF POLYELECTROLYTES FOR SLUDGE DEWATERING



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FOR SLUDGE DEWATERING

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[stowa@stowa.nl](mailto:stowa@stowa.nl) [www.stowa.nl](http://www.stowa.nl)

TEL 033 460 32 00

Stationsplein 89 3818 LE Amersfoort

POSTBUS 2180 3800 CD AMERSFOORT

Publicaties van de STOWA kunt u bestellen op [www.stowa.nl](http://www.stowa.nl)

# COLOFON

UITGAVE Stichting Toegepast Onderzoek Waterbeheer  
Postbus 2180  
3800 CD Amersfoort

## PROJECTUITVOERING

Patrizio Raffa (Wetsus)  
Leon Korving (Airforo)  
Francesco Picchioni (university of Groningen)

## BEGELEIDINGSCOMMISSIE

Wilbert Oltvoort – Waterschap Rijn en IJssel  
Hans Reith – Waterschap Vechtstromen  
David van der Elst – Waterschap Noorderzijlvest  
Gerrit Post – Hoogheemraadschap Hollands Noorderkwartier  
Alex Veltman – Waternet  
Thijs van Osch – Waterschap Aa en Maas  
Cora Uijterlinde - STOWA

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# TEN GELEIDE

Slibontwatering en slibafzet zijn voor de waterschappen belangrijke kostenposten. De kosten voor de noodzakelijke dosering van chemicaliën of polyelektrolyten of polymeren, zijn daar een onderdeel van. Eerder STOWA-onderzoek laat zien dat het ontwateren van slib steeds meer moeite kost waardoor het gebruik van polyelektrolyt en daardoor de kosten van ontwatering toenemen. De zuiveringsbeheerders zijn daarom voortdurend op zoek naar mogelijkheden om efficiënter om te gaan met polyelektrolyt met behoud van hetzelfde ontwateringsresultaat.

Tijdens het onderzoek naar de kwaliteit van polyelectrolyten is een protocol voor de karakterisering van polyelektrolyten voor slibontwatering opgesteld om de kwaliteit van de gebruikte polyelectrolyten te kunnen monitoren. Dit protocol maakt als het ware een "vingerafdruk" van de polyelectrolyten en maakt het mogelijk om verschillende producten te onderscheiden en eventuele veranderingen in de kwaliteit van een bepaald product vast te stellen. Een dergelijke methode draagt bij aan de controle van de kwaliteit van het polyelectrolyt dat door waterschappen ingekocht wordt.

Er zijn verschillende analytische technieken getest om informatie over de bepalende eigenschappen van een polyelectrolyt te verkrijgen. In de studie zijn voor twaalf verschillende polyelectrolyten de eigenschappen bepaald met de diverse technieken.

Op basis van deze studie wordt aanbevolen om in overleg met de zuiveringsbeheerders de interesse voor het toepassen van de kwaliteitsbepaling te inventariseren. Bij voldoende interesse kan de methode verder ontwikkeld worden en kan op basis van een dergelijk protocol in de praktijk ervaring opgedaan worden met het intensiever testen van de polyelectrolyten.

Met de resultaten van dit project krijgen zuiveringsbeheerders een middel in handen om de kwaliteit van polyelectrolyten te controleren en daarmee het gebruik te optimaliseren zodat chemicaliën en kosten bespaard kunnen worden.

J.J. Buntsma  
directeur

# SAMENVATTING

Dit project beoogde een experimentele methode te ontwikkelen voor het karakteriseren van op polyacrylamide gebaseerde polyelectrolyten die door de Nederlandse waterschappen worden gebruikt voor slibontwatering. Een dergelijke methode zou bruikbaar moeten zijn als middel om de kwaliteit van het polyelectrolyt (PE) dat men inkoopt te controleren.

Voor deze verkenning zijn verschillende analytische technieken getest om informatie over de bepalende eigenschappen van een PE te verkrijgen, namelijk: het molecuulgewicht, de chemische samenstelling, de structuur en de ladingdichtheid. Voor deze aanpak is onder andere gebruik gemaakt van element analyse, proton-NMR, gelpermeatiechromotografie (GPC), geleidbaarheid, afschuifviscositeit en dynamische reologische metingen.

In de studie zijn voor twaalf verschillende PE's de eigenschappen bepaald met de diverse technieken. Deze eigenschappen resulteerden in een dataset met eigenschappen waarmee een "fingerprint" van de verschillende PE's werd verkregen. Met behulp van een principale componenten analyse is vervolgens het minimum aantal parameters onderzocht dat nodig is om de spreiding in de dataset te beschrijven. Deze analyse liet zien dat een combinatie van de meting van de elementsamenstelling en afschuifviscositeit bij verschillende concentraties voldoende is om de twaalf PE's van elkaar te onderscheiden. Deze bepalingen moeten plaats vinden met het pure PE dat verkregen wordt door een extractie met aceton om zo de storende invloed van zouten of andere componenten in de emulsie uit te sluiten.

Deze aanpak is vervolgens verder getest door in een quickscan de meetfout van de meetmethode vast te stellen. Vervolgens is de methode gebruikt om van de kwaliteit van één PE soort afkomstig van verschillende batches met elkaar te vergelijken. Deze scan liet zien dat de methode voldoende nauwkeurig was om verschillen aan te tonen tussen zes monsters van hetzelfde PE. De studie ging niet zo ver dat ook onderzocht kon worden of deze verschillen zodanig groot zijn dat zij leiden tot een andere prestatie van het PE.

De gevolgde aanpak is in twee workshops teruggekoppeld aan vertegenwoordigers van waterschapslaboratoria, commerciële laboratoria en PE-leveranciers. Deze terugkoppeling leverde geen zwaarwegende inhoudelijke bezwaren op tegen de voorgestelde methode. De PE-leveranciers geven aan dat zij vertrouwen op hun eigen ISO gecertificeerde kwaliteitssystemen om de kwaliteit van hun product te garanderen. Verder wijzen zowel de laboratoria als de PE leveranciers op het belang van verdere standaardisatie en normering van de aanpak. Voor de laboratoria is het verder van belang dat er een reëel perspectief is op omzet voor deze aanpak, wil het voor hen zin hebben om een commercieel pakket aan te bieden. Zij zullen namelijk moeten investeren in meetapparatuur voor bepaling van de viscositeit van het PE en in de ontwikkeling van de methode. Een eerste schatting laat zien dat een kwaliteitsbepaling 300-400 €/monster kost bij een omzet van ongeveer 500 monsters per jaar.

Op basis van deze studie wordt aanbevolen om in overleg met de zuiveringsbeheerders de potentiële markt voor een dergelijke kwaliteitsbepaling te kwantificeren. Bij voldoende interesse kan de methode verder ontwikkeld worden zodat de meetfout zo klein mogelijk wordt. Op basis van een dergelijk protocol zou dan een pilot project kunnen worden gestart

om ervaring op te doen met de methode en ook meer inzicht te krijgen in variaties in de kwaliteit en de invloed daarvan op de slibontwatering. Uiteindelijk zou dit dan kunnen leiden tot het vaststellen van acceptabele toleranties voor de variatie in de kwaliteit.

# DE STOWA IN HET KORT

STOWA is het kenniscentrum van de regionale waterbeheerders (veelal de waterschappen) in Nederland. STOWA ontwikkelt, vergaart, verspreidt en implementeert toegepaste kennis die de waterbeheerders nodig hebben om de opgaven waar zij in hun werk voor staan, goed uit te voeren. Deze kennis kan liggen op toegepast technisch, natuurwetenschappelijk, bestuurlijk-juridisch of sociaalwetenschappelijk gebied.

STOWA werkt in hoge mate vraaggestuurd. We inventariseren nauwgezet welke kennisvragen waterschappen hebben en zetten die vragen uit bij de juiste kennisleveranciers. Het initiatief daarvoor ligt veelal bij de kennisvragende waterbeheerders, maar soms ook bij kennisinstellingen en het bedrijfsleven. Dit tweerichtingsverkeer stimuleert vernieuwing en innovatie.

Vraaggestuurd werken betekent ook dat we zelf voortdurend op zoek zijn naar de 'kennisvragen van morgen' – de vragen die we graag op de agenda zetten nog voordat iemand ze gesteld heeft – om optimaal voorbereid te zijn op de toekomst.

STOWA ontzorgt de waterbeheerders. Wij nemen de aanbesteding en begeleiding van de gezamenlijke kennisprojecten op ons. Wij zorgen ervoor dat waterbeheerders verbonden blijven met deze projecten en er ook 'eigenaar' van zijn. Dit om te waarborgen dat de juiste kennisvragen worden beantwoord. De projecten worden begeleid door commissies waar regionale waterbeheerders zelf deel van uitmaken. De grote onderzoeklijnen worden per werkveld uitgezet en verantwoord door speciale programmacommissies. Ook hierin hebben de regionale waterbeheerders zitting.

STOWA verbindt niet alleen kennisvragers en kennisleveranciers, maar ook de regionale waterbeheerders onderling. Door de samenwerking van de waterbeheerders binnen STOWA zijn zij samen verantwoordelijk voor de programmering, zetten zij gezamenlijk de koers uit, worden meerdere waterschappen bij één en het zelfde onderzoek betrokken en komen de resultaten sneller ten goede van alle waterschappen.

De grondbeginselen van STOWA zijn verwoord in onze missie:

*Het samen met regionale waterbeheerders definiëren van hun kennisbehoeften op het gebied van het waterbeheer en het voor én met deze beheerders (laten) ontwikkelen, bijeenbrengen, beschikbaar maken, delen, verankeren en implementeren van de benodigde kennis.*

# SUMMARY

This project aims at suggesting some guidelines for the development of an experimental protocol for the characterization of polyacrylamide-based polyelectrolytes (PE), used by the Dutch water authorities for sludge dewatering.

Various experimental techniques have been used, in order to gain information about key properties of these materials, such as molecular weight, chemical composition and structure, charge density. In particular elemental analysis, proton-NMR, Gel Permeation Chromatography, conductance measurements, shear viscosity and dynamic rheological measurements have been performed. This study generated a set of data for several samples, allowing to obtain an experimental “fingerprint”, which allows to distinguish between different PE and assess the quality of a product coming from different batches. A Principal Component Analysis has been performed on the data, to establish the minimum number of independent variables able to distinguish among different samples. As a result, a relatively simple experimental protocol based on elemental analysis and viscosity measurements at different concentrations is suggested.



# STOWA IN BRIEF

The Foundation for Applied Water Research (in short, STOWA) is a research platform for Dutch water controllers. STOWA participants are all ground and surface water managers in rural and urban areas, managers of domestic wastewater treatment installations and dam inspectors.

The water controllers avail themselves of STOWA's facilities for the realisation of all kinds of applied technological, scientific, administrative legal and social scientific research activities that may be of communal importance. Research programmes are developed based on requirement reports generated by the institute's participants. Research suggestions proposed by third parties such as knowledge institutes and consultants, are more than welcome. After having received such suggestions STOWA then consults its participants in order to verify the need for such proposed research.

STOWA does not conduct any research itself, instead it commissions specialised bodies to do the required research. All the studies are supervised by supervisory boards composed of staff from the various participating organisations and, where necessary, experts are brought in.

The money required for research, development, information and other services is raised by the various participating parties. At the moment, this amounts to an annual budget of some 6,5 million euro.

For telephone contact number is: +31 (0)33 - 460 32 00.

The postal address is: STOWA, P.O. Box 2180, 3800 CD Amersfoort.

E-mail: [stowa@stowa.nl](mailto:stowa@stowa.nl).

Website: [www.stowa.nl](http://www.stowa.nl).

# CHARACTERIZATION OF POLYELECTROLYTES FOR SLUDGE DEWATERING

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# 1

## DESCRIPTION OF THE PROJECT

Dutch water authorities make extensive use of polyacrylamide-based polyelectrolytes (PE), but usually the suppliers provide little information about key attributes such as molecular weight, structure and charge distribution. This makes it difficult for the water authorities to understand differences between products and even more difficult to ensure a consistent quality of the delivered product, in terms of reproducible performances of a product coming from different production batches.

Ideally, the water authorities would like to have a simple method to obtain a “fingerprint” of the PE’s, which would allow to detect any changes in quality. The measured properties should have a clear relationship with the application of the PE’s. Secondly, the measured differences in properties could also be used to compare products with each other, allowing a pre-selection of potential candidates for a given use.

This project aims at testing some techniques applicable in this context to polyacrylamide-based PE’s.

The focus is on techniques that would be simple and inexpensive to implement by a water laboratory or at the site of a sludge dewatering plant. Testing of these techniques has been carried out for four months by Dr. Patrizio Raffa of Wetsus, under the supervision of prof. Picchioni of the research “Product Technology” of the University of Groningen (RUG). This group at the University of Groningen has carried out much research into polyacrylamides for use in the oil industry, for example, gaining a lot of knowledge in their analysis and applications. In addition, the research group has the necessary analytical setup and experience in using it. In particular elemental analysis, proton-NMR, Gel Permeation Chromatography, conductance measurements, shear viscosity and dynamic rheological measurements have been performed.

Leon Korving of Aiforo provided the translation of results to use in water authorities. He performed a principal component analysis of the collected data, which gave the basis for the design of an efficient experimental protocol based on few targeted experimental techniques.

The research led to a recommendation for an appropriate standard “fingerprint” technique and procedure for characterization of PE.

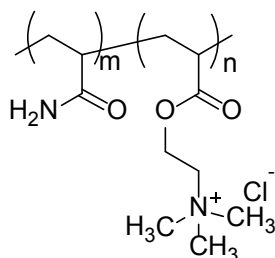
## 2

## RESEARCH APPROACH

## 2.1 POLYMERS GENERAL CHARACTERISTICS

Polyelectrolytes used for sludge dewatering can be of various nature. Water-soluble, cationic, high molecular weight polymers, proved to be very effective flocculants and thus found large use in this process.<sup>1,2</sup> Among the most used polymers are cationic polyacrylamides (c-PAM), which usually are copolymers of acrylamide and substituted acrylates, bearing quaternary ammonium groups as the source of the positive charges (Figure 1).

FIGURE 1 CHEMICAL STRUCTURE OF A C-PAM



These polymers can vary in chemical composition, molecular weight, structure (linear, branched, cross-linked), and charge density. Those characteristics will determine their performance in the application, even though the literature in structure-properties relationships is quite rare.<sup>1</sup> This investigation aims at developing an experimental protocol to obtain a “fingerprint” for various commercially available polyelectrolytes for sludge dewatering (sources: SNF, Kemira, Solenis-Necarbo) and try to relate the measured properties to the mentioned molecular characteristics, to gain insight on structural differences between the different polymers. The samples have been obtained as oil/water emulsions containing 42-58 weight % of active matter. In total twelve different polymers have been investigated. For one polymer two different samples were analyzed. They have been labeled with capital letters from A to M, which will be used from now on to refer to them. Sample L and M have the same polymer. Table 1 reports the names of the different polymers in random order, i.e. the order in table 1 has no relation to the coding. This is done to prevent discussions on quality differences between the different polymer suppliers, as this is not the scope of this study.

1 Bolto, B.; Gregory, J.; Water Research, 2007, 41, 2301 – 2324

2 Teh, C.-Y.; Budiman, P.-M.; Shak, K. P.-Y.; Wu, T.-Y.; Ind. Eng. Chem. Res. 2016, 55, 4363 4389

TABLE 1 POLYMERS ANALYZED IN THIS RESEARCH (IN RANDOMIZED ORDER)

Sample	Provider
C 82090	Kemira
SD 2081	Kemira
EM 3101	SNF
EM 5108	SNF
EM 2315	SNF
EM 803	SNF
EM 997	SNF
EM 3103	SNF
K133L	Solenis/Necarbo
K 166	Solenis/Necarbo
K 242	Solenis/Necarbo
K 233 L	Solenis/Necarbo

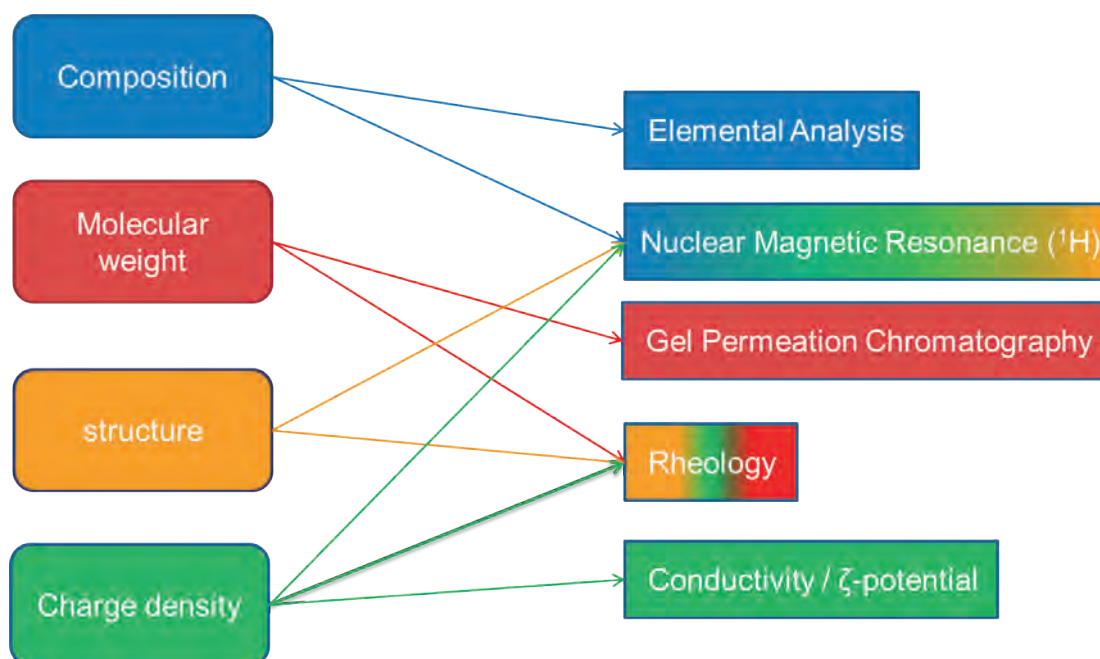
n.r. = not reported

## 2.2 RESEARCH PLAN

Various experimental techniques have been selected, based on the kind of information required from the project and the availability of experimental setup. The relationship between the kind of experiments and the relevant polymer properties are summarized in Scheme 1. Each experimental method will be briefly introduced in the following sections, before discussing the results obtained. The collected experimental procedures furnished datasets for each sample, which were further elaborated in a Principal Component Analysis (PCA). This allowed to propose an experimental protocol able to distinguish among different samples, based on a minimum number of variables.

Finally, a quick scan of the reproducibility of measurement and consistency of measurements across different batches of a specific commercial product was performed.

SCHEME 1 PROPERTIES OF INTEREST FOR THIS STUDY AND THEIR RELATIONSHIP TO THE EXPERIMENTAL TECHNIQUES USED. COLORS ARE USED TO BETTER SHOW THE CONNECTIONS BETWEEN STRUCTURAL INFORMATION NEEDED AND THE CORRESPONDING EXPERIMENTAL TECHNIQUES USED TO OBTAIN THEM.



# 3

## EXPERIMENTAL PROCEDURES AND RESULTS

### 3.1 SAMPLES TREATMENT

As already mentioned, the samples are obtained as emulsions. It is not convenient to measure and compare the properties of the materials as received, because the composition of the complex mixture is ill-defined and varies for each sample in terms of chemical composition and relative amount of components: polymer, water, oil, salts, other additives such as surfactants and emulsion stabilizers. A simple procedure has been used to isolate the polymer from the other components, which consists in precipitating the polymer by adding the mixture to an excess of acetone (technical grade).

A weighed amount (approximately 5-6 g) of the suspension is added dropwise to an excess of acetone (around 50 mL) kept under vigorous stirring (with a magnetic stirring bar). The polymer precipitates as a white solid (Figure 2).

FIGURE 2

EXAMPLE OF POLYMER PRECIPITATE IN ACETONE



The solid is separated by decantation or filtration with a paper filter (Munktell grade 15, 65 g m<sup>2</sup>, flow rate 25s/10 mL, retention 8-12 μm), rinsed with acetone, then dried at 70°C overnight (10 hours). The liquid phase, containing the oil, is concentrated with a rotary evaporator when available, or by gently evaporating the solvent at 40-50°C under air flow, to determine the oil content.

*NB: the solid is usually highly hygroscopic, thus it should be stored in a sealed container to minimize take up of atmospheric water, which can introduce errors in the successive operations.*

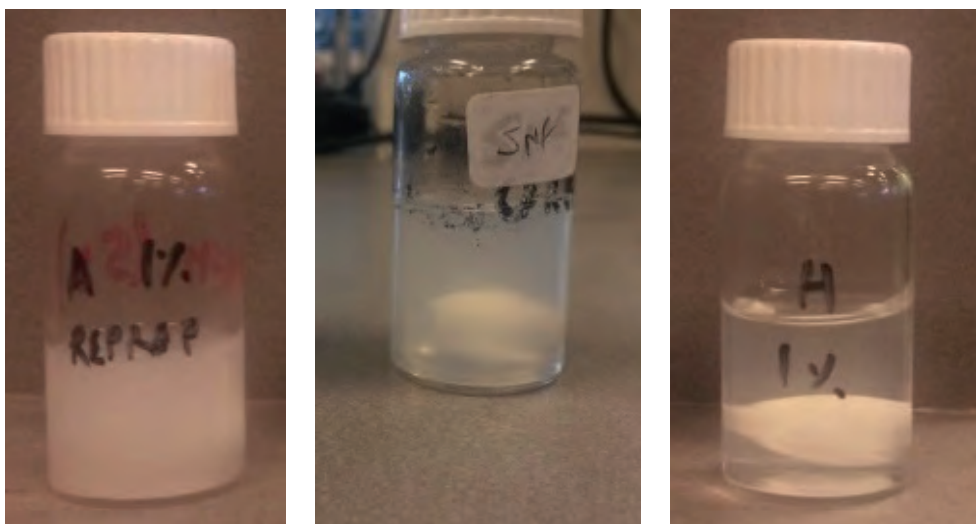
Depending on the sample, the emulsions were from white to yellowish, the solid upon precipitation were all white in color but presented different textures. 1 wt % water solutions

used for further characterization (see following sections) were different in turbidity, ranging from very clear to very turbid (see Figure 3 for examples).

TABLE 1 VISUAL FEATURES OF ANALYZED SAMPLES

Sample	observations emulsion	observations solid	observations 1 wt % solution
A	white	gum	very turbid
B	white	powder	turbid
C	white	sticky chunks	turbid
D	white	sticky chunks	turbid
E	white	powder	clear
F	yellow	flakes	turbid
G	white	sticky chunks	slightly turbid
H	white	powder	clear
I	heterogeneous (stirred before use)	sticky chunks	very turbid
J	white	sticky chunks	very turbid
K	white	chunks	very turbid
L	whitish	powder	clear
M	whitish	powder	clear

FIGURE 3.1 WT % SOLUTIONS OF SAMPLES A, B AND H (FROM LEFT TO RIGHT), WHICH SHOWS THE DIFFERENCE IN TURBIDITY



### 3.2 SAMPLES COMPOSITION

The composition of samples, in terms of amount of solid and oil, was determined for all samples. After precipitation and drying, the solid content can be calculated by the formula:

$$\text{solid \%} = \frac{\text{dry solid weight}}{\text{emulsion weight}} * 100$$

Also the amount of non-volatile oil fraction can be determined, by evaporating the acetone and water present in the liquid phase (it can be done with a rotary evaporator when available, or by gently evaporating the solvent at 40-50°C under air flow) and weighting the residual liquid. Results are presented in Table 2. For comparison, values declared by the providers are also given, when available. In some cases, significant discrepancies can be observed.



TABLE 2 SOLID AND OIL CONTENT MEASURED FOR THE ANALYZED SAMPLES. MEASUREMENT ERRORS ARE ESTIMATED BASED ON THE NORMAL ACCURACY OF THE APPLIED METHODS

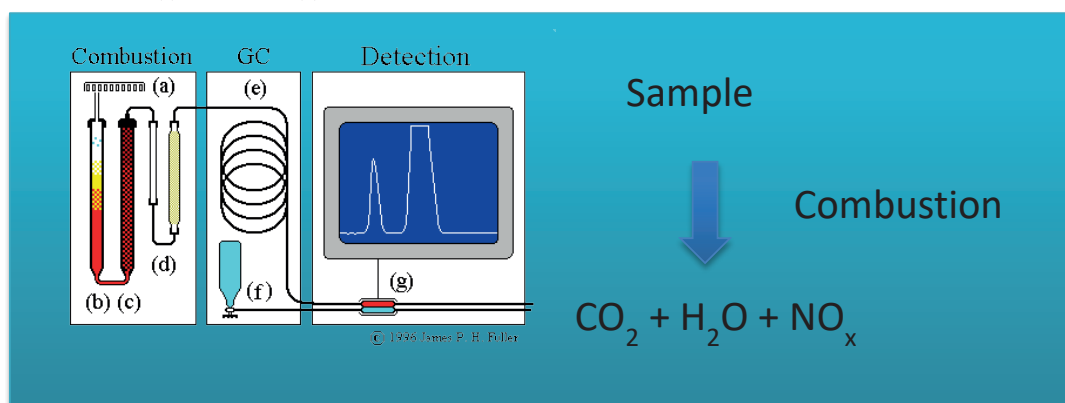
Sample	Nominal active matter %	Measured solid content %	Measured oil content %
A	48	51±2	18±2
B	45	54±2	16±2
C	45	50±2	6±2
D	49	47±2	8±2
E	48	41±2	25±2
F	45	43±2	25±2
G	42	45±2	8±2
H	48	49±2	27±2
I	45	50±2	11±2
J	45 - 52	53±2	17±2
K	49 - 56	59±2	8±2
L	Not specified	45±2	26±2
M	Not specified	45±2	26±2

### 3.3 ELEMENTAL ANALYSIS

#### 3.3.1 INTRODUCTION

Elemental analyses (CHN) were performed with an Eurovector EA coupled to a TCD (Thermal Conductivity). The instrument in its standard setup can determine the content of Carbon, Nitrogen, Hydrogen and Sulfur in a sample. Analysis of other elements such as metals and halogens are sometimes possible, but additional parts are usually required. The technique is based on combusting the sample in a furnace and analyzing the combustion gases after separating them through GC columns. A schematic of the instrument is given in Figure 4. For more details about the technique the reader can find information in analytical chemistry textbooks.

FIGURE 4 SCHEMATIC OF A GENERIC ELEMENTAL ANALYSIS INSTRUMENT. (A) FURNACE; (B), (C), (D) PACKED COLUMNS FOR ABSORPTION; (E) GC COLUMN; (F) REFERENCE GAS; (G) CONDUCTIVITY DETECTOR

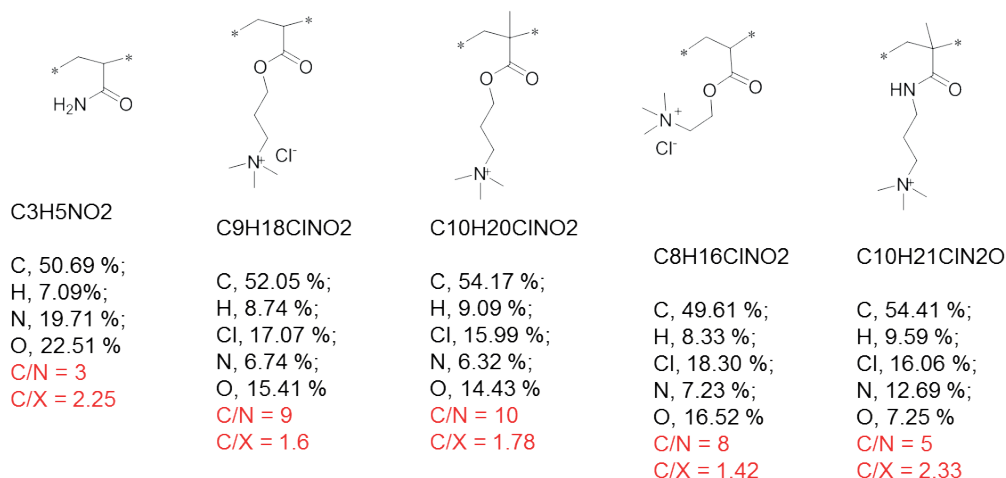


#### 3.3.2 RESULTS AND DISCUSSION

For the polymers analyzed in this work, contents of C, H and N were determined. The two other elements surely present in the samples are Oxygen, which cannot be determined directly, and Chlorine (see structure is figure 1), which cannot be determined with a standard setup. Assuming that no other elements are present, the content of O and Cl can be estimated by difference to 100% of the values obtained for C, H and N. Depending on the composition

of the polymers (kind of monomers and relative amounts), the values of C, H, N and X will be different. In figure 5 some example of possible monomeric units present in the analyzed sample and their corresponding amount of C, H, N and X are given.

FIGURE 5 POSSIBLE MONOMERIC UNITS PRESENT IN THE ANALYZED SAMPLE AND THEIR CORRESPONDING THEORETICAL ELEMENTAL ANALYSIS



The results obtained for the investigated samples are reported in Table 3.

TABLE 3 ELEMENTAL ANALYSIS OF THE ANALYZED SAMPLES. MEASUREMENT ERRORS ARE ESTIMATED BASED ON THE NORMAL ACCURACY OF THE APPLIED METHOD

sample	N (wt %)	C (wt %)	H (wt %)	X (O, Cl)	C/N mol	C/Het
A	7.00±0.05	44.6±0.1	8.6±0.1	39.7±0.1	7.4	1.1
B	6.63±0.05	41.4±0.1	8.0±0.1	43.6±0.2	7.3	0.9
C	6.92±0.05	46.7±0.1	8.6±0.1	37.7±0.1	7.9	1.2
D	8.27±0.05	48.4±0.1	8.5±0.1	34.8±0.1	6.8	1.4
E	10.64±0.05	45.6±0.1	8.0±0.1	35.7±0.1	5.0	1.3
F	5.85±0.05	40.5±0.1	8.6±0.1	45.1±0.1	8.0	0.9
G	7.55±0.05	40.7±0.1	8.1±0.1	43.5±0.1	6.2	0.9
H	7.58±0.05	39.4±0.1	8.1±0.1	44.8±0.1	6.1	0.9
I	6.97±0.05	44.4±0.1	8.5±0.1	40.2±0.1	7.4	1.1
J	7.72±0.05	47.1±0.1	8.6±0.1	36.4±0.1	7.1	1.3
K	7.70±0.05	45.7±0.1	8.6±0.1	38.0±0.1	6.9	1.2
L	8.64±0.05	40.1±0.1	7.8±0.1	43.3±0.1	5.4	0.9
M	8.62±0.05	40.1±0.1	7.9±0.1	43.2±0.1	5.4	0.9
Expected	6.7 - 19.7	50 - 52	7.0 - 8.7	22.5 - 32	3 - 9	1.6 - 2.25

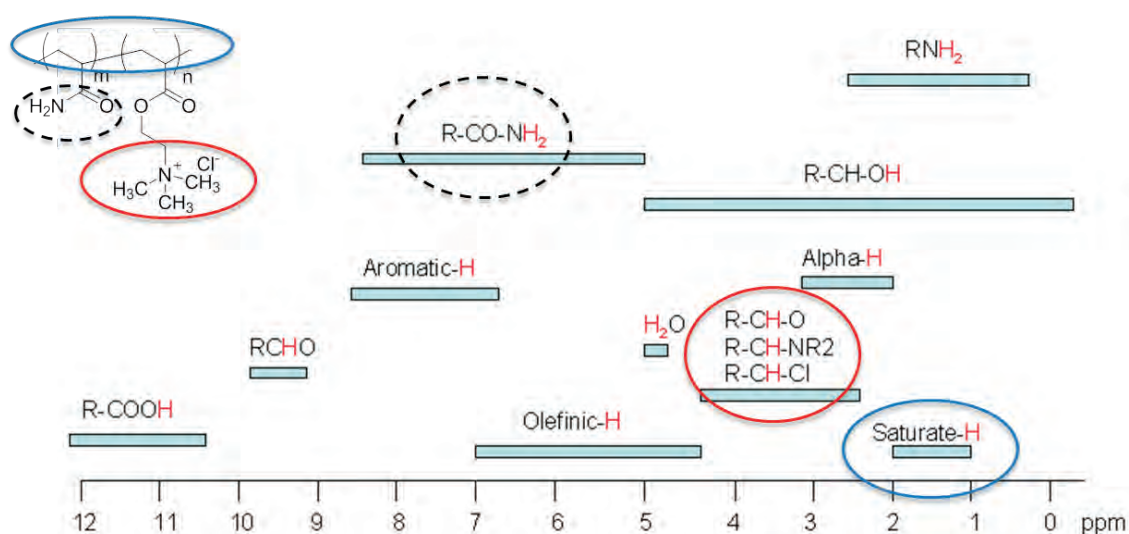
In the last entry of Table 3, the values expected theoretically based on the numbers in Figure 5 are reported. It can be observed that the values for C are systematically lower than the theoretical ones and the X values are higher. This can be explained by the presence of impurities in the sample, the most plausible one being water. The solid samples were carefully dried before being sent to the analysis lab, but as already stated the materials are very hygroscopic and they can uptake water from the atmospheric moisture if not stored properly. For this reason, the most reliable value that can be taken from this analysis is the C/N ratio (expressed in moles in this work), which is independent from the amount of water present in the sample.

### 3.4 PROTON NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

#### 3.4.1 INTRODUCTION

Proton nuclear magnetic resonance ( $^1\text{H-NMR}$ , simply NMR from now on) is a powerful spectroscopic technique for the determination of chemical structures. The theory is extensively treated in many textbooks and will not be discussed here. Shortly, it is based on the characteristic resonance frequencies of certain nuclei, when introduced in a strong magnetic field. The instrument allows to differentiate protons possessing different chemical environment in a molecule, by their different frequency. Thus, protons connected to different functional groups have a different value of frequency. These values are given in an NMR spectra as “chemical shifts”, which are defined as differences of frequency with respect to a reference (protons in tetramethylsilane) and expressed in ppm. Figure 6 shows some typical values of chemical shift for protons in organic molecules, highlighting the ones of interest for this study.

FIGURE 6 TYPICAL NMR CHEMICAL SHIFTS

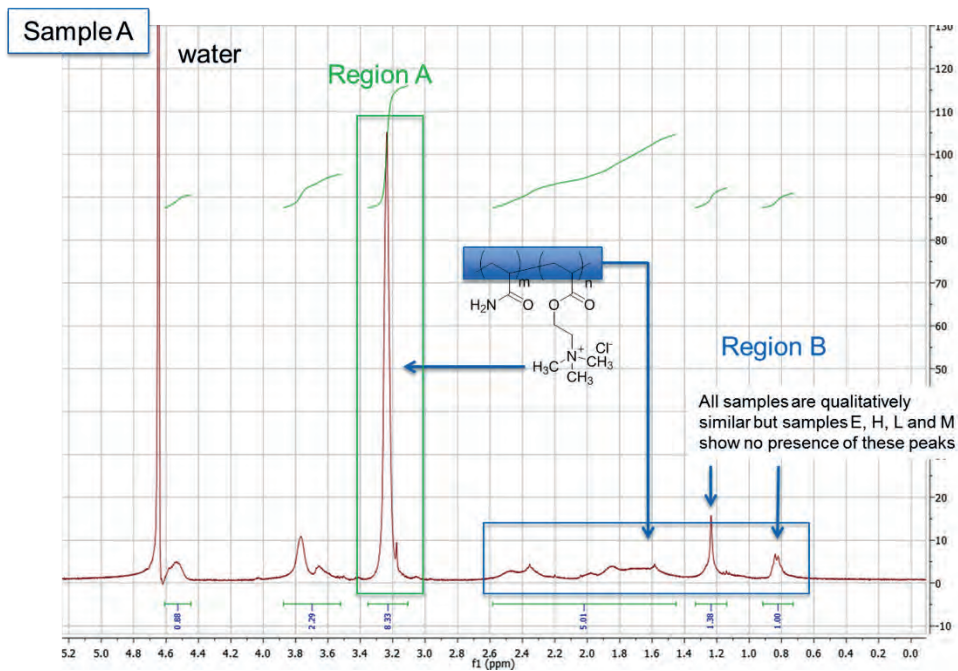


The sample is prepared by dissolving the chemical in a deuterated solvent (the solvent shouldn't contain protons, which would cover the other signals),  $\text{D}_2\text{O}$  in this case. Spectra in this research were recorded on a Varian Mercury Plus 400 MHz spectrometer and the data elaborated with MestReNova 9.1 software.

#### 3.4.2 RESULTS AND DISCUSSION

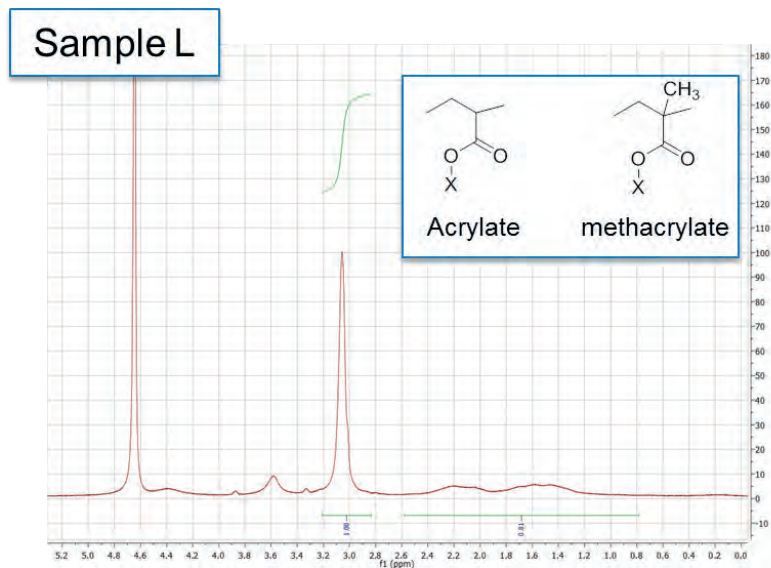
Figure 7 shows spectra of sample A. Most samples resemble qualitatively this sample A. Signals are usually broad, as expected for polymeric systems. Two regions can clearly be identified. Region A contains proton from the quaternary ammonium groups, while region B contains aliphatic protons from the backbone (Figure 6). Integration of the peaks gives values which are proportional to the amount of the corresponding kind of protons. Thus, the A/B integral ratio can give an estimate of the cation group present in the polymer, which is proportional to the charge density. This has been done for all the polymers.

FIGURE 7

NMR SPECTRA OF POLYMER A IN D<sub>2</sub>O

Spectra from samples E, H, L, M show qualitatively different spectra, characterized by the absence of peaks at around 0.8 and 1.2 ppm, which are instead present in the other samples (Figure 8). This might be attributed to the use of different monomers in the synthesis of the polymers, in particular, acrylates instead of methacrylates (insert in Figure 8).

FIGURE 8

NMR SPECTRA OF POLYMER L IN D<sub>2</sub>O

All NMR spectra of polymers A-M are shown in appendix C.

### 3.5 CONDUCTANCE

#### 3.5.1 INTRODUCTION

Conductance is by definition the inverse of resistance. According to SI, conductance is measured in Siemens, which is the inverse of the Ohm ( $S = 1/\Omega$ ). In case of solutions the conductance expresses the amount of electrolytes present. In the specific case, it will be related to the charge density of the polymers. Measurements of conductance were performed for solutions of the studied polymers, at 0.1 wt % concentration in demineralized water. Measurements were performed with a ZetaPALS (B.I.C.) zeta potential analyzer, which is able to measure both conductance and zeta potential.

#### 3.5.2 RESULTS AND DISCUSSION

Results for conductance of the analyzed samples (at 20°C are reported in Figure 9). Since both NMR peak ratio (as defined in section 3.4) and conductance should both increase with the charge density, it is interesting to compare the two sets of data. Results are shown in Figure 10. It is possible to observe a general loose correlation between the two variables, but the scatter is pronounced, because of the heterogeneous chemical structures.

FIGURE 9 CONDUCTANCE VALUE FOR 0.1 WT % SOLUTIONS OF THE STUDIED POLYMERS AT 20 °C. MEASUREMENT ERROR IS ESTIMATED BASED ON THE NORMAL ACCURACY OF THE APPLIED METHOD

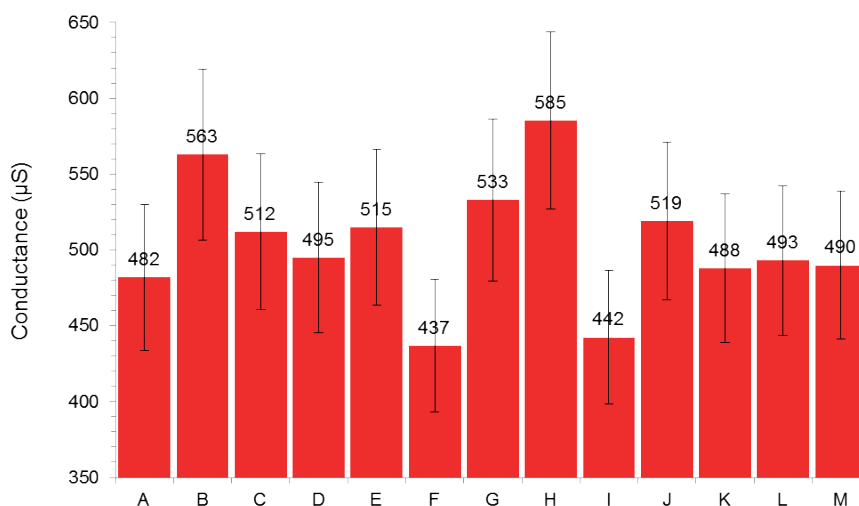
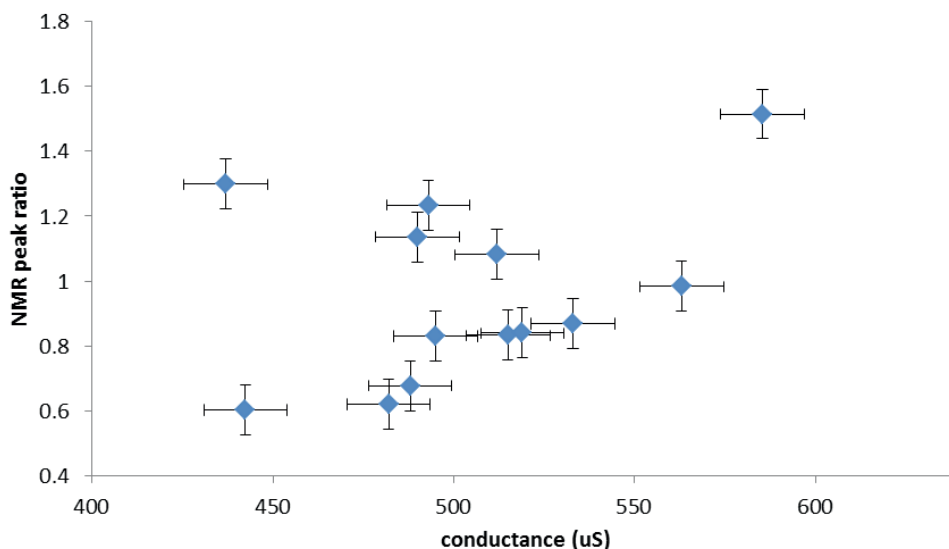


FIGURE 9 PLOT OF CONDUCTANCE VERSUS NMR PEAK RATIO



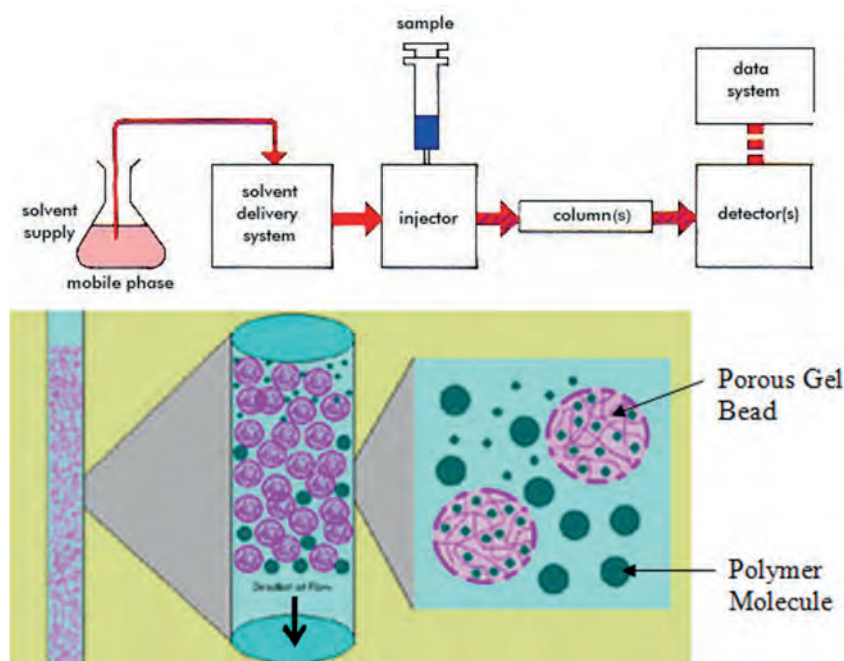
### 3.6 GEL PERMEATION CHROMATOGRAPHY

#### 3.6.1 INTRODUCTION

Gel permeation chromatography (GPC) or size-exclusion chromatography (SEC) is a routine technique in polymer chemistry, used to estimate polymers molecular weight. A schematic GPC apparatus is shown in Figure 10. The polymers are eluted through a column packed with porous gel beads. The elution volume is inversely proportional to the hydrodynamic volume, which in turn depends on the molecular weight.

In this research the analysis was performed on a Agilent 1200 system with Polymer Standard Service (PSS) columns (guard, 104 and 103 Å) with a 50 mM NaNO<sub>3</sub> aqueous solution as the eluent. The columns were operated at 40 °C with a flow rate of 1.00 mL/min, and a refractive index (RI) detector (Agilent 1200) was used at 40 °C. The apparent molecular weights and polydispersity index (PDI) were determined using a polyacrylamide (PAM)-based calibration with WinGPC software.

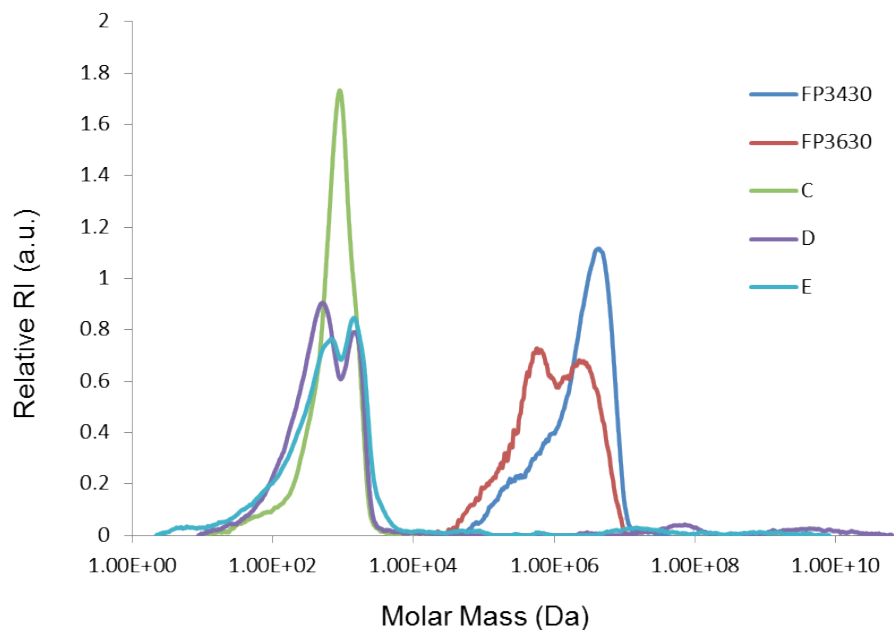
FIGURE 10 SCHEMATIC REPRESENTATION OF A GPC INSTRUMENT



#### 3.6.2 RESULTS AND DISCUSSION

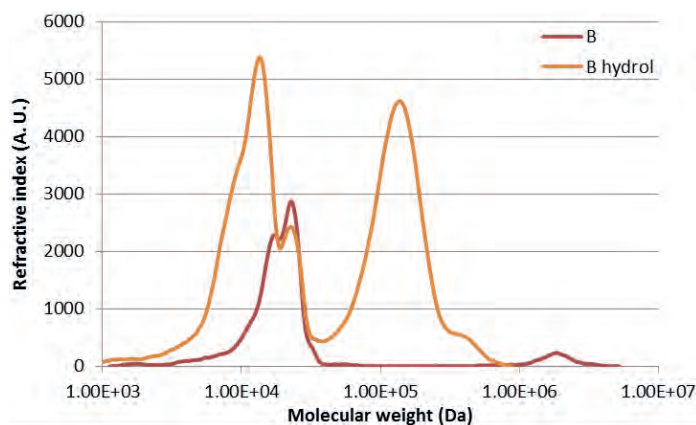
GPC measurements of the studied polymers proved to be unreliable. This kind of polymers should have molecular weights in the range  $10^6$ - $10^7$  Daltons. Figure 11 show the eluogram for samples C, D and E. For comparison, two samples of different anionic polyacrylamides (not from this study) with comparable nominal molecular weight are also shown. It is evidenced that only low-molecular weight peaks are visible, as opposed to samples FP3430 and FP3630, that shows values in the expected range. Possible causes for this observation are: the samples are cross-linked and thus do not go through the column; there is some strong electrostatic interaction between the polymers and the column, which also may cause the polymers not to be eluted.

FIGURE 10 GPC ELUGRAM FOR SAMPLES C, D AND E. TWO POLYMERS FROM A DIFFERENT STUDY (FP3430 AND FP3630) ARE SHOWN FOR COMPARISON



Another attempt was made at determining the molecular weight with GPC, by performing an hydrolysis of the polymer before injection, in order to convert amide functionalities in carboxylic groups, which surely would not interact with the column. Hydrolysis of polymer B was performed by stirring the polymer in a 1 % NaOH solution for 3 days. GPC of polymer B before and after hydrolysis are shown in Figure 11. The appearance of a peak at higher molecular weight, can be observed but low-molecular weight products are still predominant. GPC characterization was abandoned as the time available for this study did not allow further optimization of this approach.

FIGURE 11 GPC OF POLYMER B BEFORE AND AFTER HYDROLYSIS



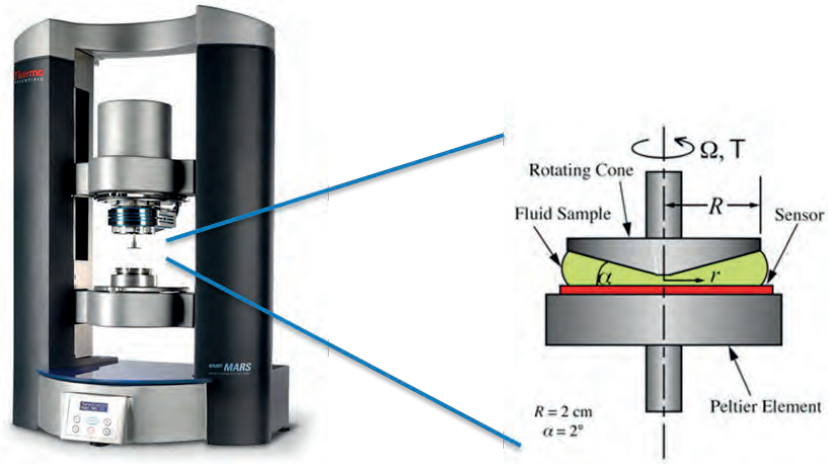
### 3.7 RHEOLOGY

#### 3.7.1 INTRODUCTION

Rheology is the study of the flow of matter. This kind of study is of great interest for viscous fluids, like polymer melts or solutions and for solids that exhibit visco-elastic response, such as rubbers and plastics. There are various commercially available instruments specifically designed to measure rheological properties. For this study, a by Haake Mars III rotational rheometer with a cone-and-plate geometry was used (Figure 12).



FIGURE 12 HAAKE MARS RHEOMETER, SHOWING A SCHEMATIC REPRESENTATION OF THE CONE-AND-PLATE GEOMETRY



For this investigation three different kind of experiments were performed:

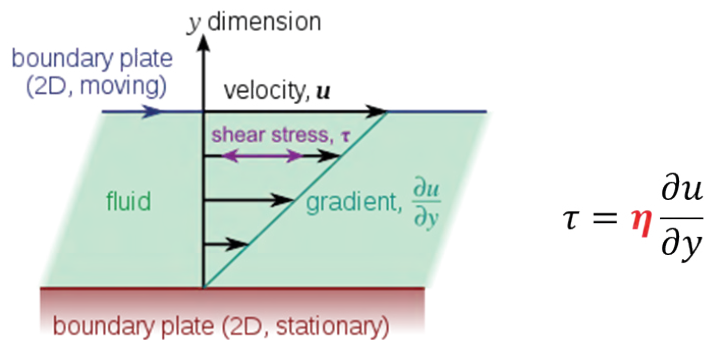
- Viscosity as function of shear
- Stress amplitude sweep (SAS)
- Oscillation frequency sweep (OFS)

They will be described in detail in the following sections.

### 3.8 SHEAR VISCOSITY

#### 3.8.1 INTRODUCTION

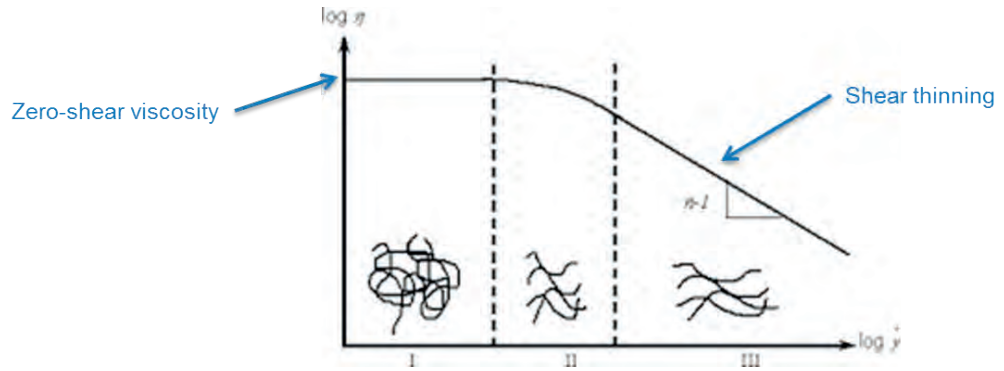
The viscosity of a fluid is a measure of its resistance to flow when a stress is applied. Depending on how the stress is applied, different kinds of viscosity can be defined. In the case of shear viscosity, a shear stress is applied (Figure 13). Viscosity is measured in Pas in the SI, but the cgs-derived unit cP (centipoise) is often used (1 cP = 1 mPas).

FIGURE 13 GRAPHICAL REPRESENTATION OF SHEAR VISCOSITY ( $\eta$ )

The simplest case is given by Newtonian fluids, where  $\eta$  is independent on the applied stress. Most fluids show non-Newtonian behavior, at least in some range of shear stress. Polymer solutions often exhibit a pseudo-plastic viscosity response, with a near-Newtonian behavior at low shear and shear thinning behavior at high shear (Figure 14).



FIGURE 14 REPRESENTATION OF SHEAR VISCOSITY PROFILE FOR TYPICAL POLYMER SOLUTIONS



At low shear a zero-shear viscosity value can sometimes be extrapolated ( $\eta_0$ ). In the shear thinning region, these solutions can be approximated to so-called power-law fluids, thus the curve can be fitted with:

$$\eta = K\gamma^{n-1}$$

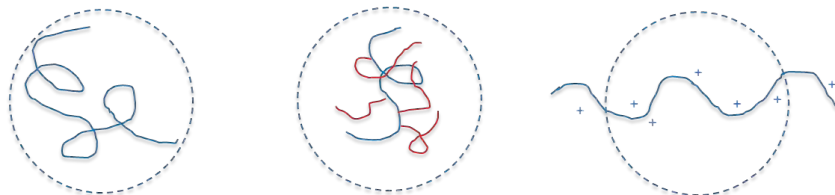
where  $\gamma$  is the shear rate and K and n are the two fit parameters.

Since the shear viscosity profile of polymer solutions is related to the hydrodynamic volume and entanglement of polymeric chains in solution, the parameters  $\eta_0$ , K and n are dependent on solution concentration and polymer properties (Molecular weight, branching and charge density). The structure-properties relationships are not obvious but some considerations can be made. Some of them are illustrated in Figure 15.

FIGURE 15 SCHEMATIC REPRESENTATION OF STRUCTURE-PROPERTIES RELATIONSHIP OF INTEREST FOR THIS STUDY

Molecular property	Effect on volume	Effect on entanglement	viscosity
Molecular weight	↑	↑	↑
branching	↓	↑	Depends on concentration
Charge density	↑	?	?

Low concentration      High concentration



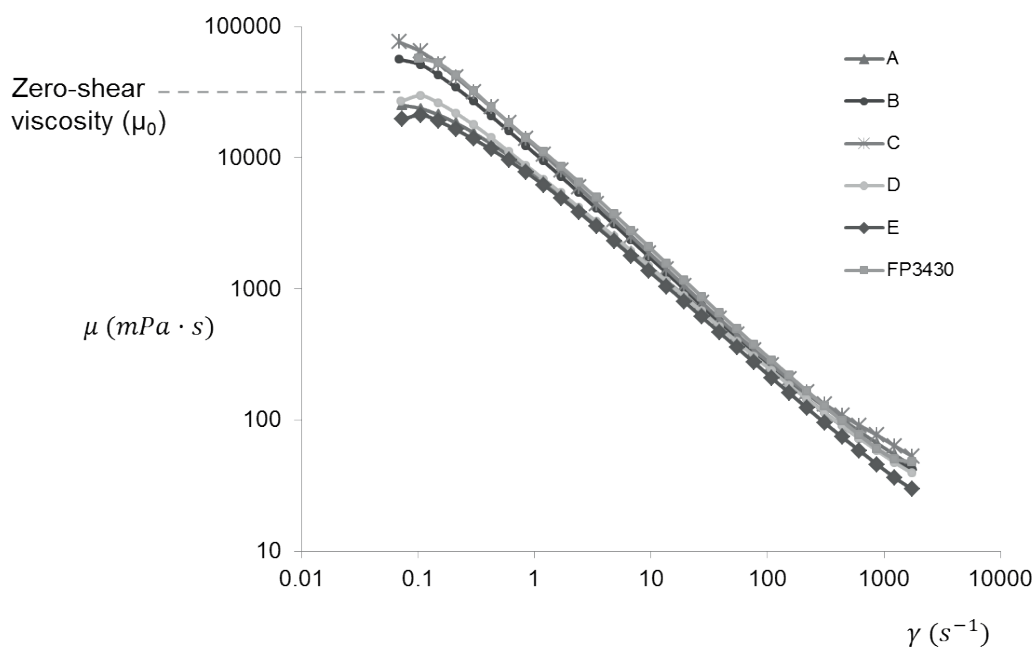
The parameters  $\eta_0$  and K should be mostly related to the magnitude of the viscosity, thus with molecular weight, while the parameter n gives an indication of deviation from Newtonian behavior, thus it should be mostly related to branching, charge density and polydispersity of the sample. In any case, one must keep in mind that it is difficult to separate different contribution, thus the data has to be interpreted carefully.

### 3.8.2 RESULTS AND DISCUSSION

Given the importance of concentration effects (at low concentration the hydrodynamic volume should have a prevalent effect on viscosity, while at high concentration the entanglement density should be the most important), measurements in concentrated (1 %) and diluted conditions (0.1 %) were performed and the 3 parameters  $\eta_0$ ,  $K$  and  $n$  have been estimated for all samples at the different concentrations.

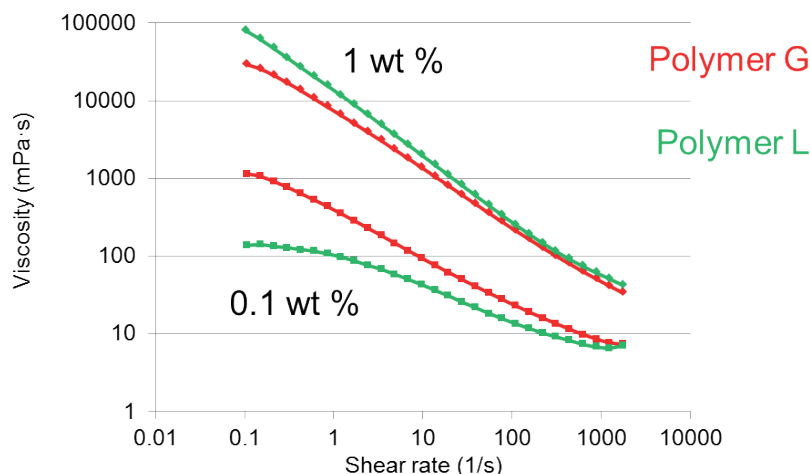
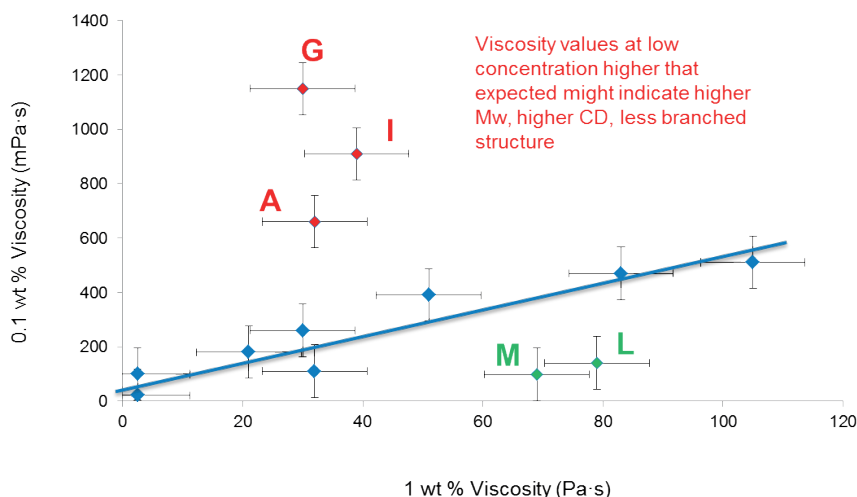
Shear viscosity measurements for polymers from A to E at 1 % concentration are reported in Figure 16. All the other samples show comparable curves. It can be observed that all the samples possess shear thinning behavior. However, a plateau region is not visible, thus the zero-shear viscosity cannot be estimated. The values at a shear of 0.1 s<sup>-1</sup> (close to the lower limit for the machine) were taken instead ( $\eta_{0.1}$ ). Comparison with a sample of FP3430, that has a Mw of about 12 MDa, shows that the investigated polymers should fall in the same range. Values of  $\eta_{0.1}$ ,  $K$  and  $n$  were evaluated for all samples. The data were used as input for the PCA.

FIGURE 16 SHEAR VISCOSITY FOR SAMPLES A TO E 1 WT % SOLUTIONS. FP3430 IS ALSO REPORTED FOR COMPARISON



Analogous measurements were taken for 0.1 wt % solutions, obtained by 10-fold dilution of the 1 % ones. To show the relevance of measuring viscosity at different concentrations, polymers G and L are compared (Figure 17). It can be observed that the trend at 1 wt % is the opposite of the trend at 0.1 %. This is clear indication that polymer structures affect the viscosity behavior differently in diluted or concentrated regime. Plotting  $\eta_{0.1}$  viscosity at 1 wt % vs 0.1 wt % shows a direct proportionality for most samples (Figure 18). It can be speculated that polymers A, G and I, that show unexpectedly high values of viscosity at low concentration might have higher molecular weights, higher charge density and/or more linear structures, but these observations must be taken carefully.

FIGURE 17 SHEAR VISCOSITIES FOR POLYMERS G AND L AT 1 WT % AND 0.1 WT %

FIGURE 18 VISCOSITY ( $\eta_{0.1}$ ) AT 1 WT % VS 0.1 WT %

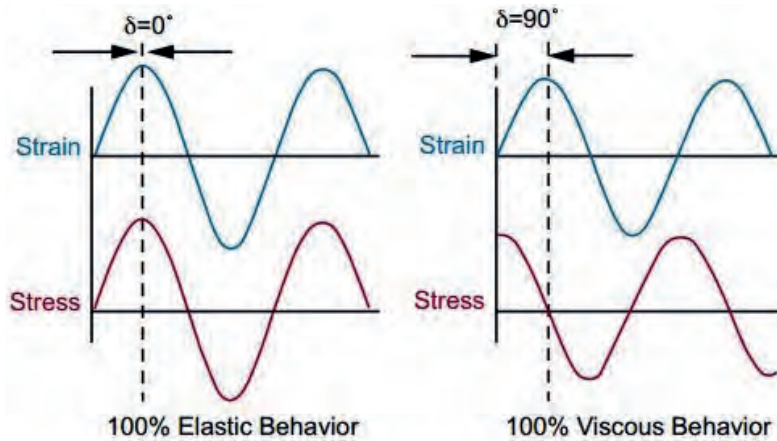
### 3.9 STRESS AMPLITUDE SWEEP

#### 3.9.1 INTRODUCTION

Stress amplitude sweep experiments fall under the category of oscillatory rheological experiments. These experiments are particularly useful for materials (such as polymer solutions) that exhibit visco-elastic response. These materials present a two-component response to stress: a quick, reversible one (elastic response) and a slow, irreversible one (viscous response). This response is characterized by a modulus ( $G$ ) that has two components:  $G'$  (or storage modulus) corresponds to the elastic response and  $G''$  (or loss modulus) corresponds to the viscous response. The first component is conservative (the energy is stored as elastic energy and the deformation is not permanent), while the second is not (the energy is lost as heat and the deformation is permanent). Figure 19 illustrates how with oscillatory application of stress it is possible to distinguish between elastic and viscous behavior, given the different response time of the deformation.  $G'$  and  $G''$  possess different values, depending on the frequency used and the characteristic of the material. A complex modulus  $G^*$  is defined as  $G^* = G' + iG''$ . The ratio  $G'/G''$ , known as  $\tan\delta$  (tangent of  $\delta$ , where  $\delta$  is the phase angle or loss angle) is an indication of the elastic-to-viscous behavior. The highest  $\tan\delta$ , the more elastic the material.

FIGURE 19

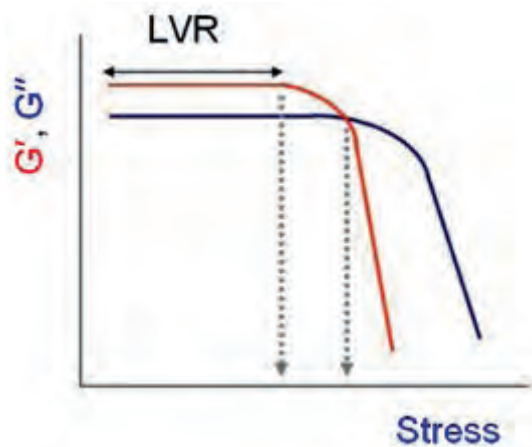
ELASTIC AND VISCOUS RESPONSE TO STRESS



The absolute values of  $G'$  and  $G''$  (and thus of  $\tan\delta$ ) are in general dependent on the applied stress and on the frequency. The dependence from the applied stress is the object of SAS experiments. In a typical SAS experiment, increasing stress is applied to the solution at a constant frequency. The typical result for a concentrated polymer solution is represented in Figure 20. For low values of stress,  $G'$  is higher than  $G''$  (elastic behavior) and both values are constant. After a certain value of stress, the material “yields” and both moduli decrease abruptly (the material start flowing). The interval where both moduli are constant is called linear viscoelastic region (LVR). The point where the  $G'$  start deviating from linearity is called yield stress.

FIGURE 20

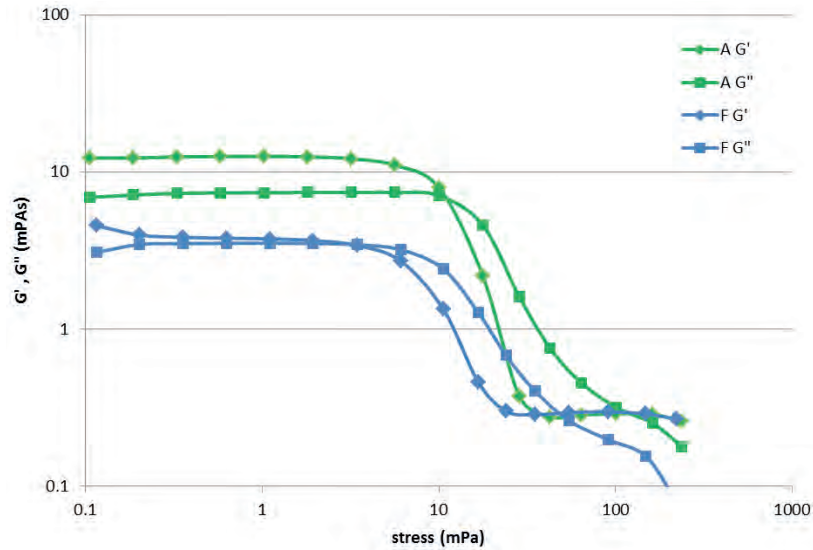
TYPICAL SAS PLOT FOR CONCENTRATED POLYMER SOLUTION



### 3.9.2 RESULTS AND DISCUSSION

SAS experiments were performed for all samples at 1 wt % concentration, at a fixed frequency of 1 Hz (typical value for these experiments). Values of  $G'$ ,  $G''$  and yield point of all polymers were used as input for the PCA. Again, visco-elastic behavior is dependent on polymer structure, but exact relationship are very difficult to establish. Stronger gels (high  $G'$ ,  $G' \gg G''$ , high yield stress) should be formed by polymers with higher molecular weight and entanglement density. SAS of polymer A and F are shown as an example in Figure 21.

FIGURE 21 SAS OF POLYMERS A AND F (1 WT %)

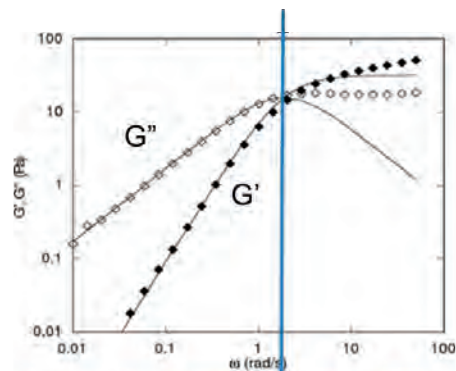


### 3.10 OSCILLATION FREQUENCY SWEEP

#### 3.10.1 INTRODUCTION

This is another oscillatory rheological experiment, where the applied stress is kept constant and the visco-elastic response of the material is investigated in a large range of frequencies. In order to have meaningful results the applied stress should be chosen in the LVR (see previous section) and samples should be compared at the same applied stress. Typical curves for polymer solutions are shown in Figure 22.

FIGURE 22 TYPICAL OFS EXPERIMENT FOR POLYMER SOLUTIONS



Low frequency (long time)  
Viscous behavior  $G'' > G'$

high frequency (short time)  
Elastic behavior  $G' > G''$

In the region at low frequency, the viscous response ( $G''$ ) prevails over the elastic response ( $G'$ ). Low frequency means long times, thus the delayed response predominates over the quick one. Both values are strongly frequency dependent. In the terminal region, at very low frequencies, the value of  $G''/\omega$  should approach a constant value, which according to the current theory corresponds to  $\eta_0$ . As the frequency increases, a cross-over point is reached ( $G' = G''$  or, equivalently,  $\tan\delta = 1$ ) where the behavior switch from viscous to elastic. In the elastic region,  $G'$  should reach a plateau value.

### 3.10.2 RESULTS AND DISCUSSION

OFS experiments on 1 wt % solutions were performed. The applied stress used was 1 mPa, which is in the LVR for all investigated polymer solutions. The measurements were performed in the range of frequencies 0.01 – 100 Hz. For all polymers values of cross-over points (both  $G'$  and  $\omega$ ) and  $\eta_0$  (extrapolated as  $G''/\omega$  at low frequencies) were estimated and used for the PCA. Plateau values of  $G'$  were not observed in the studied interval. The cross-over points, as for SAS experiments, indicates the strength of the gel and thus is again related to molecular characteristics of the polymers. The values of  $\eta_0$  are always higher, as expected, from the  $\eta_{0,1}$  directly measured (section 3.8), but the differences can be an indication of the non-ideality of the systems (because of the high polydispersity, presence of charges and possibly cross-linking).

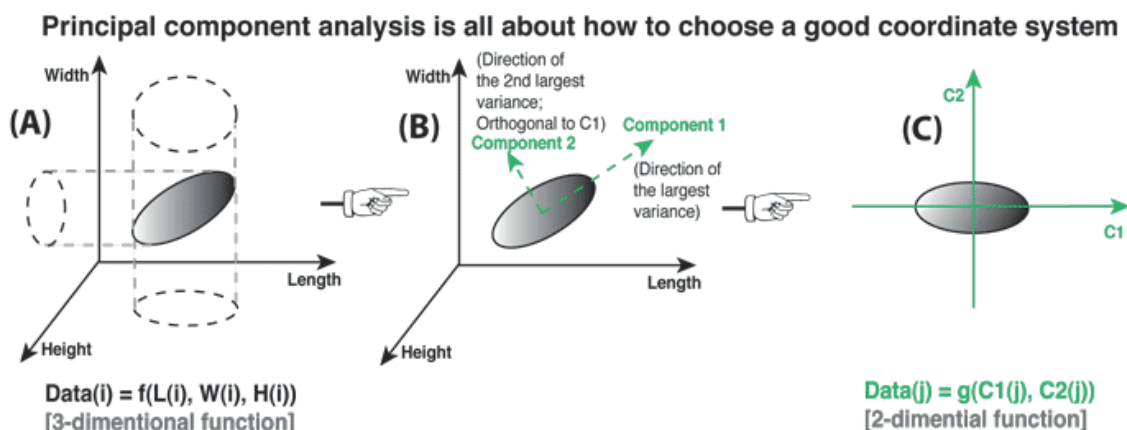
## 4

## PRINCIPAL COMPONENT ANALYSIS

## 4.1 INTRODUCTION

All the different measurements performed within the scope of this study give a total of 17 different properties that can be measured for the different polymers (not taking account polymer content and oil percentage of the emulsion). All these parameters have a relation with relevant polymer properties as discussed before. However it is not practical to determine all these parameters. Therefore it is interesting to understand the minimal amount of parameters that still characterize the full dataset. A principle component analysis (PCA) is a statistical way to analyze a multi-dimensional data set and to project this data set onto a new set of parameters (the principle components) of a lower dimension. The new set of parameters is composed by grouping parameters that have a high correlation into a new coordinate system (Figure 23). This analysis therefore gives insight into the minimum amount of parameters that is required to describe the variance in the dataset.

FIGURE 23 GENERAL PRINCIPLE BEHIND A PRINCIPLE COMPONENT ANALYSIS (\*\*ADD SOURCE\*\*)



(Figure taken from <http://mengnote.blogspot.nl/2013/05/an-intuitive-explanation-of-pca.html>).

## 4.2 DATA AND APPROACH

The data used for the PCA is summarized in Appendix B. Parameters that are obviously correlated, like the ratios between certain parameters (for instance  $\tan \delta$ ), were removed from this dataset to get a dataset of 17 parameters for 13 data points. The statistical software Sigmaplot (v13.0) was used to perform the principal component analysis on the dataset.

### 4.3 PRINCIPLE COMPONENT DETERMINATION

The principle component analysis provides a number of sub results that give information about the dataset.

First of all a correlation matrix is made that shows the correlation between all the different parameters in the dataset (Table 4). Already this matrix shows that a number of parameters have a high correlation with each other. This suggests that they give similar information about the variation in the data set. The table shows that especially the different viscosity parameters have high correlations.

TABLE 4 CORRELATION MATRIX FOR THE PARAMETERS. STRONG CORRELATIONS ARE HIGHLIGHTED

		zsv	K	n	cof	coG	zsvG	G'	G''	YS	zsv01	K01	n01	Cond	C	CN	CX	NMR
$\eta_{0.1}$ (1 wt%)	zsv	1,00																
K (1 wt %)	K	0,93	1,00															
n (1 wt %)	n	-0,83	-0,95	1,00														
cross-over $\omega$	Cof	-0,63	-0,80	0,89	1,00													
cross-over G	CoG	0,41	0,34	-0,17	-0,14	1,00												
$\eta_{0.1}$ (lim G''/ $\omega$ )	zsvG	0,91	0,90	-0,78	-0,51	0,35	1,00											
G' (LVR)	G'	0,96	0,92	-0,85	-0,66	0,53	0,86	1,00										
G'' (LVR)	G''	0,82	0,72	-0,64	-0,56	0,72	0,61	0,90	1,00									
yield stress	YS	0,74	0,91	-0,90	-0,75	0,13	0,81	0,76	0,46	1,00								
$\eta_{0.1}$ (0.1 wt%)	zsv01	0,12	0,15	-0,26	-0,42	-0,13	-0,01	0,07	0,04	0,06	1,00							
K (0.1 wt %)	K01	-0,22	-0,31	0,43	0,57	0,02	-0,09	-0,19	-0,16	-0,24	-0,84	1,00						
n (0.1 wt %)	n01	0,13	0,17	-0,23	-0,44	0,04	-0,03	0,09	0,12	0,04	0,94	-0,90	1,00					
conductance	Cond	0,41	0,45	-0,43	-0,39	0,24	0,30	0,49	0,44	0,45	0,13	-0,07	0,14	1,00				
C %	C	-0,29	-0,38	0,32	0,11	-0,21	-0,49	-0,32	-0,08	-0,51	-0,14	0,31	-0,19	-0,11	1,00			
C/N	CN	-0,17	-0,39	0,38	0,37	-0,15	-0,36	-0,24	-0,04	-0,65	0,18	-0,10	0,23	-0,35	0,31	1,00		
C/X	CX	-0,31	-0,37	0,30	0,09	-0,25	-0,48	-0,34	-0,14	-0,42	-0,22	0,33	-0,28	-0,07	0,97	0,12	1,00	
NMR peak ratio	NMR	0,47	0,37	-0,20	0,14	0,26	0,58	0,46	0,27	0,43	-0,29	0,10	-0,24	0,23	-0,65	-0,20	-0,57	1,00

Using linear algebra the correlation matrix is used to determine new directions (eigenvectors) in the data set that described the largest variations in the dataset. Basically the eigenvectors are new axes on which the data can be projected. For each eigenvector an eigenvalue can be calculated and this value indicates how much of the variance in the dataset is explained by this eigenvector. Table 5 gives the eigenvalues for the different eigenvectors of the dataset in this study. The "principle components" are those eigenvectors that explain the largest amount of the variation in this dataset. Table 5 shows that 86% of the variation in this dataset can be explained by the first four principle components. The first principle component already explains 46% of the variance in the dataset. This result suggests that only four parameters would be sufficient to explain most of the variation in the dataset. Interestingly, four properties were determined as the most relevant characteristics of the different polymers (molecular weight, charge density, structure and composition) and measurements were selected that have a relation these four properties.



TABLE 5

EIGENVALUES OF THE CORRELATION MATRIX

	Eigenvalue	Proportion(%)	Cumulative(%)
1	7,81	45,9	45,9
2	3,15	18,5	64,5
3	2,17	12,8	77,3
4	1,54	9,0	86,3
5	0,95	5,6	91,9
6	0,70	4,1	96,0
7	0,28	1,6	97,6
8	0,25	1,5	99,1
9	0,09	0,5	99,6
10	0,04	0,2	99,8
11	0,02	0,1	99,9
12	0,01	0,1	100
13	0,00	0,0	100
14	0,00	0,0	100
15	0,00	0,0	100
16	0,00	0,0	100
17	0,00	0,0	100

The principle component analysis also shows which parameters contribute to the new coordinate system based on the principle components. Each principle component is a vector that is composed of different contributions of the various parameters. Table 6 gives the “loadings” of the different parameters to the four first principle components. The table shows that the viscosity parameters are the most important parameters in the data set and explain the largest variance in the data set. Both the shear viscosity measurements at 1 wt%, the stress amplitude sweep data and the oscillatory frequency data all end up in the same principal component. Of this data only the cross-over G ends up in the fourth principle component together with the C/N ratio. This could suggest that this viscosity parameter gives some information on the charge density of the polymers.

TABLE 6

LOADINGS OF THE FIRST FOUR PRINCIPLE COMPONENTS

	PC 1	PC 2	PC 3	PC 4
$\eta_{0,1}$ (1 wt%)	0,916	0,107	0,154	0,192
K (1 wt %)	0,971	0,030	0,135	-0,079
n (1 wt %)	-0,918	0,125	-0,193	0,222
cross-over $\omega$	-0,759	0,387	-0,381	0,267
cross-over G	0,434	0,241	0,052	0,622
$\eta_{0,1}$ (lim $G''/\omega$ )	0,884	0,265	-0,078	-0,003
$G'$ (LVR)	0,939	0,15	0,177	0,216
$G''$ (LVR)	0,754	0,103	0,357	0,509
yield stress	0,888	0,115	-0,026	-0,431
$\eta_{0,1}$ (0.1 wt%)	0,215	-0,921	-0,095	0,033
K (0.1 wt %)	-0,379	0,857	0,175	-0,017
n (0.1 wt %)	0,245	-0,923	-0,131	0,166
conductance	0,512	0,037	0,222	-0,073
C %	-0,514	-0,032	0,836	0,071
C/N	-0,403	-0,312	0,013	0,65
C/X	-0,499	0,051	0,821	-0,096
NMR peak ratio	0,464	0,509	-0,548	0,15

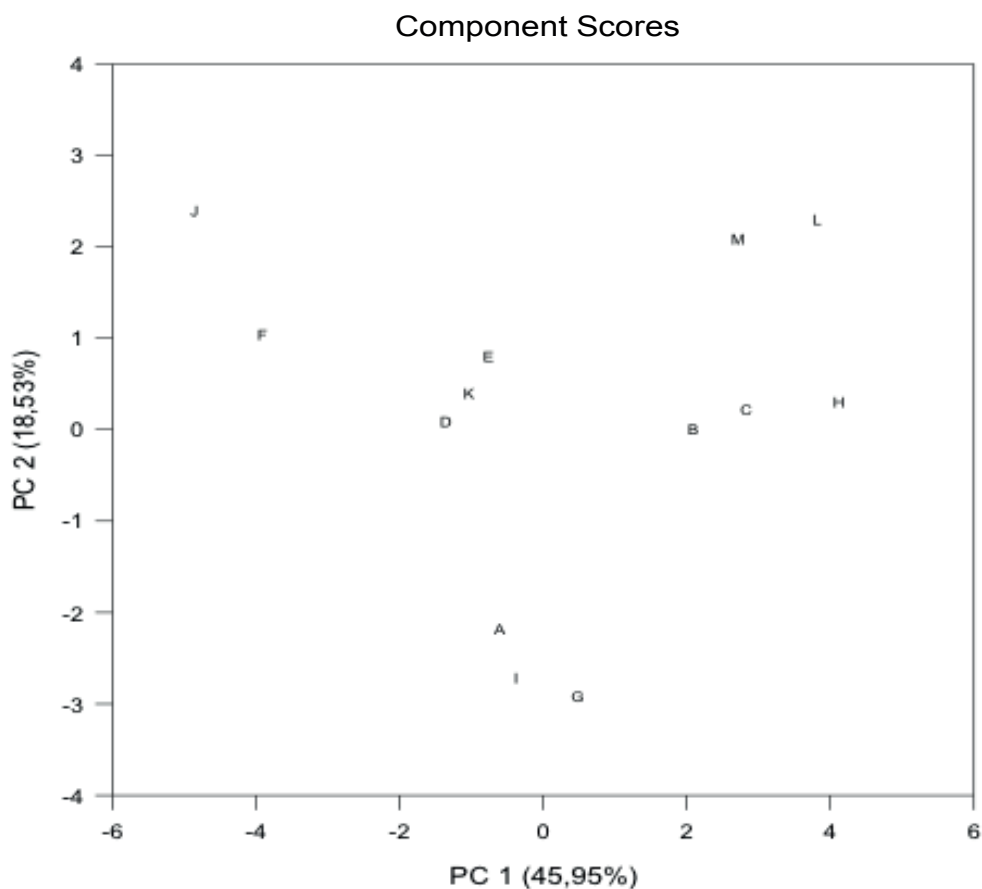
The second principal component is mainly determined by the shear viscosity measurements at 0,1 wt% and this result confirms that dilution of the samples indeed gives distinctly different information about the polymers as explained in section 3.8. The third principal component mainly relates to the chemical composition of the polymer, but interestingly the C/N ratio gives different information as it is grouped into the fourth principal component. The NMR peak ratio and the conductance do not contribute significantly to one of first four principle components. The largest contribution of the conductance is to the first component, suggesting that it gives similar information as the viscosity data. The measurement error for this parameter was relatively large and that could also explain this relatively low contribution. The NMR peak ratio contributes to the first 3 parameters but the contribution is much lower than for the other parameters. Also here the measurement error or “noise” in the data may explain this low contribution to the principal components. It might imply that the chosen ratio is not accurate enough and that a more detailed analysis of the NMR spectra is required. Such an analysis is however difficult to transform into data that can used a quality parameter.

#### 4.4 GRAPHICAL REPRESENTATION

The dataset can be plotted in a graph using the principal components as the new axes. Figure 24 shows the plot for the first two principal components. This plot shows for instance that polymers E, K and D have similar properties based on these two components. Other groups of polymers are (B, C, H), (A, I, G) and (J, F). L and M were the same polymer but different samples. They also appear as their own group.

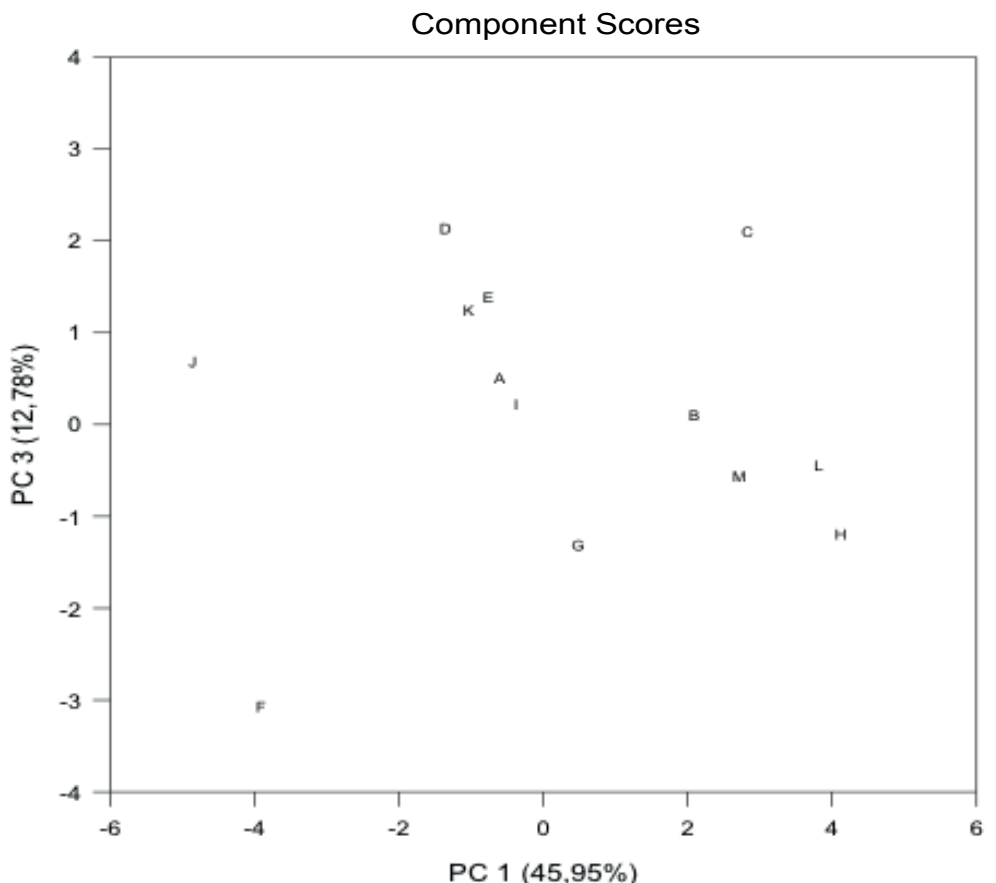
FIGURE 24

PLOT OF THE DATASET FOR THE FIRST TWO PRINCIPLE COMPONENTS



When the third principal component is plotted against the first principal component new information is added. This third component for instance shows that where J and F first where group using principal component 1 (PC1) and PC2, the now can be distinguished from each other using PC3. Similarly also B, C and H are separated from each other in this way.

FIGURE 25 PLOT OF THE DATASET FOR THE FIRST AND THE THIRD PRINCIPAL COMPONENT



#### 4.5 CONCLUSION

The principle component analysis shows that there are correlations between the different parameters that were measured to determine the properties of the different polymers. The analysis suggests that four parameters are enough to describe the variation in the data set. The main determining parameters were the viscosity measurements and the elemental analysis. The conductance measurements and the NMR parameters did not contribute significantly to the principal components, suggesting this information is either not relevant or has too much noise in the data. Furthermore the analysis showed that the different results of the viscosity measurements are correlated. The most important contributions were obtained via the shear viscosity measurements at two different concentrations. The stress amplitude sweep data and the oscillatory frequency sweep data ended up in the same first principal component, suggesting that they are correlated to the shear viscosity measurements. This suggests that only measurement of the shear viscosity data would be sufficient in order to minimize the analytical effort.

#### 4.6 PRACTICAL TRANSLATION

The results of the principal component analysis suggest that shear viscosity data (at 1 wt% and 0,1 wt%) in combination with the elemental analysis would give enough information to distinguish the different polymers from each other. This hypothesis was tested to see if it would indeed

be possible to find differences between the different polymers using only these parameters. Figure 26 shows that determination of the K value using shear viscosity measurements in a 1 wt% solution makes it possible to roughly distinguish three groups of polymers: (J, F), (A, D, E, K, G, I) and (B, C, H, L, M). The additional measurement of the K value in a solution of 0,1 wt% makes it is then possible to further distinguish between polymers that were first grouped in the same group. For instance: (L, M) are then different from (B, C, H) although they appeared in the same group using the K-value at 1 wt%. Also (A, G, I) now show different properties from (D, E, K). Finally, addition of the C/N ratio makes it possible to further distinguish between the polymers in the subgroups (figures 27 & 28). Addition of the n-values, (near) zero shear viscosity and C/X ratio may then further help to distinguish the polymers and their fingerprint as suggested by the principal component analysis.

FIGURE 26 NORMALIZED VALUES FOR K USING SHEAR VISCOSITY MEASUREMENTS AT 1,0 (LEFT BARS) AND 0,1 WT% SOLUTIONS (RIGHT BARS)

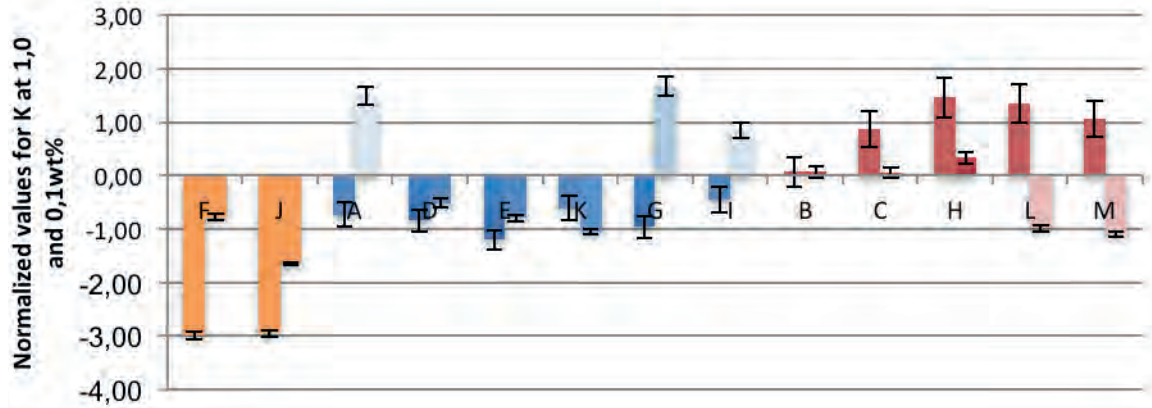


FIGURE 27: COMPARISON OF THE K VALUES AT 1,0 (LEFT), 0,1 WT% (MIDDLE) AND THE C/N RATIO'S (RIGHT) FOR THE POLYMER GROUP (A, D, E, K, G, I)

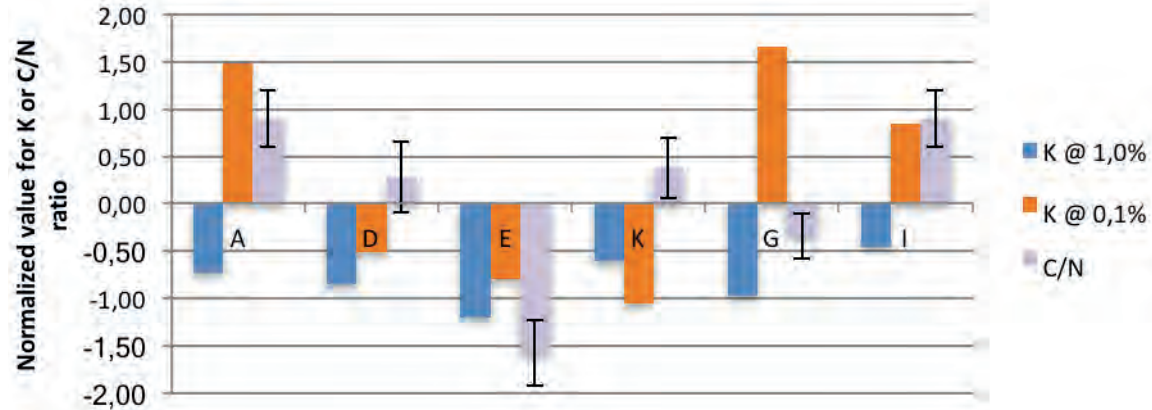
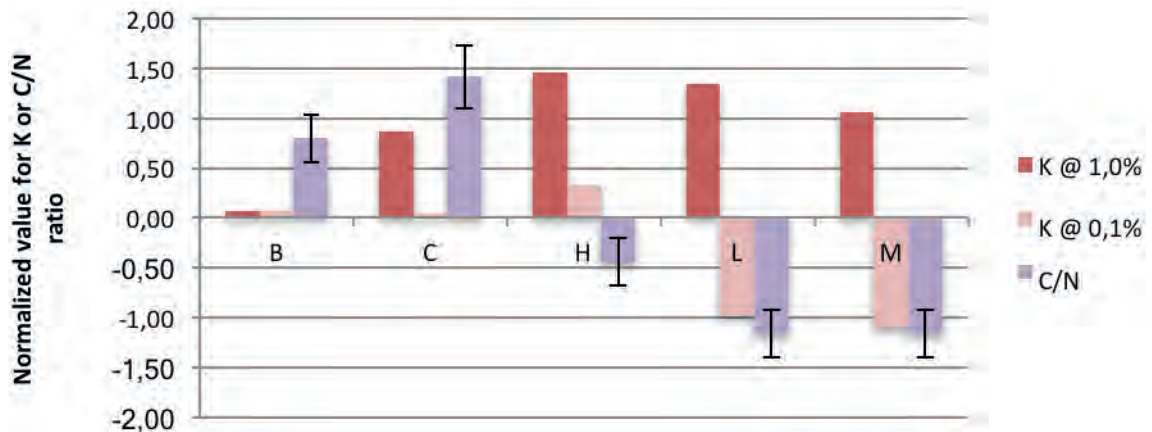


FIGURE 28: COMPARISON OF THE K VALUES AT 1,0 (LEFT), 0,1 WT% (MIDDLE) AND THE C/N RATIO'S (RIGHT) FOR THE POLYMER GROUP (B, C, H, L, M)



# 5

## REPRODUCIBILITY STUDY

As a conclusion of this study, a preliminary reproducibility study was performed. This consisted of two parts. First, the accuracy of the experiments was estimated. Analyses were performed 3 times on a same sample and the standard deviation was taken as error. Secondly, 5 different batches of the same product were received and tested for the same properties, to see if there are any significant differences between different batches of the supposedly same product. This product is the same as the previously investigated polymer G. The new 5 batches are indicated as: G1, G2, G3, G4 and G5. The samples were received from two different water authorities: sample G, G3, G4 and G5 from one water authority, G1 and G2 from another water authority.

For this study certain analyses were selected as the most significant (based on the results obtained by the PCA) and established as a standard experimental protocol to obtain a “fingerprint” for each polymer. Those are:

- Extraction of the polymer in acetone to determine polymer and oil content
- Elemental analysis (CHN)
- Shear viscosity at 1 wt % ( $\eta_{0,1}$ ,  $K$  and  $n$  parameters)
- Shear viscosity at 0.1 % ( $\eta_{0,1}$ ,  $K$  and  $n$  parameters)

### 5.1 MEASUREMENT REPRODUCIBILITY

Sample G1 was used for this study. Operations described in sections 3.1 and 3.2, to calculate the composition in solid and oil content gave the results shown in Table 7.

TABLE 7 COMPOSITION OF SAMPLE G1 AND STANDARD DEVIATION

Code	Total weight (g)	Solid (g)	Oil (g)	Solid (wt %)	Oil (wt %)
G1a	7.24	3.58	0.52	49.4	7.2
G1b	6.05	2.98	0.578	49.3	9.5
G1c	5.70	2.57	0.60	45.1	10.5
Average				48.0	9.1
St. dev.				2.4	1.7
St. dev %				5%	19%

Values for the solid content seem to be quite reproducible, while for the oil content the deviations are significantly high. This can be ascribed to the presence of volatile fractions in the oil, that can evaporate along with acetone and water in the drying phase, thus giving high variations if the drying time or even the flask used<sup>3</sup> are not kept always constant.

<sup>3</sup> different flask, with different size, gives different evaporating surface, which affect evaporation rates

Sample G1a was used to prepare three different 1 wt % solutions. Results of shear viscosity measurements are reported in Table 8. Standard deviations for  $\eta_{0.1}$ , K and n are all reasonably low.

TABLE 8 SHEAR VISCOSITY MEASUREMENT AND STANDARD DEVIATION FOR 1 WT % SOLUTION OF 1A5

Sample	$\eta_{0.1}$ (Pas)	K (Pas)	n
G1a_1	45.97	9.25	0.226
G1a_2	46.72	9.058	0.225
G1a_3	42.68	8.617	0.231
average	45.1	9.0	0.23
St. dev	2.1	0.32	0.003
St. dev %	4.7%	3.6%	1.4%

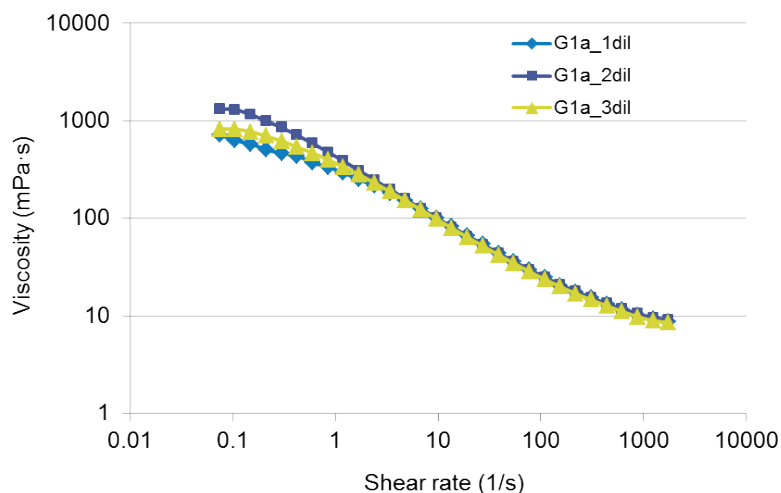
Finally, each 1 wt % solution was diluted to 0.1 wt % and viscosity measurements were performed. Results are in Table 9.

TABLE 9 SHEAR VISCOSITY MEASUREMENT AND STANDARD DEVIATION FOR 0.1 WT % SOLUTION OF G1

Sample	$\eta_{0.1}$ (mPas)	K (mPas)	n
G1a_1dil	626	333	0.46
G1a_2dil	1297	398	0.42
G1a_3dil	817	365	0.43
average	913	365	0.43
St. dev	346	33	0.021
St. dev %	38%	9%	4.8%

In this case, standard deviations are generally higher, especially for the value of  $\eta_{0.1}$ . The complete shear viscosity curves are shown in Figure 23, evidencing the deviations at low shear.

FIGURE 29 SHEAR VISCOSITY CURVES FOR 0.1 WT % VISCOSITY



## 5.2 BATCHES REPRODUCIBILITY

The same techniques were used to test the other 4 different batches of the product, using the standard deviations obtained in section 5.1 as measurement error. Data for sample G from the previous study are also added. Table 10 and 11 summarize the data obtained. The same data are given as graphical representations in figures 30, 31 and 32.

TABLE 10 SOLID AND OIL CONTENT AND ELEMENTAL ANALYSIS OF ALL BATCHES. \* = VALUES FOR G1 ARE AVERAGE OF 3 MEASUREMENTS (SEE PREVIOUS SECTION)

Sample	solid (wt %)	oil (wt %)	N (wt %)	C (wt %)	H (wt %)	X (O, Cl)	C/N mol	C/Het
G1*	48.0	9.1	7.91	43.8	8.3	39.9	6.4	1.1
G2	48.1	11.9	7.56	43.9	8.4	40.1	6.8	1.1
G3	49.5	15.0	7.94	43.9	8.1	39.9	6.4	1.1
G4	46.8	19.0	7.96	42.6	7.9	41.5	6.2	1.0
G5	49.6	15.2	8.12	45.0	8.2	38.7	6.5	1.1
G	45.0	7.9	7.55	40.7	8.1	43.5	6.2	0.9

TABLE 11 VISCOSITY DATA FOR ALL THE BATCHES. \* = VALUES FOR G1 ARE AVERAGE OF 3 MEASUREMENTS (SEE PREVIOUS SECTION)

Sample	$\eta_{0.1}$ (mPas)	K (mPas)	n	$\eta_{0.1}$ (mPas)	K (mPas)	n
conc		1 wt %			0.1 wt %	
G1*	45.1	9.0	0.23	913	365	0.43
G2	32.6	7.4	0.26	1246	384	0.42
G3	43.8	9.0	0.23	376	242	0.47
G4	48.7	9.7	0.23	1476	427	0.40
G5	40.6	8.9	0.23	334	229	0.48
G	29.3	7.4	0.25	1150	375	0.41

FIGURE 30 POLYMER AND OIL CONTENT OF THE DIFFERENT BATCHES

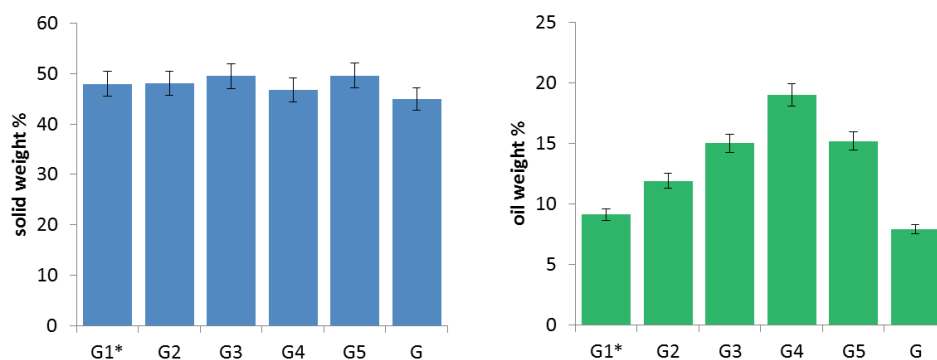
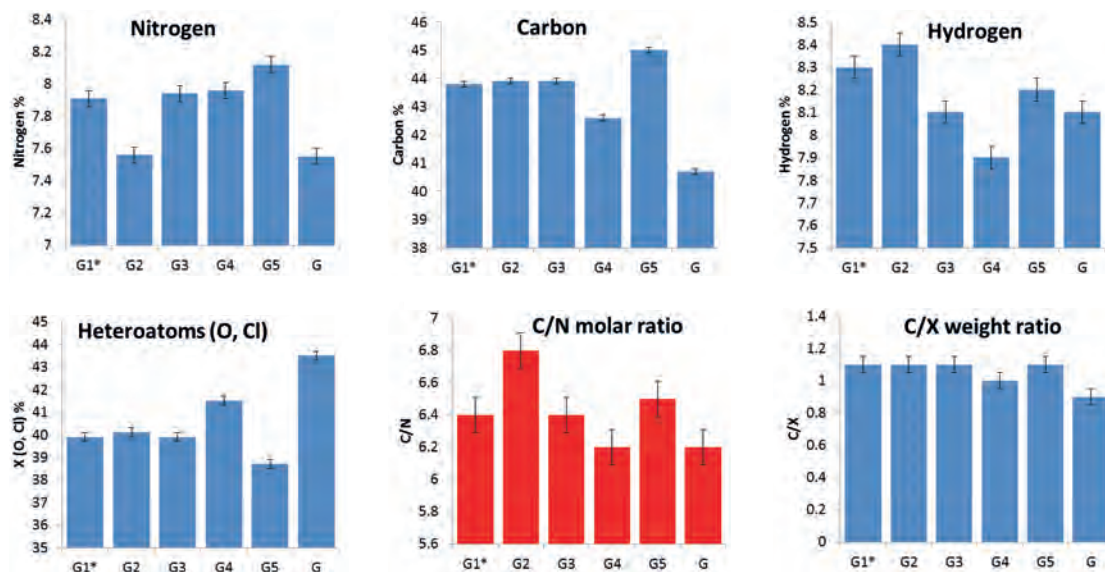
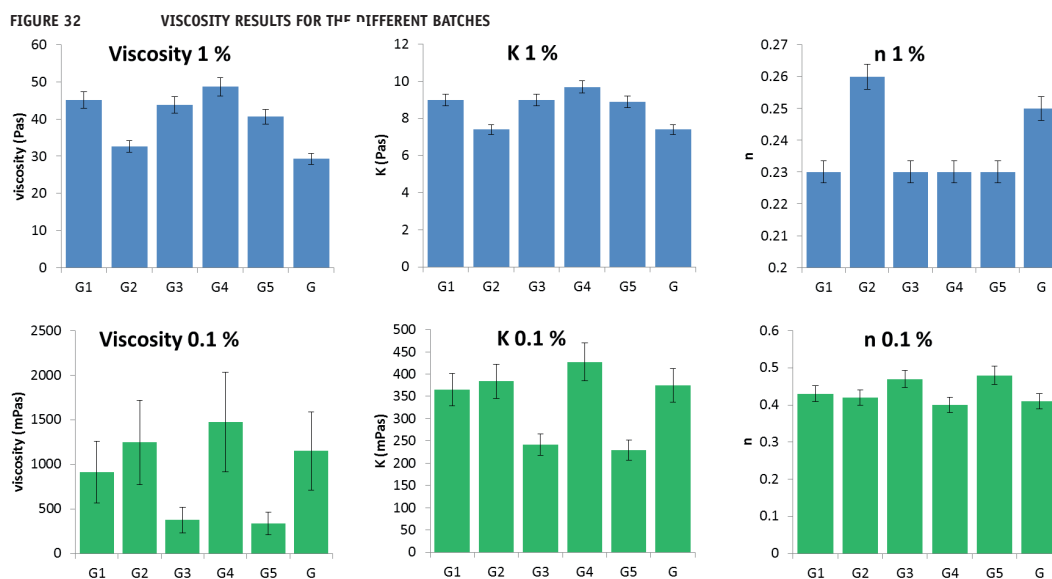


FIGURE 31 ELEMENTAL ANALYSIS OF THE DIFFERENT BATCHES





Some differences within the batches can be observed. They seem to be significantly above the experimental error, thus proving that there is some variation between different batches of the same product. The viscosity measurements at 1% show that samples G2 and G are different from the other samples, whereas the measurements at 0,1% show that samples G3 and G5 differ from the other samples in a different way. Furthermore there is a large variation in the oil content of the different samples, even taken into account the large measurement error. For the polymer content no large deviations were found given the measurement error for the applied method.

The different batches differ from each other in different ways and no batch has all properties similar to another batch. Table 12 visualizes the differences between the properties of the different batches. For the preparation of the table the batches were classified in three categories (low value (-), average value (0) and high value (+)). The table shows that every batch has some differences from the other batches. Batch G1 shows the most average composition, but has a low oil content it shares with sample G. Batch G3 and G5 differ mainly from the other batches in their viscous properties at a low concentration of 0,1 wt%. The viscous properties of samples G2 and G3 at a concentration of 1 wt% differ from the other batches, but G3 also differs from G2 in the measured C/N ratio. Sample G4 differs from the other samples in its' C/N ratio and high oil content.

**TABLE 12 GROUPING OF THE PROPERTIES OF THE DIFFERENT G SAMPLES IN THREE DIFFERENT CATEGORIES PER PROPERTY (LOW VALUE (-), AVERAGE VALUE (0) AND HIGH VALUE (+))**

	G1	G2	G3	G4	G5	G
Dry matter	0	0	0	0	0	0/-
Oil content	-	0/-	0	+	0	-
C/N ratio	0	+	0	-	0	-
Low shear viscosity, 1%	0	-	0	0	0/-	-
K value 1%	0	-	0	0	0	-
n value 1%	0	+	0	0	0	+
Low shear viscosity, 0,1%	0/-	0	-	+	-	0
K value 0,1%	0	0	-	+ / 0	-	0
n value 0,1%	0 / +	0	+	0	+	0



# 6

## MARKET CONSULTATION

The results of this study were presented in two workshops to two target groups in order to get feedback on the results and the conclusions. A first target group were representatives of five laboratories of the Dutch water authorities as well as three commercial laboratories. A second target group were representatives of suppliers of polyelectrolytes for the Dutch water authorities. Six different suppliers were invited and representatives of four suppliers were present in the meeting.

The objective of the laboratory workshop was to understand possible obstacles for implementation of the proposed approach into a commercial analytical package. In general all participants thought the followed approach to be feasible. One representative from a commercial lab had followed a similar approach to characterize polyacrylamides used in the oil industry. The representatives stressed that it is important to develop a standardized and certified protocol if this approach is to be used as a quality check. Viscosity measurements are essential in this approach, but all labs would need to invest in equipment to be able to offer this service. The involved investment will be roughly 100-200 k€. Therefore a minimum turnover is required to be able to earn back these investments. Rough calculations indicate that the proposed approach would be possible at a price of 300-400 €/sample, provided that there is turnover for 500 samples/year for at least 3-5 years.

The objective of the workshop with the polyelectrolyte producers was to understand how they control the quality of their products and if the proposed approach matches their own quality control approach. This workshop showed that the PE producers do not immediately see the need for an external verification of the quality. They stressed that they have their own ISO-certified quality control systems in place to identify off-spec production batches. They also invite water authorities for external audits of their quality systems to verify these systems. For the producers the production recipe is often the most important quality control parameter, but also quality checks are performed on the produced polyelectrolytes. In general there is consensus that rheology based measurements (i.e. viscosity) are the best approach to characterize polyelectrolytes. GPC failed in this study to characterize the polymers and it is also the experience of the producers that GPC may provide inconsistent data. There were some concerns about the acetone extraction that was used to extract the polymer from the emulsion. This extraction may lead to a change in the polymer behaviour. According to the authors of this study the extraction is however necessary to separate the polymer from other ingredients in the emulsion (salts, emulsifiers, etc.). The authors do not expect that the extraction influences the molecular structure of the polymer. The producers were very surprised by the high variations in the oil content. This should not be the case and they recommended verifying the determination procedure, as the error in the procedure was relatively high. Finally it was commented that the current approach needs further development (protocol development, error determination) to be able to use it as a quality control method.

# 7

## CONCLUSIONS

The goal of this project was to propose an experimental protocol for the characterization of polyelectrolytes used for sludge dewatering. This protocol should be able to provide a “fingerprint” of the polymers, that would allow to distinguish among different samples and monitor any changes in the quality of a given product. Ideally, the selected experiments should also give some information about the important properties of the polymers, such as molecular weight, charge density and presence of branching or cross-linking. The samples are provided as emulsions, so the polymer is first isolated by precipitation in acetone. This allows also to determine the composition of the emulsion (solid and oil amounts). Several analyses were then performed: elemental analysis (CHN), H-NMR, conductance, GPC and various rheological measurements. All the techniques employed were used to determine numerical parameters related to structural properties of the polymers (in a non-obvious way), which constitutes the desired “fingerprint”. The principal component analysis allowed to narrow down the number of measurements necessary to distinguish among different polymers. As a result, an experimental protocol based on precipitation of the polymer, elemental analysis and shear viscosity measurement at the two different concentrations of 1 wt % and 0.1 wt % was proposed. Appendix A contains a description of such protocol. Furthermore, a quick scan of the reproducibility of the experimental method was performed and the obtained standard deviations were used to check if the differences observed among samples were significant. Finally, 5 different samples of a same product were tested to determine the reproducibility of properties among batches. The quick scan of the measurement error confirmed that the reproducibility of the proposed methods are acceptable. With the available measurement accuracy some significant differences were observed between different deliveries of the same type of polymer. In conclusion, with some effort in finding the right equipment, analytical laboratories could be able to setup a working protocol for the characterization of polyelectrolytes for sludge dewatering.

# 8

## RECOMMENDATIONS

### 8.1 FURTHER OPTIMIZATION OF THE ANALYTICAL TOOLS

Although the performed analysis can give some indication about the molecular properties of the polymers, any attempt at providing structure-properties relationships remain quite speculative at this stage. This is because it was not possible to obtain direct information on the mentioned properties. In particular, GPC failed to provide estimation of molecular weight and polydispersity of the samples, from which any other characteristic is strongly dependent. Therefore, the causes of the observed problems should be identified and solved in order to gain better insight on the molecular properties.

Naturally, many other experimental methods could be implemented to measure properties of interest. For example a more accurate determination of charge density could be done by using a polyelectrolyte titration. Gel electrophoresis could also give some indications on charge density. This is a less direct method but it has the advantage of being implemented in many laboratories (mostly biological ones though). Since a cone-and-plate rheometer is not of easy access, alternative viscosity measurements could also be performed by using other instruments such as Brookfield viscometer, but these are usually less accurate and more time consuming, they require much higher amount of material and the shear cannot be easily varied.

### 8.2 TOWARDS A CHARACTERIZATION TOOL FOR WATER AUTHORITIES

This study was a first step towards the development of a characterization tool for the water authorities and has lead to a suggestion to such an approach. However several steps are still necessary before the results of this study can made available as a standard characterization tool that can routinely be used by the Dutch water authorities.

First of all it is important to get more data on the measurement error (accuracy) for the proposed methods. To get reliable data a standardized protocol should be developed first in order to make such a study meaningful for a following phase. Once the protocol and the associated accuracy is determined it will be possible to start following the quality differences in the poly-electrolyte deliveries and this data will then make it possible to evaluate acceptable tolerances in quality differences based on practical data and discussions with the suppliers of the poly-electrolytes.

The results of this study were discussed with representatives of five analytical labs of the Dutch water authorities (Aquon, Aqualysis, Waterproef, Hunze en Aa's, Fryslan) and three commercial labs (SGS, Eurofins and Alcontrol). The viscosity shear measurements and elemental analysis equipment are not readily available at these labs, except for one commercial lab. Nevertheless the labs were open to discuss together ways to develop such a tool. Their willingness to invest in new equipment will depend on the expected market volume (expected volume ca. 1000 characterizations/year, assuming 80 dewatering locations with a delivery once/month).

The following steps are recommended as a follow-up to this study:

- 1 Share the results of this study and the next steps with the **polyelectrolyte producers**.
- 2 Verify the total **market volume** for characterizations of polyelectrolytes.
- 3 Development of a **standardized analytical protocol**, including a more detailed verification of the measurement errors. This step should be taken in cooperation with an analytical lab (commercial lab/water authority lab).
- 4 Perform a **pilot phase** at 3-4 different sewage treatment plants where the quality of the polyelectrolyte deliveries is followed during a year. Changes in quality should be related to changes in dewatering performance (full scale and maybe also using lab-scale dewatering equipment) to get a feeling for acceptable *tolerances* for deviations in quality.
- 5 Introduce a **commercial** and **standardized** characterization method with recommendations for acceptable tolerances. Standardization may be possible in cooperation with NEN. Water authorities may choose to do the analysis themselves or demand that a certified analysis is supplied for each delivery by the supplier of the polyelectrolyte.

## APPENDIX A

# EXPERIMENTAL PROTOCOL FOR THE CHARACTERIZATION OF PE FOR SLUDGE DEWATERING

## 1. SAMPLE TREATMENT

The samples are received as emulsions (active matter 42-56 % according to the providers). They appear as milky and viscous liquids. A weighted amount (approximately 5 g) of the suspension<sup>4</sup> is added dropwise to an excess of acetone (technical grade, around 50 mL) kept under vigorous stirring (with a magnetic stirring bar). The polymer precipitates as a white solid (Figure 1).

FIGURE 1

EXAMPLE OF POLYMER PRECIPITATE IN ACETONE



The solid is separated by decantation or filtration with a paper filter (Munktell grade 15, 65 g/m<sup>2</sup>, flow rate 25s/10 mL, retention 8-12 μm), then dried at 70°C overnight (10 hours). The solid content can be calculated by:

$$\text{solid \%} = \frac{\text{dry solid weight}}{\text{emulsion weight}} * 100$$

<sup>4</sup> Since the emulsion is viscous and sticky, a convenient way to perform this operation is to use a 5 mL plastic syringe for the precipitation. Fill the syringe with the liquid, weight it, then weight it again after it is emptied.

Also the amount of non-volatile oil fraction can be determined, by evaporating the acetone and water present in the liquid phase (it can be done with a rotary evaporator when available, or by gently evaporating the solvent at 40-50°C under air flow) and weighting the residual liquid.

NB: the solid is usually highly hygroscopic, thus it should be stored in a sealed container to minimize take up of atmospheric water, that can introduce errors in the following operations.

## 2. ELEMENTAL ANALYSIS

There are several commercial instruments for elemental analysis. They are all based analogous principles, that is combustion of the sample and GC analysis of the resulting gases (CO<sub>2</sub>, H<sub>2</sub>O, NO<sub>x</sub>). A weighted amount of sample (few mg are often sufficient, usually around 20 mg) is put in a combustion chamber. The machine burns the sample and the formed gas is carried by an inert gas into a GC column. The results are obtained in the form of chromatograms, which the software included with the instrument converts into numerical values expressed as % of C,H,N (and sometimes S). By difference the values of other atoms are obtained (O and Cl in case of the polymers in object).

## 3. VISCOSITY MEASUREMENTS

Viscosity measurement are performed for solutions at 1 weight % and 0.1 weight % concentration in DEMI water. The procedure is exactly the same.

To prepare the solution, a weighted amount of solid polymer<sup>5</sup> (around 100 mg) is added to a vigorously stirred (> 500 rpm) flask filled with the right amount of water (around 10 mL). In order to ensure complete solubilization and homogenization of the solution, the stirring is kept for 24 hours.

NB: the solutions have limited stability, thus at the moment of the measurement the solution should be freshly prepared.

The 0.1 % solution is prepared by dilution 1:10 of the 1 % one. The solution is stirred overnight (approx. 10 hours) before the measurement.

The viscosity measurement procedure is dependent on the instrument used and it can vary a lot.

5 the solid obtained after the drying procedure sometimes needs to be grinded in order to obtain a fine powder.

## APPENDIX B

SUMMARY OF PARAMETERS OBTAINED FOR  
SAMPLES A-M

parameter	unit	A	B	C	D	E	F	G	H	I	J	K	L	M	discussiein section
$\eta_{0,1}$ (1 wt%)	Pas	32	51	105	30	21	2.5	30	83	39	2.5	32	79	69	3.8
K (1 wt %)	Pas	8	10	12	7.7	6.8	2.3	7.4	13.5	8.7	2.4	8.3	13.2	12.5	3.8
n (1 wt %)	none	0.29	0.2	0.19	0.26	0.26	0.39	0.25	0.16	0.2	0.4	0.22	0.17	0.188	3.8
cross-over $\omega$	Hz	0.27	0.08	0.02	0.1	0.52	5	0.08	0.01	0.03	5	0.027	0.012	0.014	3.10
cross-over G	Pa	4.5	4.5	4.3	2.4	4	3	2.7	3	2.1	3	1.9	4.7	3.5	3.10
$\eta_{0,1}$ (lim $G''/\omega$ )	Pas	72	130	328	40	24	2.4	100	370	145	2.1	130	460	330	3.10
$\eta_{0,1}$ ratio		0.44	0.39	0.32	0.75	0.88	1.04	0.30	0.22	0.27	1.19	0.25	0.17	0.21	3.10
$G'$ (LVR)	Pa	12	26	33	14	13	3.7	13	26	13	3.5	12	29	24	3.9
$G''$ (LVR)	Pa	7	10	12	6	6.5	3.5	5	7	4.5	3.5	5	8.7	7.2	3.9
$\tan\delta$		0.58	0.38	0.36	0.43	0.5	0.94	0.38	0.27	0.35	1	0.42	0.3	0.3	3.9
yield stress	mPa	10	20	17	18	18	3.5	18.5	33	18	2	18.5	30	32	3.9
$\eta_{0,1}$ (0.1 wt%)	mPa	660	390	510	260	180	100	1150	470	910	21	110	140	98	3.8
K (0.1 wt %)	none	48.48	130.8	205.9	115.4	116.7	25	26.1	176.6	42.9	119.0	290.9	564.3	704.1	3.8
n (0.1 wt %)	none	0.43	0.49	0.50	0.53	0.51	0.53	0.41	0.44	0.41	0.70	0.54	0.55	0.57	3.8
$\eta_{0,1}$ (1 %/0.1%)	mPas	357	216	214	158	130	132	375	242	293	45	104	111	100	3.8
conductance	microS	482	563	512	495	515	437	533	585	442	519	488	493	490	3.5
C %		44.6	41.4	46.7	48.4	45.6	40.5	40.6	39.4	44.4	47.6	45.6	40.1	40.1	3.3
C/N		7.4	7.3	7.9	6.8	5	8	6.2	6.1	7.4	7.1	6.9	5.4	5.4	3.3
C/X		1.1	0.9	1.2	1.4	1.3	0.9	0.9	0.9	1.1	1.3	1.2	0.9	0.9	3.3
NMR peak ratio		0.62	0.981	1.082	0.833	0.833	1.30	0.87	1.52	0.60	0.84	0.68	1.23	1.14	3.4

APPENDIX C

# H-NMR SPECTRA OF ALL SAMPLES



