Department of Biotechnology and Chemical Technology

Amphiphilic cationic polymethacrylates: synthesis, characterization and interactions with cellulose

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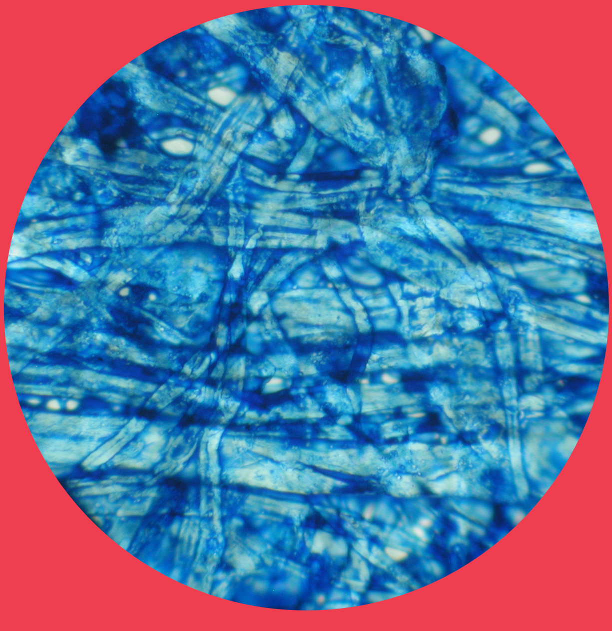
Arja-Helena Vesterinen



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Amphiphilic cationic polymethacrylates: synthesis, characterization and interactions with cellulose

Arja-Helena Vesterinen

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Abstract

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Abstract

Amphiphilic cationic co-polymers, containing poly([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide) (polyMETAI) or poly[2-(dimethylamino) ethyl methacrylate] (PDM) segment, were synthesized through two different main routes. Block co-polymers containing poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) were synthesized with oxyanionic polymerization, whereas radical polymerization was used to obtain statistical co-polymers with stearyl methacrylate (SMA) and fluorodecyl methacrylate (FMA).

The melt and thermal transition properties of the polymers were studied with dynamic scanning calorimetry and rheometry. PDM decreased crystallinity of the polymer and increased the melt strength of the polymers. The solution properties were studied with a surface tension measurement, with dynamic light scattering equipment, and with rheometry. Polymers containing highly hydrophobic segments, such as stearyl, formed charge stabilized aggregates in a water solution, whereas polymers with a less hydrophobic block, such as PEO, formed a micellar structure.

The suitability of the prepared polymers, as well as a set of commercial polymers, on cellulose fiber systems was studied. The polymers containing a cationic segment formed permanent adhesion on the anionic surface, and strong bonding with the cellulose fibers. The mechanical strength of the cellulose fiber sheets was increased more with polymers containing cationic segments than the ones with corresponding nonionic segments. Strain hardening behaviour was introduced into the fiber-polymer sheets that did not contain cationic segments and the bonding between the fiber and the polymer was weak enough. A mechanically strong cellulose fiber network could also be prepared with a hydrophobic cationic polymer, but the strength was decreased with the high density of the hydrophobic side group in the polymer.

The polymers containing a highly hydrophobic segment formed a thin layer coating on the paper surface and a small amount of polymer was enough for a complete thin layer coverage of the surface. Additionally, the higher amount of the polymer did not change the chemical or physical properties of the surface, which supported the assumption of a nanolayer formation.

Keywords polyelectrolyte, cellulose, strength additive, surface modification, rheology, DMA

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Tekijä
Arja-Helena Vesterinen

Väitöskirjan nimi
Amfifiiliset kationiset metakrylaatit: synteesi, karakterisointi ja vuorovaikutus selluloosan kanssa

Julkaisija Kemian tekniikan korkeakoulu

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Tiivistelmä

Amfifiilisiä kationisia ko-polymeerejä, jotka sisälsivät kationisen poly([2-(metakryylioksy)etyyli] tri-metyyli ammonium jodidi) (polyMETAI) tai poly-[(2-(dimetyyliamino) etyyli)metakrylaatti] (PDM) segmentin, valmistettiin kahdella polymerointitavalla. Poly(etyleeni oksidi) (PEO) tai poly(propyleeni oksidi) (PPO) lohkopolymeerit syntetisoitiin oksyanionisella polymeroinnilla, kun taas stearyyli metakrylaatti (SMA) tai fluorodekyyli metakrylaatti (FMA) kopolymeroitiin satunnaisjakautuneesti radikaalipolymeroinnilla.

Polymeerien sulaominaisuuksia ja lämpötilatransitiokäyttäytymistä tutkittiin dynaamisella pyyhkäisykalorimetrilla ja rotaatioreometrilla. PDM vähensi polymeerien kiteisyyttä ja lisäsi sulalujuutta. Polymeerien liuosominaisuuksia tutkittiin pintajännitysmittauksella, dynaamisella valonsirontalaitteella ja reometrilla. Polymeerit, jotka sisälsivät voimakkaasti hydrofobisen segmentin, kuten stearyyliryhmän, muodostivat ionisin varauksin stabiloituja aggregaatteja vesiliuoksessa kun taas hydrofiilisemmät lohkokopolymeerit, kuten PEO muodostivat misellejä.

Valmistettujen polymeerien käytettävyyttä selluloosakuidun sovelluksissa tutkittiin ja verrattiin kaupallisiin polymeereihin. Polymeerit, jotka sisälsivät kationisen segmentin, adsorboituivat voimakkaasti anioniselle pinnalle ja muodostivat voimakkaista vuorovaikutuksia selluloosakuidun kanssa. Selluloosakuitukalvojen mekaanisia ominaisuuksia voitiin parantaa enemmän näillä polymeereillä kuin vastaavilla neutraaleilla polymeereilla. Venymälujittuvia ominaisuuksia selluloosakalvoille saatiin polymeereillä, jotka eivät sisältäneet kationisia ryhmiä, ja joissa polymeerin ja kuidun välinen vuorovaikutus oli heikko. Mekaanisesti vahva kuituverkko saatiin aikaiseksi myös amfifiilisellä kationisella polymeerillä. Lujuus kuitenkin heikkeni, kun hydrofobisen ryhmän määrää lisättiin.

Samalla polymeerillä saatiin myös päällystettyä paperi siten, että se muodosti ohuen tasaisesti levittyneen kerroksen paperin pintaan. Tasainen polymeerikerros saatiin aikaiseksi jo hyvin pienellä polymeerimäärällä, eikä polymeerin määrän lisääminen enää muuttanut paperin pinnan kemiallisia tai fysikaalisia ominaisuuksia. Tämän perustella oletetaan, että menetelmällä on mahdollista saada aikaiseksi nanomittakaavan päällyste paperin pintaan.

Avainsanat polyelektrolyytti, selluloosa, lujuuspolymeeri, pintamodifiointi, reologia, DMA

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PREFACE

Work of this thesis was carried out in the Polymer Technology Research group at Aalto University School of Chemical Technology. I would like to express my gratitude to Prof. Jukka Seppälä for offering me the opportunity to do doctoral thesis in his group and for his way of supervising my thesis.

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Finally I want to thank my family and friends for being around for me, and not pushing too much, nor demanding. Friendship with you helps me to find joy and light in my life. It is easier to be productive, successful and positive in mind when surrounded by your love.

LIST OF PUBLICATIONS

I A. Vesterinen, P. Myllytie, J. Laine, J. Seppälä; The effect of water-soluble polymers on rheology of microfibrillar cellulose suspension and dynamic mechanical properties of paper sheet, J Appl Polym Sci. 116 (**2010**) 2990-2997.

II A. Vesterinen, J. Rich, P. Myllytie, J. Laine, J. Seppälä; Poly(ethylene oxide)-*block*-poly[2-(dimethylamino) ethyl methacrylate] as strengthening agent in paper: dynamic mechanical characterization, Macromol Mater Eng. 295 (**2010**) 269-275.

III A. Vesterinen, J. Rich, J. Seppälä; Synthesis and solution rheology of poly[(stearyl methacrylate)-stat-([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide)], J.Colloid Interface Sci. 351 (**2010**) 478-484.

IV A. Vesterinen, S. Lipponen, J. Rich, J. Seppälä; Effect of Block Composition on Melt Viscosity of Poly[2-(dimethylamino)ethyl methacrylate], Poly(ethylene oxide) and Poly(propylene oxide) Block Co-polymers, Express Polym Lett. 5 (**2011**) 754–765.

V A .Vesterinen, M. Anttila, K. Littunen, J. Rich, J. Seppälä; Chemical modification of fine paper base with amphiphilic copolymer, Nord Pulp Pap Res J. (Accepted July **2011**).

VI M. Peresin, Y. Habibi, A. Vesterinen, O. Rojas, J. Pawlak, J. Seppälä; Effect of Moisture on Electrospun Nanofiber Composites of Polyvinyl Alcohol and Cellulose Nanocrystals, Biomacromolecules 11 (**2010**) 2471–2477.

VII X. Liu, A. Vesterinen, J. Genzer, J. Seppälä, O. Rojas; Adsorption of PEO–PPO–PEO Triblock Copolymers with End-Capped Cationic Chains of Poly(2-dimethylaminoethyl methacrylate), Langmuir 27, (**2011**) 9769–9780.

THE AUTHOR'S CONTRIBUTION IN THE APPENDED PUBLICATION

I, II Arja-Helena Vesterinen planned and carried out the experiments, excluding the preparation of the cellulose samples, and wrote the manuscript with the assistance of the co-authors.

III Arja-Helena Vesterinen planned and carried out the experiments, and wrote the manuscript.

IV Arja-Helena Vesterinen planned and carried out the experiments, excluding DSC measurements, and wrote the manuscript together with the co-authors.

V Arja-Helena Vesterinen planned and carried out the experiments, excluding the pilot scale coating and ToF-SIMS, and wrote the manuscript together with the co-authors.

VI Arja-Helena Vesterinen planned and carried out the DMA measurements and participated in writing the manuscript with the co-authors.

VII Arja-Helena Vesterinen planned and carried out the polymer synthesis, and DLS studies, participated in planning adsorption studies, and wrote the manuscript together with the co-authors.

ABBREVIATIONS AND SYMBOLS

AIBN	azobis isobutyro nitrile
CMC	carboxy methyl cellulose
CNs	cellulose nanocrystals
CPAM	cationic poly(acryl amide)
CS	cationic starch
DC	charge density
DLS	dynamic light scattering
DMA	dynamic mechanical analysis
DMAEMA	2-(dimethylamino) ethyl methacrylate
dn/dc	specific refractive index increment [ml/g]
DPE	1,1-dimethyl ethylene
DS	degree of substitution
DSC	differential scanning calorimetry
FMA	fluorodecyl methacrylate
G’	storage modulus [Pa]
G”	loss modulus [Pa]
HR	hydrodynamic radius [nm]
LS	light scattering
LVE	linear viscoelastic
MALLS	multi-angle laser light scattering
METAI	[2-(methacryloyloxy)ethyl] trimethyl ammonium iodide
M_n	number average molecular weight [g/mol]
M_w	weight average molecular weight [g/mol]
MFC	microfibrillar cellulose
NMR	nuclear magnetic resonance
PEO	poly(ethylene oxide)

PDA	poly[(ethylene oxide)-*block*-(2-[dimethylamino] ethyl methacrylate)]
PDM	poly(2-(dimethylamino) ethyl methacrylate)
PFMAQ	poly((fluorodecyl methacrylate)-*stat*-([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide))
PPO	poly(propylene oxide)
PSMAQ	poly((stearyl methacrylate)-*stat*-([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide))
PVA	polyvinyl alcohol
Q	quaternary ammonium
QCM-D	quartz crystal microbalance with dissipation
RI	refractive index
RR	rotational rheometry
SEC	size exclusion chromatography
SMA	stearyl methacrylate
TEG	tetraethylene glycol dimethyl ether
ToF-SIMS	time of flight secondary ion mass spectrometry
T_c	crystallization temperature [°C]
T_g	glass transition temperature [°C]
T_m	melting temperature [°C]
η	viscosity [Pa s]
η_{sp}	specific viscosity
η_{rel}	relative viscosity

CONTENTS

1. INTRODUCTION

The pulp and paper process contains several steps. It begins with breaking down the wood structure chemically or mechanically to different fractions, and then paper or board is produced using different additives, many of which are polymers. [1] It is of interest to increase the understanding of this process, which would enable removing unnecessary processing steps or reduce the chemicals used in the process, resulting in environmentally less polluting processes. The novel cellulose fiber research, including this thesis, combines to a large extent two fields of research; polymer technology and forest biomaterial research. This research adds to the fundamental understanding of the phenomena, but it is still focusing on possible applications.

Polymers are used as additives in the papermaking process for a number of purposes; e.g. as a retention agent, strength additive, and coating chemical. [1, 2] For the most part, the polymers and other additives used in cellulose fiber applications are cationic, [3] since the surface of cellulose fiber is anionic. The different nature of a charge enables strong ionic bonding between these components and strong adhesion. It would be desirable to achieve also other properties, such as hydrophobicity, by means of adding hydrophobic groups in the polymer structure. This multi-functionality would improve several properties of a paper sheet, e.g. work as a hydrophobicing agent, and also as a strengthening agent. These tailored structures can be prepared in small amounts for studying fundamental properties. However, they are often difficult and expensive to synthesise, and for applications the possibility to upscale must be taken into account.

Structure-property correlations can be studied if the polymers are well characterized; in this thesis, that means solution properties, such as particle sizes and rheology. It is also important to know, for example, the polymer's adhesion properties on surfaces. With this background information, it makes it easier to tailor suitable polymers for strength additives, as well as for paper coatings.

1.1 The choice of molecular composition

Polymers used in paper applications usually contain a highly hydrophilic segment. Hydrophilicity can be increased with ionic groups, and, mostly, the polymers that are used in the paper industry are cationic, since most of the other components, are anionic. [4] The purpose of the ionic group is not only to increase the hydrophilicity of the polymer, but also to increase its bonding on fibers. The strength of paper [5] is normally improved with various highly hydrophilic high molecular weight polyelectrolytes, e.g. cationic (methacrylate) polymers. Even though the cationic part increases the bonding between the cellulose fiber and polymer, moderate charge density is desired. A polymer-fiber adhesion which is too strong can reduce the strength of the fiber network by having a negative effect on the uniformity of the fiber network.[6]

Interest in studying polymers with an amphiphilic character has increased considerably during the last decade.[7] Block co-polymers can have, for example, the ability to form self-organized structures.[8] The performance of a cationic group could be improved if they were concentrated at the ends of polymer chain, where they are needed. However, the synthesis of amphiphilic polymers can be challenging if the different components which are used in reaction form a heterogeneous system. In this thesis, this challenge was addressed with post-modification.

Co-polymers consisting of [2-(methacryloyloxy)ethyl] trimethyl ammonium iodide (METAI) and a hydrophobic monomer have found applications in the field of hydrophobizing hydrophilic surfaces. [9] METAI was chosen as the cationic segment and it was introduced into the polymer by co-polymerizing 2-(dimethylamino)ethyl methacrylate (DMAEMA) [8] with a non-ionic prepolymer or monomer, followed by methylation of the amine group [10, 11]. DMAEMA itself is also cationic in a water solution at a neutral and low pH, when an amine group is protonated. [12] The polymer structures which were chosen as non-ionic segments were poly(ethylene oxide) (PEO), poly(propylene oxide) PPO and stearyl methacrylate (SMA). The use of PEO was motivated since they have found applications as a hydrophilic component in the field of hydrophobizing paper. [13] A long aliphatic carbon chain is typical of hydrophobic components used in industrial paper production processes. [14] Water soluble polymers containing long aliphatic side chains have the potential to be used as dispersing agents for strongly hydrophobic materials such as polyethylene [15] and carbon nanotubes, [16] and SMA was mainly chosen for applications where a hydrophobic segment was needed.

1.2 Solution properties

Relatively high concentrations of PEO, PPO, PDM (poly[2-(dimethylamino)ethyl methacrylate]), and their block copolymers can easily be dissolved in water. [8, 12, 17] In contrast to these hydrophilic polymers, the solubilisation of highly hydrophobic poly(alkyl methacrylates) in water demands copolymerization with the hydrophilic monomer. [18] Typically, this requires more than 80 mol% hydrophilic monomer [10], but stearyl methacrylate especially obtains water solubility when copolymerized with ionic co-monomers. [15] The solubility of polymers containing a highly hydrophobic segment can be further improved by using a suitable organic co-solvent, [19] however; such an approach should usually be avoided, from an application perspective.

It is important to study polymer behavior in a water solution in order to predict its behavior as an additive. Typically, the viscosity of a polymer solution decreases when the solubility of the polymer in the solvent decreases and the reduction in viscosity is caused by a decrease in the hydrodynamic radius [20] or the radius of gyration. [21] However, solubility is not always easy to determine. Even though PEO visibly dissolves in water, it remains as clusters, and the larger the cluster, the better the adsorption on fibers and fine particles. [3] In addition, some special solution properties have been found for amphiphilic polymers. For example block co-polymers from stearyl methacrylate and 2-(dimethylamino)ethyl methacrylate exhibit self-organising behaviour in different organic solvents, [18] and at high pH, PEO-b-PDM will aggregate at the temperature where the PDM sequence is totally deprotonated and sufficiently hydrophobic. [12]

From an application point of view, the rheological properties are more critical than the actual particle size. Solution viscosity is strongly dependent on the nature of the polymer, but the solvent also plays an important role [21] as it affects the hydrodynamic size of the polymer. The hydrodynamic size can decrease due to the polymer structure, e.g. branching [21], or it can decrease due to a solvent in which the polymer has limited solubility, i.e. not all of the segments are completely dissolved [22]. However, the rheological behaviour of amphiphilic polymers deviates from that of more homogeneous polymers [23]. The most typical difference is an atypically strong concentration dependence [22], where a sharp increase in viscosity is observed above a certain concentration [24]. This concentration dependence [25] is observed when the hydrophobic segment is long enough [26] , so that the polymer may form an associated structure in the solution [24].

1.3 Fiber suspension rheology

Rheology is commonly used in research on pulp and paper processes, with simple viscosity measurements being done both for polymer and fiber suspensions. [27] In this study, rheology was used to predict how a polymer additive affects paper strength. In many rheological studies, storage modulus of fiber suspension has been used as a synonym for strength. [28] In this thesis, we are studying strongly yielding materials, which can be said to be unstable. Therefore, the focus is on the structure break down.

The surface of cellulose fiber consists of microfibrillar material and the characteristically shear thinning behavior of microfibrillar cellulose (MFC) [28] is close to macroscopic fibre. [29] Here, MFC was used as a model compound of macroscopic fibres [30] because the particle size of MFC is small enough [31] to be suitable for conventional rotational rheometers with narrow gap sizes. [32] Repeatability of rheological measurements of the MFC suspension was confirmed by using same MFC batch and careful preparation of the suspensions.

1.4 Polymers as strengthening agents in cellulose fiber sheets

A generally accepted mechanism behind the development of paper strength is to increase fiber-fiber bonding, [33] which can be achieved by adding a hydrophilic polymer. [5] According to adhesion theory, [34] polymers which are used as a strengthening agent in paper should be as hydrophilic as possible. There are, however, a number of other factors in a polymer molecule that can affect the strength of a paper sheet, such as charge density or molecular weight. [35] Cationic water soluble polymers, like cationic poly(acryl amide) (CPAM), [36, 37] and cationic polysaccharides [35] are used in the paper industry since they have a good affinity to cellulose fiber. [4] Paper strength is most effectively increased by anchoring the highest possible amount of polymer on the surfaces of fibers. This can be achieved with a polymer having a moderate charge density. [35]

The polymers used as strengthening agents are typically of a high molecular weight. Very small molecules may penetrate into the fiber pores, [34] whereas polymers of a higher molecular weight remain on surfaces, [4] where the fiber-fiber bondings are formed. The affinity to particles can also be increased by increasing the entanglement formation of the polymer. [38] It is also known that fiber-fiber bonding can be strengthened by decreasing the amount of easily removable water in a fiber suspension. [5] Most importantly, a good strength enhancing polymer should form a uniform distribution of fibers, without causing undesired flocculation.[6, 39]

Poly(ethylene oxide) (PEO) is not a typical strength enhancing polymer. It is widely used in the paper industry to improve retention, but it also increases the paper strength if the molecular weight is high enough. [3] The adsorption mechanism of PEO on the surface is proposed to be an association induced bridging, [38] and PEO is assumed to act as a dispersing agent. The problem with using PEO is its lack of adhesion to fibers. To improve its affinity to fibers in pulp and paper processes, PEO is typically used together with so called co-factors, such as molecules containing aromatic rings and acid groups, hydroxyl groups or cationic groups. [40, 41] When PEO is modified by introducing cationic anchors to it, adsorption of the polymer on fibers only at chain ends would prevent the polymer from forming flat conformation on the surface, and maintain a three-dimensional conformation and enhance strength. [39]

The mechanical strength of a cellulose fiber sheet decreases in a humid environment. The mechanical properties were mostly studied in this thesis with dynamic mechanical analysis (DMA) in controlled humidity in film tension mode. DMA, at varying humidities, has been performed for paper [42-44] and cellulose [45] applications, mainly focusing on mechanosorptive effects and creep [46]. A dynamic mode also enables the study of reversible deformation. In oscillatory measurements, the focus has been on changes in tan delta, but changes in mechanical strength in humid conditions are most clearly seen in changes in the storage modulus. [47]

1.5 The chemical modification of paper surfaces

Paper surface coatings are typically mixtures that consist of different components, including pigments, binders and different additives. Coating amounts are generally rather high, about 15 g/m^2. [48] After coating, the paper surface is calendared in order to improve, for example, the gloss and surface smoothness. [49] The properties of calendared paper can be enhanced by wetting the surface of the paper prior to calendaring, [50] so one way to further improve paper surface properties could be to include additives in the moistening water.

Several groups have reported chemical modification of hydrophilic surfaces with water soluble amphiphilic polymers. [9, 13] Stearyl methacrylate polymers have been reported to be effective modifiers of boxboard, [14] but not from a water solution. Stearyl methacrylate has also been used to stabilize long aliphatic chains in a water solution [51]. Additionally, a number of hydrophobic compounds are used to decrease sticking in the pulp and paper processes and to hydrophobize fibers.

Hydrophobization of a paper surface can be characterised by contact angle measurements, but the chemical analysis of the surface is also possible with time of flight secondary ion mass spectrometry (ToF-SIMS). ToF-SIMS is widely used in biopolymer analytics [52], but it is also a practical tool to characterize paper surfaces. [53-55] The carbon in cellulose fibre provides a strong signal during analysis, but in order to study the coating of the paper surface, the coating polymer has to have a molecular structure with a signal that deviates from that of cellulose. [55] Many of the polymers used in paper applications, such as cationic starch, contain a cationic group originating from an ammonium ion which can be identified with ToF-SIMS [56]. Another good component to identify on paper surfaces is fluorine-containing molecules, [57] and high tendency to ionize fluorine makes it a good marker polymer. [52]

ToF-SIMS is a surface-sensitive mass spectrometry [58], having a measuring depth of 1-2 nm, [59] and a horizontal resolution originating from the primary beam of 150 nm. [52] It can be used for the identification of mass segments and for chemical imaging. [52] One problem with ToF-SIMS can be its lack of quantitativeness. The surrounding matrix affects the susceptibility to ionization, but this is often not a significant problem in polymer analytics.

1.6 The scope of the thesis

The aim of the thesis was to 1) synthesize block and statistical co-polymers, which have a tailored structure, 2) enhance the properties of cellulose fiber sheets with polymer additives, and 3) to find a structure-property correlation between polymer structure and properties of cellulose fiber sheets modified with these polymers. This thesis consists of two parts: first, the polymer synthesis and characterization are described, and a second part, where these polymers are used to modify cellulose fiber sheets and the paper surface.

Polymer synthesis and characterization is described in publications II, III, IV and V. The goal was to synthesize polymers having a cationic segment that would attach to anionic groups, but also having a non-ionic segment with the level of hydrophobicity depending on the application. A set of poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO) and PEO-PPO-PEO macroinitiators were used to synthesize block polymers with PDM segments. [IV] Additionally, a hydrophilic cationic PEO was synthesized to be used as a strength additive. [II] Water soluble methacrylate polymers, with a hydrophobic side group, were tailored to introduce a hydrophobic nanolayer coating on the fine paper base surface. [III, V] These statistical co-polymers contained [2-(methacryloyloxy)ethyl] trimethyl ammonium iodide (METAI) as the cationic part and stearyl methacrylate (SMA) or fluorodecyl methacrylate (FMA) as the hydrophobic part.

The solution properties of the polymers were studied in publications I, II, III, V and VII. The focus was on the rheological properties [I, III, V], but also other solution properties such as the particle sizes and surface tension were characterized. [II, VII] The effects of hydrophobic groups, [III, V] molecular weight, [V] and ionic strength [I, V] on the rheological properties of the solution are discussed. Additionally, adhesion properties are described. [VII]

Fiber sheets consisting of cellulose fiber and polymer were prepared in publications I, II and VI. The main target was to study the strength enhancing properties, but also the effect of humidity on the mechanical strength was evaluated. Some of the sheets were cellulose fiber sheets, in which anionic, cationic or noionic strength enhancing polymers were used [I, II], but also poly(vinyl alcohol) reinforced with cellulose nanocrystals were prepared, and the mechanical properties were studied with DMA. [VI] Also, the rheological properties of the fiber suspension and dynamic mechanical properties of the paper sheets were compared to evaluate whether the strength properties of the paper sheets can be estimated from the rheological behavior of dilute suspensions. [I] Additionally, the effect of nonionic interactions between poly(vinyl alcohol) and cellulose fiber is discussed [VI], , as well as the effect of hydrophobicity. [60, 61]

In publication II, the theme around the paper strength is continued with a study on how cationization could improve the strength enhancing properties of PEO, and make it as a wet strength additive in paper without a co-factor. The use of a weakly and highly cationized PEO as a strengthening agent was studied by using these polymers as additives with pine pulp fibers.

Hydrophobically-modified water soluble polymers were also used in coating applications. [V] These polymers were applied to paper sheets on a laboratory scale, and on pilot scale as an additive in the moistening water of the calendaring process. The effect of the molecular composition, as well as the effect of the coating amount, was discussed. The distribution of polymers on the surface was studied by chemical imaging and the physical properties of the modified paper surface were also measured.

2. THE SYNTHESIS OF CATIONIC METHACRYLATE POLYMERS

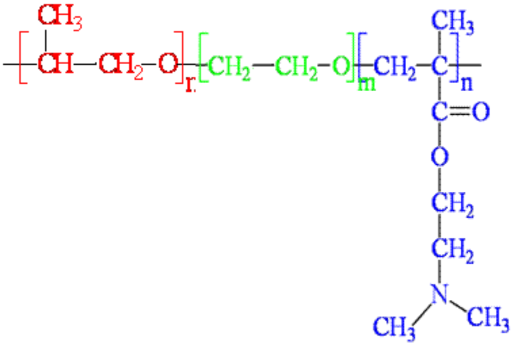
Amphiphilic co-polymers, containing a cationic methacrylate segment, were synthesized through two different main routes. Block co-polymers were synthesised with oxyanionic polymerization, whereas radical polymerization was used to obtain statistical polymers. Polymers were characterized with nuclear magnetic resonance (NMR) spectroscopy, as well as with size exclusion chromatography (SEC) using a light scattering detector (MALLS). The thermal characterization of the resulting polymers was performed with differential scanning calorimetry (DSC) and rotational rheometry (RR). Further, the polymer particle sizes in solutions were measured with dynamic light scattering (DLS). Solution rheology was done for two reasons, as a tool to study polymer solution behaviour and to measure the viscosity for application purposes. [II, III, IV, V, VII]

2.1 Cationic poly(ethylene oxide) and poly(propylene oxide)

There are several different ways reported in literature to introduce cationic groups into poly(ethylene oxide) PEO and poly(propylene oxide) PPO. [11, 62-65] The simplest way to prepare cationic PEO is through end group functionalization. [66] More efficiently cationic properties can be obtained through the grafting of PEO into cationic dendrimer [67] or through block co-polymer formation. One way to synthesize block polymers, introduced by Nagasaki et al. [68], is to use potassium alcoholate RO^-K^+ as an initiator. [69] The method is called oxyanionic synthesis, [68, 70-72] and different macroinitiators containing a hydroxyl group, [73-75] such as PEO, can act as such an initiator.[76, 77] The method has been used for the polymerization of methacrylates containing particular heteroatoms, such as nitrogen or oxygen, [69, 71] e.g. 2-(dimethylamino)ethyl methacrylate (DMAEMA) [78].

2.1.1 Thermal transition behavior

Block co-polymers consisting of poly[2-(dimethylamino)ethyl methacrylate] (PDM), PEO and PPO were synthesized through oxyanionic polymerization. DMAEMA was polymerized into the end groups of a set of macroinitiators with a varying ratio of PEO and PPO. [IV] The polymer structure was PDM-*block*-PEO-*block*-PPO-*block*-PEO-*block*-PDM; the structures of the corresponding blocks are presented in Scheme 1, and the characterization details in Table 1.



Scheme 1 The block structures of PPO (left), PEO (middle), and PDM (right). [IV]

Table 1 Molecular weight characterization of the synthesized block polymers using MALLS SEC. [IV]

Polymer	dn/dc ᵃ ml/g	dn/dc ᵇ ml/g	Molecular weight (g/mol) M_n	M_w	PD
PDM	0.07	0.07	14600	19900	1.37
PDM-PEO-PDM	0.064	0.07	26500	28300	1.07
PDM-PEO-PPO-PEO-PDM-H [c]	0.057	0.06	32300	48400	1.50
PDM-PEO-PPO-PEO-PDM-L [d]	0.055	0.06	11000	17000	1.55
PDM-PPO-PDM	0.06	0.06	13900	14300	1.03

a) theoretical values
b) values from SEC
c) H = higher molecular weight of PEO segment
d) L = lower molecular weight of PEO segment

Thermal transitions were determined by dynamic scanning calorimetry (DSC). Additionally, rheometry was used to confirm thermal properties, (Figure 1) and the results were consistent with each other (Table 2). The thermal behaviour, with obvious glass transitions and melting endotherms, indicated that poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) segments are mostly phase separated in these copolymers at a solid state. Modification with poly[2-(dimethylamino)ethyl methacrylate] (PDM) only slightly affected the thermal transition temperatures of the PEO-rich pre-polymer, whereas more significant changes were observed in PPO-rich polymers. The thermal behavior indicates that PDM is phase separated from PEO, but forms a mixed phase with PPO. Additionally, a cold crystallization behavior for PPO-rich PDM-PEO-PPO-PEO-PDM-L could be observed in DSC measurements, as well as in a temperature scan in a rheometer. [IV]

Table 2 Thermal transition temperatures and enthalpies (**ΔH)** of the studied block-copolymers. The values in parenthesis are thermal transitions observed with a rheometer. [IV]

	DSC (Rheometer)			
Pre-polymer	**T_g °C**	**T_c °C**	**T_m °C**	**ΔH $_{\text{PEO-phase}}$ J/g**
PEO	-	41	66 (62)	180
PEO-PPO-PEO-H[a]	-61	39	61 (58)	150
PEO-PPO-PEO-L[b]	-65	17	39 (38)	170
PPO	-67	-	-	
Reference				
PDM	1 (5)	-	-	
Polymer				
PDM-PEO-PDM	-	35	58 (53)	220
PDM-PEO-PPO-PEO-PDM-H	-	34	53 (49)	180
PDM-PEO-PPO-PEO-PDM-L	-60	-12 (-15)	14 (10)	48
PDM-PPO-PDM	-8 (-10)	-	-	

a) H = higher molecular weight of PEO segment
b) L = lower molecular weight of PEO segment

The rheological characterization of the block co-polymers confirmed that the melt viscosity of the pre-polymers was increased by modifying them with a PDM block. (Figure 1) Additionally, PDM segments seemed to slightly increase the frequency dependence of the polymers and to modify polymers from Newtonian into shear thinning fluids. Part of the increased viscosity may originate from the increase in molecular weight, but the shear thinning nature was most likely influenced by the PDM block. [IV]

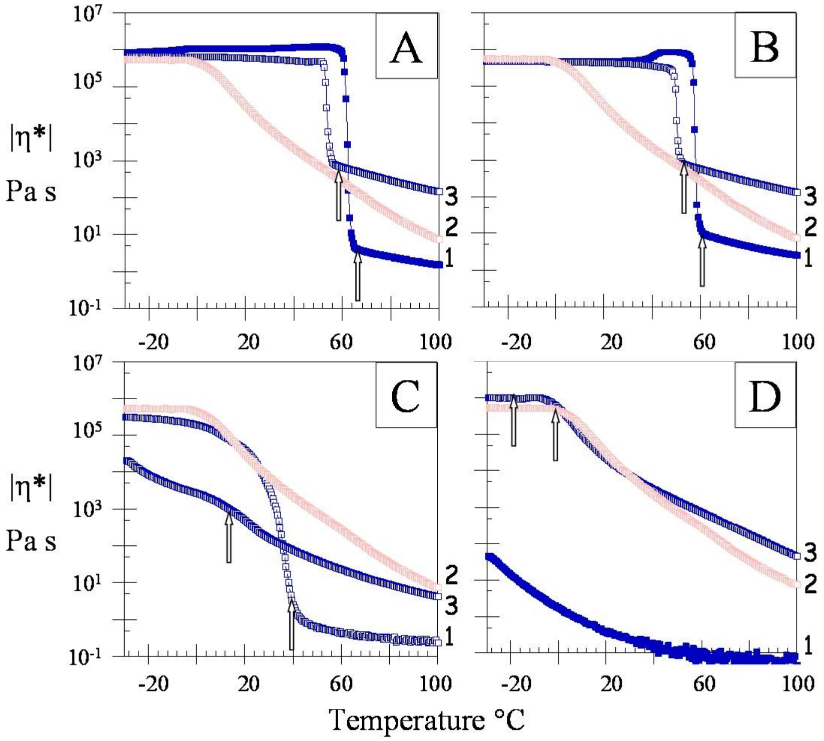


Figure 1 The effect of PDM on thermal transition behaviour, observed as the complex viscosity of A) 1 = PEO, 2 = PDM, 3 = PDM-PEO-PDM; B) 1 = PEO-PPO-PEO-H, 2 = PDM, 3 = PDM-PEO-PPO-PEO-PDM-H; C) 1 = PEO-PPO-PEO-L, 2 = PDM, 3 = PDM-PEO-PPO-PEO-PDM-L; D) 1 = PPO, 2 = PDM, 3 = PDM-PPO-PDM. The thermal transition points determined with DSC are marked with arrows. [IV]

2.1.2 Solution properties

A strongly cationic block polymer was synthesized through a reaction between tertiary amine in a PDM block and methyl iodide. After modification the tertiary amine groups became quaternary, where after, their solubility in organic solvents was strongly reduced, so that the polymers precipitated from the reaction solvent. The resulting [2-(methacryloyloxy)ethyl] trimethyl ammonium iodide (METAI) group is presented in Scheme 2. [II]

DLS and surface tension measurements were performed to study the micellization behaviour. Scattering intensity in DLS depends both on the aggregate size and the polymer concentration (the number of scatters). It should increase linearly with increasing concentration, as long as no aggregation occurs. Therefore, aggregation or micellization can be observed as a sharp increase in scattering intensity. Figure 2 displays the DLS of PEO-PPO-PEO-H, and the quaternary PDM-PEO-PPO-PEO-PDM-H solutions measured at 25 and 40 °C. [VII]

No differences in the critical micelle concentration between the temperatures were observed for the cationic PDM-PEO-PPO-PEO-PDM-H, but non-ionic PEO-PPO-PEO-H had a tendency to form micelles at a lower concentration when heated (Table 3). These effects are most likely due to the limited solubility of the PPO blocks at a high temperature. 79 However, the scattered light intensity of the polymers increased more at 40 °C than at 25 °C, when the critical micellization concentration was reached. [VII]

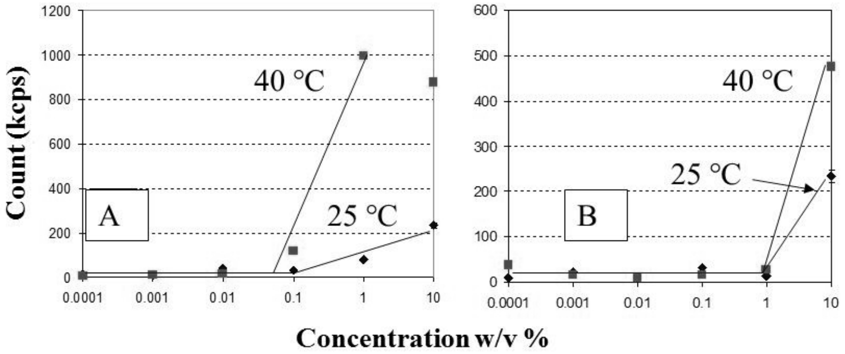


Figure 2 The critical micellisation concentrations of A) PEO-PPO-PEO-H, and B) quaternary PDM-PEO-PPO-PEO-PDM-H, measured with dynamic light scattering at 25°C and 40°C. [VII]

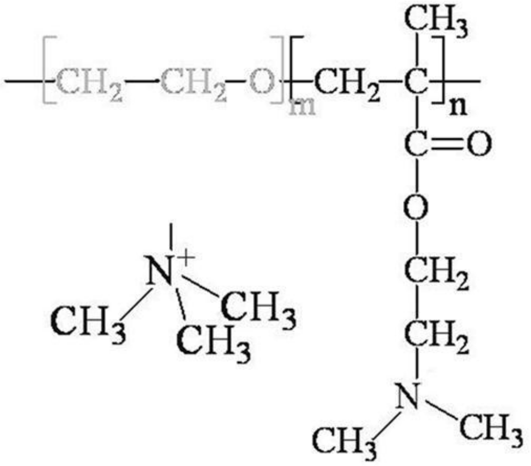
At submicellar solutions, the LS intensity of the polymer solution was lower at 40°C, compared to that at 25 °C, which is indicative of the self-association and aggregation of the PPO blocks at 40°C. In contrast, at concentrations above the micellization concentration, the macromolecular size was larger at 25°C. The smaller macromolecular size at 40 °C was most likely caused by the poor solubility and the smaller hydrodynamic size of the PPO block. Above the micellization concentration, the number of micelles in solution increased and their size was smaller as the polymer concentration increased. Additionally, the solubility of PEO-PPO-PEO-H was reduced with the increasing NaCl concentration. [VII] The phenomenon has been reported in literature and is called salt-induced micellization [80].

Table 3 The light scattering intensity and macromolecule size of aqueous solutions in a range of concentrations between 0.0001 and 10%w/v of PEO-PPO-PEO-H (P) and quaternary PDM-PEO-PPO-PEO-PDM-H (C-P), measured at 25 and 40 °C (note: "*u*" indicates unimer). [VII]

	T = 25 °C				**T = 40 °C**			
	LS intensity (a.u.)		Size (nm)		LS intensity (a.u.)		Size (nm)	
%	P	C-P	P	C-P	P	C-P	P	C-P
10	234	221	15	50	878	475	14	18
1	82	15	7	3	977	28	9	11
0.1	31	33	4	4	121	16	7	3
0.01	42	9	u	u	16	17	u	u
0.001	8	21	u	u	11	15	u	u
0.0001	14	9	u	u	10	7	u	u

2.1.3 High molecular weight poly(ethylene oxide)

Cationic PEO (poly[2-(dimethylamino) ethyl methacrylate]-*block*-poly(ethylene oxide)-*block*-[2-(dimethylamino) ethyl methacrylate]) was obtained through the end group modification of a PEO macroinitiator with DMAEMA through oxyanionic modification with a slightly modified procedure described in Section 2.1.1. Polymers were further modified into permanently cationic with methyl iodide, where after, the solution properties were measured. Molecular structures are presented in Scheme 2. These high molecular weight PEOs, with cationic anchors, were designed to be used as strengthening agents in cellulose fiber sheets. **[II]**



Scheme 2 The molecular structure of poly(ethylene oxide)-*block*-poly[2-(dimethylamino) ethyl methacrylate] (PDA) and its ammonium group after methylation (PDA Q). **[II]**

Characterized polymers are listed in Table 4. Conversion was observed with ^{1}H NMR analysis and in ^{13} C NMR analysis, no signals from $\underline{C}H_2OH$ end groups were observed. SEC analysis with a RI detector (Table 4) confirmed the end group modification, and no significant increase in polydispersity could be observed. SEC, combined with an LS detector, confirmed that both the molecular weight and the radius of PEO 100k increased, whereas changes in the mass and radius could not be detected for PEO 400k as there was only a very small increase in the theoretical molecular weight compared to the macroinitiator. **[II]** Additionally, no degradation of the PEO chain during the end group modification was observed. [81]

Table 4 Molecular data for macroinitiator and block polymers. [II]

	^{1}H NMR	SEC/RI			SEC/MALLS		DLS
Polymer[a]	M_n Block PDM (kg/mol)	M_n (kg/mol)	M_w (kg/mol)	PD	M_w (kg/mol)	R_n[b] (nm)	HR[c] (nm)
PDA400kQ	1.8	-	-	-	-	-	28
PDA400k	0.84	290	620	2.2	470	45	30
PEO400k	-	340	660	1.9	510	53	26
PDA100kQ	3.9	-	-	-	-	-	19
PDA100k	4.6	85	210	2.5	230	45	20
PEO100k	-	75	190	2.5	110	28	14

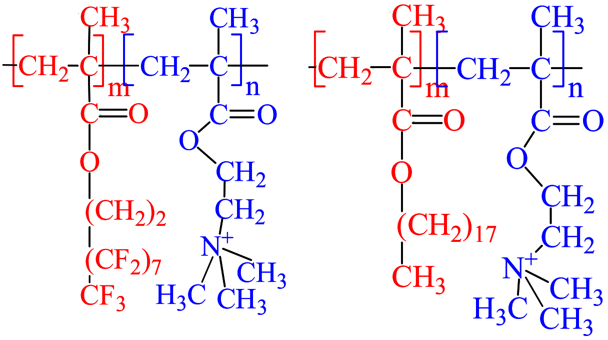
a) PDA = a block polymer of PEO and PDM
100k = a polymer formed from PEO (100 kg/mol)
400k = a polymer formed from PEO (400 kg/mol)
Q = a polymer with quaternary PDM
b) the number of the average radius of gyration R_n
c) hydrodynamic radius

The particle size in a water solution was then determined with a dynamic light scattering of modified weakly and strongly cationic versions of PEO block co-polymer (Table 4). The hydrodynamic radius indicates that these polymers also form aggregates or associated structures and the polymers exist as clusters in water solution. The hydrodynamic radius (HR) of PDA was a little higher than those of the original PEO macroinitiators, which can be explained by a slight increase in molecular weight. The HR becomes smaller when the amine group is further modified into the ammonium group. The most probable explanation is that the permanently cationic form is more water soluble and it has a lower tendency to form aggregates. [II] The typical molecular weight of a PEO used as a paper additive is more than a million, with a hydrodynamic size (HS) of 200 nm. [3] The hydrodynamic size of these polymers is smaller, but large enough to be considered as relevant strength enhancing polymers.

2.2 Hydrophobically modified water soluble methacrylate polymers

Polymethacrylates with controlled molecular weights can be prepared by group transfer polymerization [10], atom transfer radical polymerization [64], reversible addition-fragmentation chain transfer polymerization [18, 19], ring opening polymerization, etc. [82] These methods enable an accurate block structure, but for application purposes, the synthesis of hydrophobically modified water soluble methacrylates was performed with radical polymerization using AIBN as an initiator. Statistical methacrylate co-polymers containing DMAEMA and stearyl methacrylate (SMA) or a fluorodecyl methacrylate (FMA) side group were synthesized with radical polymerization in a bulk phase. Radical synthesis was further developed by using 1,1-diphenyl ethylene (DPE) as a molecular weight controlling agent [83] in order to prevent uncontrolled radical formation, and therefore reduce molecular weight resulting in reduced solution viscosity. **[III, V]**

Further, these polymers were quaternarized with methyl iodide (described previously in section 2.1). Polymer structures are presented in Scheme 3. Unlike PEO and PPO polymers, polymethacrylates, containing highly hydrophobic grafts, were not water soluble until the amine group was quaternarized into ammonium. Therefore, all water solution studies were only performed for the highly cationic polymers containing the METAI-group. **[III, V]**

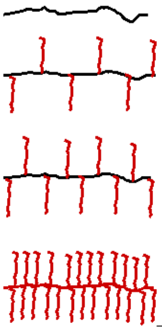


Scheme 3 Repeating units of poly(FMA-*stat*-METAI) (PFMAQ) (left) and poly(SMA-*stat*-METAI) (PSMAQ) (right). **[III, V]**

2.2.1 Stearyl containing prepolymer

A set of poly(DMAEMA-*stat*-SMA) copolymers were synthesized by varying the molecular composition from 0-100 mol% SMA (hereafter named as PDM-PSMA100, Table 5). Thermal transition temperatures were measured with DSC and rotational rheometry. The melting point of poly(DMAEMA-*stat*-SMA) can clearly be seen as a peak in DSC and as a decrease in the module in the rheometer when the molar percent of SMA is 17 % or higher. [III] Reliable T_g values of amorphous polymers could not be measured with rotational rheometry, as the stiffness of the polymers is outside the operating range of the instrument [IV].

Table 5 A schematic representation and characterization detail of P(SMA-*stat*-DMAEMA). [III]



	SMA ^{a}	M_n ^{b}	DSC		Rheometer
Polymer	Mol %	kg/mol	T_g (°C)	T_m (°C)	T_m (°C)
PDM	0	62.6	15	-	-
PSMA13	13	50.6	2	-	-
PSMA17	17	24.7	2	7	-
PSMA34	34	41.7	-15	9	-
PSMA50	50	75.6	-	24	14
PSMA100	100	195	-	36	34

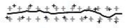
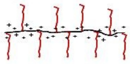
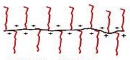
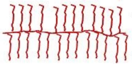
a) In feed.
b) Size exclusion chromatography against polystyrene standards.

Phase transition behaviour is consistent with the results reported in literature, where the T_m of a SMA homopolymer was reported to be 34 °C [84]. In this study, T_m increased more slowly with an increasing amount of SMA than reported elsewhere for SMA block co-polymers. [85] Since the polymerization is statistical and the reactivity ratios of the monomers are about the same, a random distribution of SMA is most likely to be expected. [64] The behavior observed earlier; a tendency of melt viscosity to increase with increasing content of DMAEMA, [IV] was also observed in this set of P(SMA-*stat*-DMAEMA) polymers. [III]

2.2.2 Cationic stearyl methacrylate co-polymer

Poly(DMAEMA-stat-SMA) was methylated with methyl iodide, giving poly(METAI-*stat*-SMA), hereafter called PSMAQ (described earlier in Section 2.1). With these polymers, the ammonium group had two functions, to increase the water solubility and introduce a cationic segment. The solution properties of the cationic co-polymers are listed in Table 6. The solubility of the PSMAQ co-polymer in water rapidly decreases when the amount of hydrophobic moieties is increased, and after 17 mol-%, the polymers became insoluble in water. This is consistent with what has previously been reported in literature [10], where the solubilisation of poly(alkyl methacrylates) in water demanded at least 80 mol% hydrophilic monomer content. Solubility in water can be improved by adding a suitable co-solvent. [15] PSMA34Q was soluble in water containing 10% tetraethylene glygol dimethyl ether (TEG), whereas PSMA50Q dissolves in water with a 15% volume ratio of TEG. **[III]**

Table 6 The solubility of poly(SMA-*stat*-METAI) polymers and zero shear rate specific viscosities of 1 % polymer solutions. **[III]**

		SMA	**Solubility**		**Water**	**Solvent mixture** [c]	
	Polymer	**Mol %**	**In water**	**Co-solvent %** [a]	η_s [b]	η_s [b]	**HR** [d] **nm**
	**PDMQ**	0	Soluble	-	1.2	1.4	-
	**PSMA13Q**	13	< 21 %	-	1.3	216	10
	**PSMA17Q**	17	< 5 %	-	11	0.9	
	**PSMA34Q**	34	Insoluble	10	-	132	15
	**PSMA50Q**	50	Insoluble	15	-	0.11	25
	**PSMA100**	100	Insoluble	100	-	-	-

a) TEG = tetraethylene glycol dimethyl ether
b) η_s = zero shear rate specific viscosity
c) 15 vol % TEG
d) HR = hydrodynamic radius measured with DLS

The poly(METAI-*stat*-SMA) does not have high surface activity, and the measured surface tension remains close to the surface tension of water (data not shown). It is most likely that these polymers form permanent aggregates in a water solution or so called “frozen micelle”, as has been discussed in literature. [9, 86] The particle size of a set of polymers was measured with dynamic light scattering to study the effect of the density of a hydrophobic side group on the particle size. [87] The measurements were performed in a solvent mixture containing 15 vol % TEG. The particle size distribution was wide and the solutions also contained aggregates up to a micron scale. However, a clear increase in the size of formed clusters was obtained with increasing hydrophobicity (Table 6).

2.2.3 Solution rheology

The rheological characterization of the polymers was one of the focus areas in this work. The viscosities of the set of poly(METAI-*stat*-SMA), containing 0-50% SMA, were measured in a solvent mixture containing 15% TEG, and the results are reported in Table 6. Additionally, rheological characteristics of the water soluble polymers were determined in water. The concentration dependence of the viscosity of the polymer solution was studied extensively, because viscosity behaviour is important from the application point of view. **[V]** The concentration dependence of a specific viscosity of the polymer solutions was compared with theoretical values. **[III]**

Typically, the specific viscosity of a polymer solution increases according to the scaling law. [25] Critical concentrations for each region were determined from specific viscosities according to the theory of entanglement viscosity [88]. The concentration dependence of a specific viscosity for polyelectrolyte solutions can typically be determined according to the following scaling relationship:

Semidilute unentangled $\eta_{sp} \sim c^a$, $c < c^*$

Semidilute entangled $\eta_{sp} \sim c^b$, $c^* < c < c^{**}$

Concentrated regime $\eta_{sp} \sim c^c$, $c > c^{**}$

Here, c^* stands for the transition concentration between semidilute unentangled and entangled, and c^{**} stands for transition concentration between semidilute entangled and concentrated regime. The concentration dependence of specific viscosities in water of two water soluble SMA co-polymers, PSMA13Q and PSMA17Q, is presented in Figure 3. The low concentration region is similar for both of the polymers, but a strong increase in viscosity is seen at higher concentrations. From the concentration curves of PSMA13Q, three different regions can be identified with different concentration dependencies, whereas only two regions can be identified for PSMA17Q. [III]

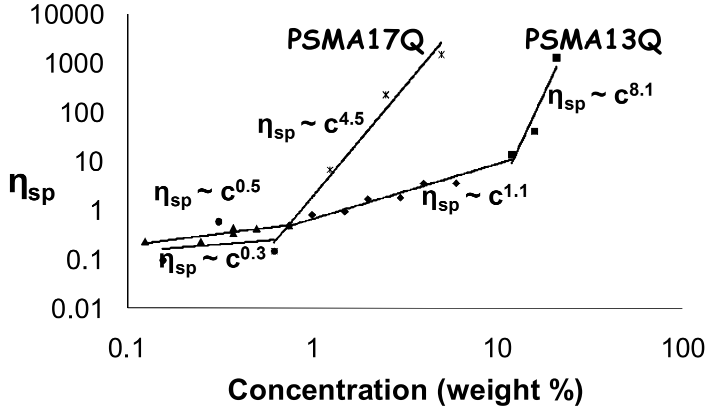


Figure 3 Specific viscosity as a mass concentration in water solution. Specific viscosity is determined: $\eta_{sp} = (\eta_o - \eta_{solvent})/\eta_{solvent}$. [III]

Transition concentrations and coefficients for concentration dependencies are listed in Table 7. First, the viscosity of PSMA13Q increases by a factor of $c^{0.5}$ and it follows the polyelectrolyte scaling law, [25] whereas the viscosity of PSMA17Q increases more slowly, by a factor of $c^{0.3}$. [III]

Table 7 The scaling relationships of polymers in a water solution. [III]

	Scaling coefficient			Transition concentration (weight %)	
	a	b	c	c*	c**
Theoretical [25]	0.5	1.5	3.75	-	-
SMA13Q	0.5	1.1	8.1	0.8	12
SMA17Q	0.3	-	4.5	-	0.7

After the unentanglement region, a separate region showing typical behaviour for an entanglement concentration of polyelectrolyte solutions was found when PSMA13Q was studied, having a concentration dependence of $c^{1.1}$. A similar region with moderate concentration dependence could not be found for PSMA17Q. In PSMA17Q, a rapid increase in viscosity occurs after the unentanglement region, and no entanglement concentration, typical for polyelectrolyte solutions, was found. A similarly rapid increase in viscosity at a high concentration was also found for PSMA13Q. In both cases, the concentration dependence after c** was atypically strong. [III]

Transition concentrations deviated significantly from each other. PSMA17Q already exhibited c** at 0.7 % mass concentration, whereas PSMA13Q reached c** at the relatively high mass concentration, 12 %. There are two likely reasons for such a sharp increase in viscosity, namely the entanglement formation of the polymer chains or associative forces between non-soluble SMA groups [24]. The frequency sweep presented in Figure 4 shows no entanglement frequency at a high concentration. It seems that PSMA17Q exhibits gel-like formation in a 5 % water solution, having a slope 0.2 of G'. It is most likely that these polymer solutions do not exhibit a melt-like behavior [21] caused by entanglement formation in concentrated regions. [89] It is most likely that the viscosity of poly(METAI-*stat*-SMA) is increased sharply due to association formation, and the proposed structure is presented as a schematic illustration (Figure 4). [III]

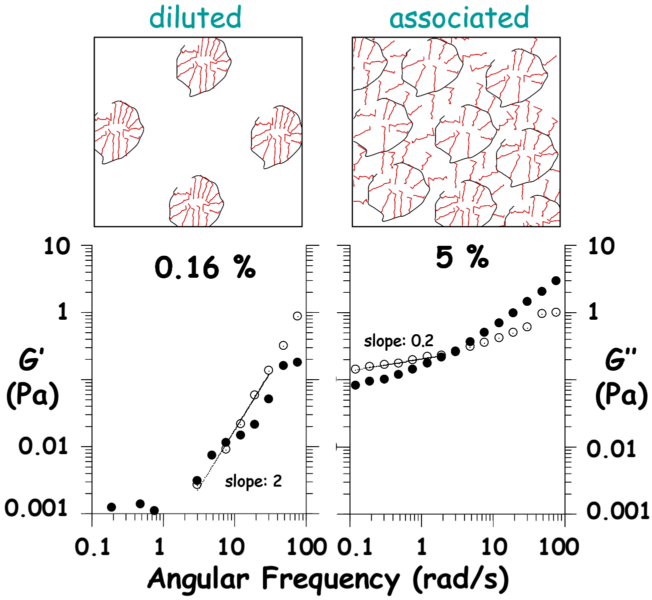


Figure 4 A frequency sweep of PSMA 17Q at low and high concentrations and a proposed structure of the polymer particles. Open bullets are G', closed bullets G". [III]

2.2.4 The viscosity of coating solutions

Polymer coatings were performed in a lab scale blade coater and in a belt calendaring process with a spray coater, and the viscosity requirements were different depending on the application method. [V] There are two main effects interfering with the rheological behavior of a polymer in a water solution; hydrodynamic radius and molecular interactions. In addition, these effects are strongly affected by solvent, polymer compositions, and polymer concentrations. [21] Electrostatic repulsion typically enlarge the hydrodynamic size of the polyelectrolyte molecule, which increases the viscosity. If the polyelectrolyte contains poorly soluble parts, the molecular interactions can cause an aggregation, resulting in low viscosity, but they can also cause intermolecular association, resulting in higher viscosity. [23] The kind of structure which is formed is strongly dependent on the polymer concentration, as well as the amount of hydrophobic segments. [V]

Since high amounts of water cannot be applied on a paper surface in conventional processes, the viscosity of the polymer solutions must be sufficiently low at relatively high concentrations. [22, 24-26] The challenge is that an increasing hydrophobicity in the copolymer increases the viscosity, [24] especially at high concentrations, but the solution viscosity of a polymer can effectively be reduced by decreasing the molecular weight. [22] The viscosity of polyelectrolytes is often higher due to intramolecular repulsion, but the repulsion can effectively be reduced by the addition of salt. [I]

The viscosity of coating solutions was tailored by three methods, namely the addition of salt, a reduction in the molecular weight, and varying the amount of the hydrophobic graft. The solution viscosities of poly(METAI-*stat*-SMA) (PSMAQ) and poly(METAI-*stat*-FMA) (PFMAQ) are reported in Table 8. A sufficiently low viscosity was obtained for high molecular weight polymers by having a 1% polymer concentration in a 7.5 mM NaCl solution. The viscosities of these polymers strongly increase as the amount of hydrophobic graft increases, as was discussed in the previous section (2.2.3). Still, the most effective method to reduce the solution viscosity was to reduce the molecular weight. [V]

Table 8 The properties of polymers and coating solutions. PFMAQ = poly (METAI-*stat*-(fluorodecyl methacrylate)), and PSMAQ = poly (METAI-*stat*-(stearyl methacrylate)). The number refers to the molar amount of fluorodecyl or stearyl side group. [V]

Polymer	Hydrophobic segment	SEC M_n	Coating solution		Coating method
			Conc.	Viscosity	
	mol %	kg/mol	mass-%	mPas	
PFMA5Q	4.9	200	1 [b]	3.2	Blade
PFMA9Q	9.1	~200 [a]	1 [b]	4.4	Blade
PFMA16Q	16.3	380	1 [b]	210	Blade
PSMA5Q	4.9	~200 [a]	1 [b]	6.0	Blade
PSMA9Q	9.1	~200 [a]	1 [b]	2300	Blade
PSMA13Q	13.0	51	4	4.1	Spray

a) some cross-linking in the sample, only indicative measurement
b) in a 7.5 mM NaCl solution

2.3 The adhesion of cationic polymers on silica surfaces

In this study, the adsorption of cationic polymers on anionic silica surfaces was monitored with quartz crystal microbalance with dissipation (QCM-D). The adsorption of hydrophilic block co-polymers (see Table 3: quaternary PDM-PEO-PPO-PEO-PDM-H and PEO-PPO-PEO-H) was done from a water solution in a batch mode. [VII] The adsorption of statistical co-polymers with a hydrophobic side group (see Table 6: PSMA13Q, PSMA34Q and PSMA50Q) was done from a 50:50 water: ethanol solution. [87] After adsorption, the unattached polymer was removed through rinsing with the same solvent.

The effect of the density of the hydrophobic side group on the amount of adsorption of poly(METAI-*stat*-SMA) was obvious as can be seen in Figure 5. The amount of the adsorbed polymer is increased by increasing the amount of the hydrophobicity. [87] This is rather natural; if we consider that the particle size (hydrodynamic radius) is increasing with the increasing hydrophobicity (Table 6) resulting in a thicker polymer layer on the surface. The proposed structure of the adsorbed layer is presented in a schematic illustration in Figure 5. It is obvious, after the rinsing step, that the cationic polymer is permanently adsorbed on an anionic surface, which is consistent with what has been reported in literature regarding different cationic polyelectrolytes. [90] A similar effect was also seen with quaternary PDM-PEO-PPO-PEO-PDM-H. It formed a permanent adhesion on a silica surface, whereas a significant amount of corresponding non-ionic PEO-PPO-PEO-H was removed by rinsing with water. [VII]

Generally, the amount of the adsorption of cationic block-copolymer PDM-PEO-PPO-PEO-PDM-H was much higher when compared to cationic co-polymers containing a highly hydrophobic side group. Additionally, the adsorption of a hydrophilic quaternary PDM-PEO-PPO-PEO-PDM-H on a silica surface increased along with an increasing polymer concentration in the adsorbing solution, [VII] but a similar effect was not seen with polymers containing a highly hydrophobic graft. The polymers containing a highly hydrophobic segment form an aggregate with strong forces, possibly having a solid core, whereas the polymers containing less hydrophobic segments form a dynamic structure that can expand or shrink depending on the conditions in the surrounding media. [VII]

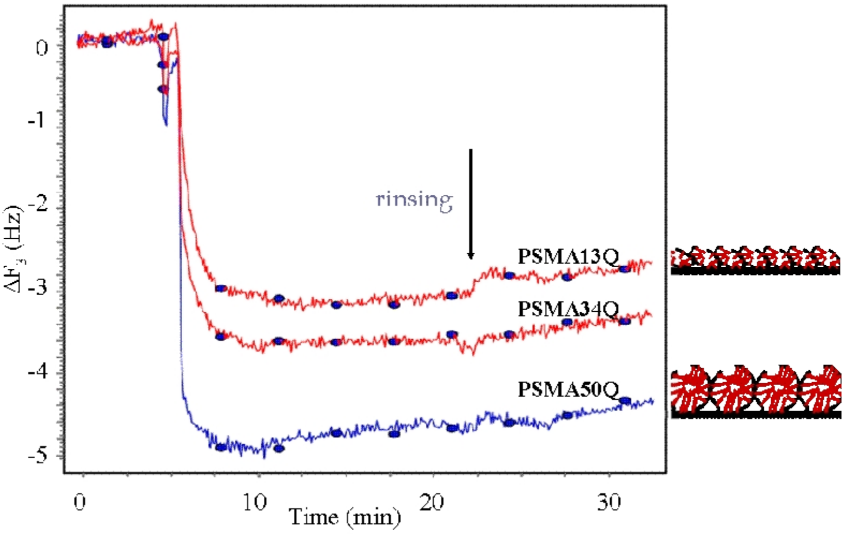


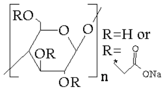
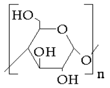
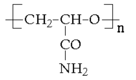
Figure 5 The adsorption on a silica surface of PSMA13Q, PSMA34Q and PSMA50Q from a 0.1% polymer solution (water: ethanol 50:50) detected with QCM-D. A schematic presentation of PSMAQ on silica surfaces (on the right).

As a conclusion, cationic polymers form adhesion on an anionic surface with strong bondings, which could be seen on a silica surface in quartz crystal microbalance. Cationic hydrophobic polymers adsorb, in rather small amounts, on surfaces, but, most importantly, they also form a permanent adhesion on the surface. Therefore, these hydrophobically modified water soluble methacrylates have a potential to be also used as applications for a cellulose fiber surface modification. Hydrophilic block co-polymers bind more water and they form thicker layer on the surfaces. Their possible application could be as a strength enhancing polymer.

3. MICROFIBRILLAR CELLULOSE SUSPENSION

Before beginning to study the mechanical properties of cellulose fiber sheets, a rheological study of a fiber-polymer suspension was performed to study molecular interactions in a dilute environment. [I] The commercial polymers which are used in this study are listed in Table 9. There are several studies where the rheological properties of fiber suspensions in water have been measured.[28, 29, 91] Rheology has been used from the paper strength point of view, [92, 93] whilst also focusing on the charge density of the polymer, the polymer concentration,[94] the salt concentration, [95] the dry substance content, [28] and the flocculation behavior. [94, 96] The suspension strength has also been studied. [97]

Table 9 The commercial polymers used as rheology modifiers and the strength additives of cellulose fiber. [I]

Polymer	Commercial name	Molecular weight	Repeating unit	Other information
CMC, Sigma-Aldrich	419338	700 000		Anionic, DS = 0.9, Mp=270 °C
CS, Ciba	Raisamyl 50021	Not known		Cationic, $R4N^+Cl^-$, DC = 0.035
CPAM, Kemira	Fennopol K3400R	6 000 000	 $[-CH_2-CH(CONH_2)-O-]_n$	Cationic, $R4N^+Cl^-$
PEO, Dow	Ucarfloc 309	8 000 000	$[-CH_2-CH_2-O-]_n$	Non-ionic

In this study, a fiber-polymer suspension is considered to be a structured fluid. [98] Structured fluids are multi-component systems, where there is not a linear correlation between rheological properties and, for example, polymer and fiber concentrations.[99] The rheological behavior of a fiber - polymer system can be explained by using several theoretical models. [100] These models have typically been used to describe the interaction between fibers, [101] usually in some polymeric matrix. [102]

Relative viscosity is used as a tool to study how different polymeric matrices affect and change the rheological nature of a microfibrillar cellulose (MFC) suspension. The relative viscosity of the suspension is determined by the ratio between the viscosities of the dispersing medium and the fiber suspension. [103] Here, the dispersing medium was a 0.5% polymer solution. Figure 6A presents relative viscosity values for the four different polymers listed in table 9. The viscosity of the MFC/CMC and MFC/PEO and suspensions follow the viscosity of the polymer solution, whereas MFC/CS and MFC/CPAM suspensions show evidence of yield stress. Also, it is remarkable that for the cationic polymers CS and CPAM, the relative viscosity is about 1 at high shear stresses. This despite the total content of the high viscosity material in the water increases from 0.5 % to 1 % when MFC is also added. The phenomenon has been reported in literature regarding CPAM, [104] and it is most likely that when fiber is added into a cationic polymer solution, the associated structure collapses. **[1]**

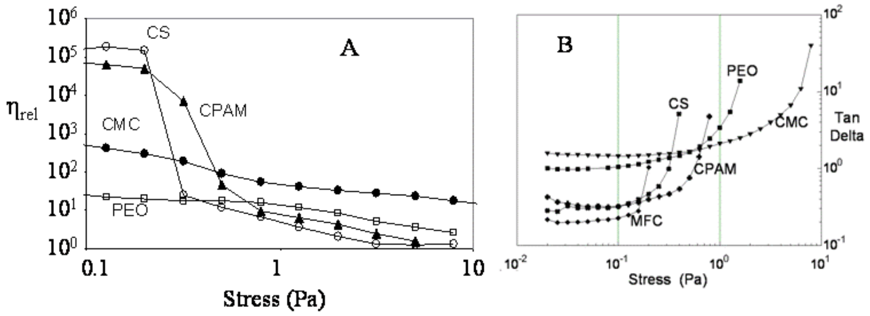


Figure 6 Suspensions containing 0.5 % polymer + 0.5 % MFC: A) relative viscosity B) tan delta. Relative viscosity = $\eta_{rel} = \eta_{susp} / \eta_{sol}$. **[1]**

In Figure 6B, the yielding behavior was determined by changes in the tan delta. If the tan delta of a structured fluid is very low, the materials are highly associated and if it is very high, they are very unassociated. [66] Presumably, at low shear rates; the adhesive forces are dominant, whereas at high shear rates, the distance between the fibers plays a key role. [101] The addition of CMC completely changes the rheological nature of the MFC suspension and the behavior of PEO is somewhat between these extremes. (Figure 6B) In pure MFC, the elastic nature dominates, whereas MFC/CMC suspension is more fluid like. The fact that a MFC/CMC suspension has practically no yield stress could be an indication that its structure is more homogeneous having an intermediate tan delta as a sign of a stable system. [66] CMC could function as some kind of stabilizer in the system, so that interactions between the continuous water phase and the fibers change. CMC seems to have a certain dispersing effect in the system, and it probably decreases the amount of free water in the suspension. [1]

It can clearly be seen that the rheology of microfibrillar cellulose suspension can be affected by the choice of polymer additive. MFC has a low tan delta, which is evidence of its gel-like nature, but when it is mixed with a polymer, the yielding behaviour of the suspension changes dramatically depending on the associating polymer. Cationic polymers form a strongly yielding structure with MFC, whereas nonionic and anionic polymers seem to have fluid-like properties which are dominant over the whole range of stresses. This indicates that cationic polymers form a strongly associated structure, but the structure formed between an anionic polymer and cellulose fiber is maintained weak enough to be flexible for changes when stress is applied. [1]

4. THE MECHANICAL PROPERTIES OF CELLULOSE FIBER SHEETS

The mechanical properties of the material depend on the compatibility of the components, and the weakest part of the paper is the fiber-fiber interface. Here, polymers, which possess supposedly different strength enhancing mechanisms, were used as strength additives, and the cellulose fiber sheets were studied with dynamic mechanical analysis. As the materials studied are hydrophilic, the presence of water in the film structure is also discussed. [I, II, VI]

4.1 Cellulose sheets with commercial polymers

The two extremes in rheological behavior, CS (cationic starch) and CMC (carboxy methyl cellulose), were chosen to be tested as a strength additive in paper, to find out whether the behavior observed in a dilute suspension can be seen in a humid paper sheet. In Figure 7, the stress-strain behavior of paper sheets containing CMC and CS are compared at three different levels of humidity. All of these paper sheets lose their strength properties when the humidity is increased, which happens as water weakens the fiber polymer interphase. Additionally, paper containing CMC is much stronger than that which contains CS and CMC tolerates the highest stress and strain levels in all conditions. The better strength enhancing properties of CMC is most likely because it improves uniformity of the fiber structure,[6] as was seen in the rheological properties. [I]

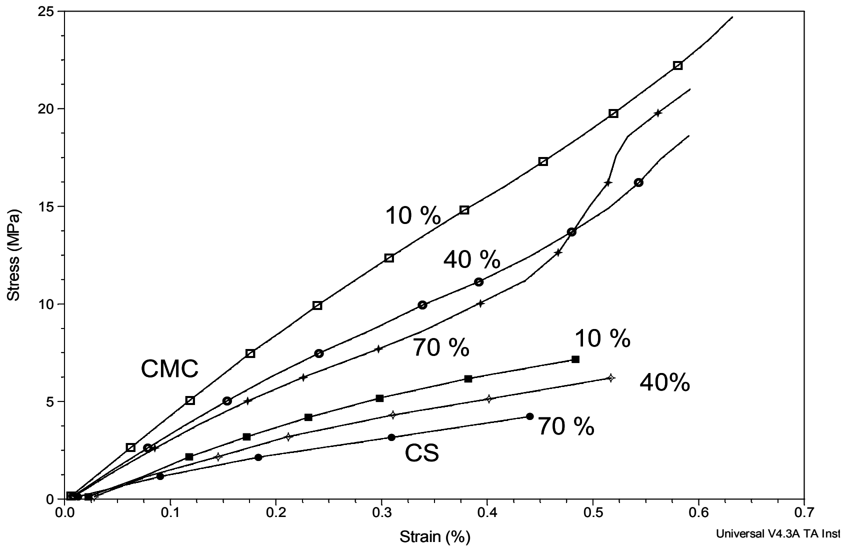


Figure 7 The stress-strain behaviors of CS and CMC at different humidity levels: 10, 40 and 70% relative humidity measured with DMA. [I]

The most remarkable differences were observed in the shapes of the stress-strain curves. CMC shows clear strengthening behavior under stress, which is not seen with CS. These DMA strength profiles were compared with those obtained with rheology measurements, and the behavior of CMC as a strength additive can be explained based on its rheological behavior. 99 MFC/CMC suspension has quite a linear stress-strain behavior in rheometry, and it maintains its ability to resist the strain and does not break as easily as CS. [I] The fluidic nature of a MFC/CMC suspension can be seen as the strain hardening of paper in DMA. Strain hardening behavior means that CMC causes internal mobility in the fiber network, so that at high stresses, the paper sheet is strongest at high humidity levels. Paper with CS seems to be quite fragile and strongly yielding, just like CS in an MFC suspension. [I]

According to literature, strain hardening in oscillative tensile measurements in DMA demands a certain amount of mobility from the material 47 and is a common phenomenon in viscoelastic polymers. 105 It has also been realized that mobility and structures that are more loosely associated can result in reduced shear thinning behaviour in rheological studies. 66 The mobility of

CMC is most likely a reason for the differences observed in both the rheological and dynamic mechanical properties. [I]

The effect of humidity on fiber-polymer interactions was also studied with hygroscopic nanofibers, containing cellulose and PVA. Nanofibers were prepared with electro-spinning from a suspension containing cellulose nanocrystals (CNs) [106] and polyvinyl alcohol (PVA). [VI] Just like macroscopic cellulose fiber samples, nanofiber sheets formed from PVA and CNs were weakened with increasing humidity. As was previously observed, a fiber sheet containing a non-ionic polymer exhibited clear strain hardening behavior. The most likely explanation to the strain hardening behavior is that the molecular interactions between the PVA and CNs are weak and water acts as a lubricant between the two components weakening interfacial adhesion. In conclusion, strain hardening behavior was observed in fiber polymer systems, where no strong ionic bondings were formed.

4.2 Paper sheets with cationic block copolymers

The hydrophilic cationic block polymers (poly(DMAEMA-*block*-(ethylene oxide)-*block*-DMAEMA)) listed in Table 4 were used as strength additives in cellulose fiber sheets. The dynamical stress-strain behavior of prepared paper sheets is described in Figure 8. The yield strength of the paper sheets decreases along with increasing humidity as previously observed with CS and CMC, and the paper were generally weaker at 80 % humidity. The behavior of the reference sample (the sample without a polymer additive) showed some material strengthening properties at a moderate humidity. The reason for the increasing strain might be that the water was working as a plasticizer, [107] bringing viscotic properties to the system. [II] Additionally, small decreases in strength levels are also observed at the higher temperature, which were not observed with CS and CMC. [I]

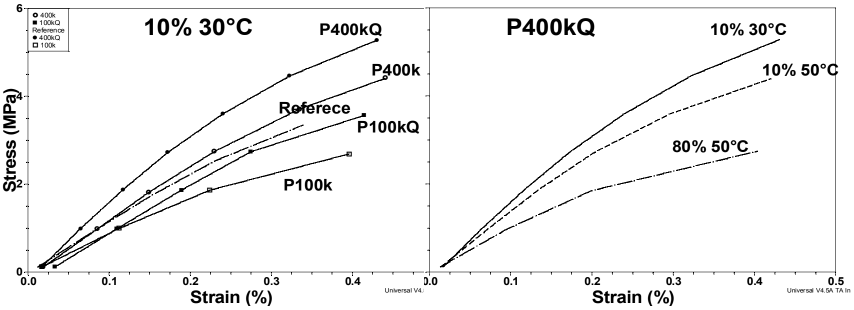


Figure 8 The Stress-Strain curves of papers with different PEO polymers at 30 °C and 10 % r.h. (left) and papers with PDA400kQ under three different sets of conditions (right). [II]

In general, the polymer which has a highly cationic form is a better strength additive than its weakly cationic analogue. The same kind of behaviour can be seen at both molecular weights. It indicates that a strong fiber network is formed by the cationic polymer. Another reason might be that the cationic segment simply makes a co-polymer more hydrophilic, which should enhance the paper strength. [5] However, it is obvious that a polymer of 100 kg/mol does not increase the strength of the paper sheet. The cause of such differing behavior, depending on the molecular weight, can be speculated upon, and the possible reason is the small particle size of the polymer aggregates. (Table 4)

Cellulose fibers are porous and polymer particles that are too small may penetrate into the porosity of cellulose fibers. [5] There might be a minimum hydrodynamic size needed for polymers used as strength additives in paper, [4] as it has been reported that an increase in the molecular weight of PEO increases the strength of a cellulose fiber sheet. [34, 67] The higher molecular weight would also contribute to adhesion, by having the possibility or tendency to form an interpenetrating structure. [5, 33]

Here, we compared two polymers that supposedly form weak or strong bonding between cellulose fibers. At higher temperatures, a weakly cationic PDA 400k appears to show a higher loss modulus, which is an indication of weaker bonds formed between fibers. **[II]** Due to these weaker bonds, the weakly cationic polymer is less yielding than a comparable highly cationic polymer. Due to the strong adhesion with cellulose fiber, none of the cationic polymers exhibited any strain hardening, which discussed in the previous section (Section 4.1). **[I]**

4.3 Microfibrillar cellulose sheets with cationic stearyl methacrylate

The water soluble poly(METAI-*stat*-SMA) polymer series (listed in Table 6) was used as an additive in a MFC sheet. Films were prepared by mixing a 1 % MFC suspension and a 1 % polymer solution, followed by solvent casting. The preparation of the films is described in more detail elsewhere. [60, 61]

The strength enhancing properties of PDMQ, PSMA13Q and PSMA17Q were studied, regarding the effects of the hydrophobic side chain and the amount of the polymer additive. The stiffness of the MFC films was measured with DMA and the results are presented as Young modulus in Figure 9. The stiffness of the MFC film was decreased with the increased addition of PSMA13Q. At the smallest amount, at a 10 mass% polymer addition, a slight increase in Young modulus was observed, but it started to decrease with an increasing amount of polymer. This is consistent with what is reported in literature, where the optimum amount of strength enhancing polymer is rather small, [35] unless polyelectrolyte complex or prolonged adsorption time is used. [108]

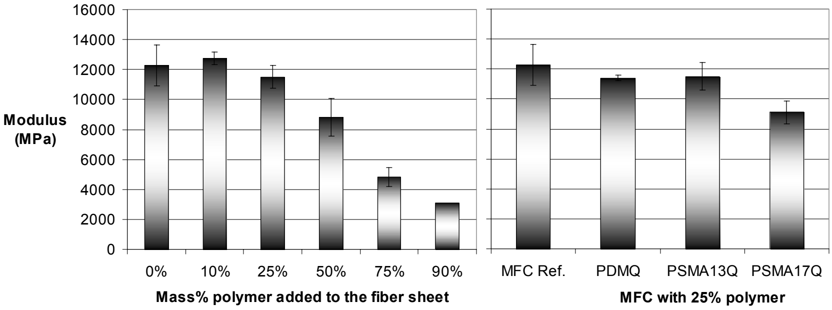


Figure 9 The young modulus of MFC sheets with poly(METAI-*stat*-SMA) as an additive. (PSMA13Q left)

The amount of hydrophobic side in the polymer chain affects the strength of MFC film, somewhat as expected. [35] The strength additives are typically highly hydrophilic polymers, and increased hydrophobicity is connected with a decreased capacity to improve the strength of a cellulose fiber network, [33, 35] even though hydrophobized fibers alone can form a strong network. [5, 39] Additionally, commercial strength enhancing polymers are not typically highly cationic, and the adsorption on surfaces is reduced with an increasing amount of cationic groups. [109] At 0-13 mol% graft density, the strength is at the same level as without a polymer addition, but a clear decrease is observed at 17 mol% graft density. Generally, none of the polymer additives markedly increased the Young's modulus of MFC film. Films prepared from MFC have a very high modulus for being strong but very brittle without any softener, [31] but a softening of these materials could not be studied because of the limited experimental window of the equipment.

5. THIN LAYER COATING OF PAPER SHEETS

The performance of water soluble polymers containing a hydrophobic side group as a coating agent was studied by applying a thin polymeric layer on the surface of a paper sheet. A fine paper base was coated with two methods: with a blade coater in a lab scale and with a spray coater which had a polymer as an additive in the moistening water of the calendaring process. The purpose was to study the effect of the amount of the hydrophobic group, as well as the effect of the amount of coating polymer on the surface chemistry. Additionally, the influence of temperature treatment on the surface chemistry was studied in belt calendaring. Polymer structures are shown in Scheme 3 (Page 17). [V]

5.1 The coating of the fine paper base with a lab scale blade coater

Lab scale coating was performed with the polymer solutions listed in Table 8. The coated fine paper base surface was analysed with ToF-SIMS, and the amount of the hydrophobic graft detected on the surface was compared with the graft density of the co-polymer. An example of a mass spectrum is presented in Figure 10. A cationic group, originating from [2-(methacryloyloxy)ethyl] trimethyl ammonium iodide (METAI), can be identified since the main signal is the same as has been identified from cationic starch. [56] Also, fluorine-based segments [57] were identified as being characteristic for the coating polymer with a systematic set of signals originating from the 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-hexadecafluoro-1-decyl methacrylate side group. Additionally, signals from the polymer backbone [52] can be identified in the higher mass region. [V]

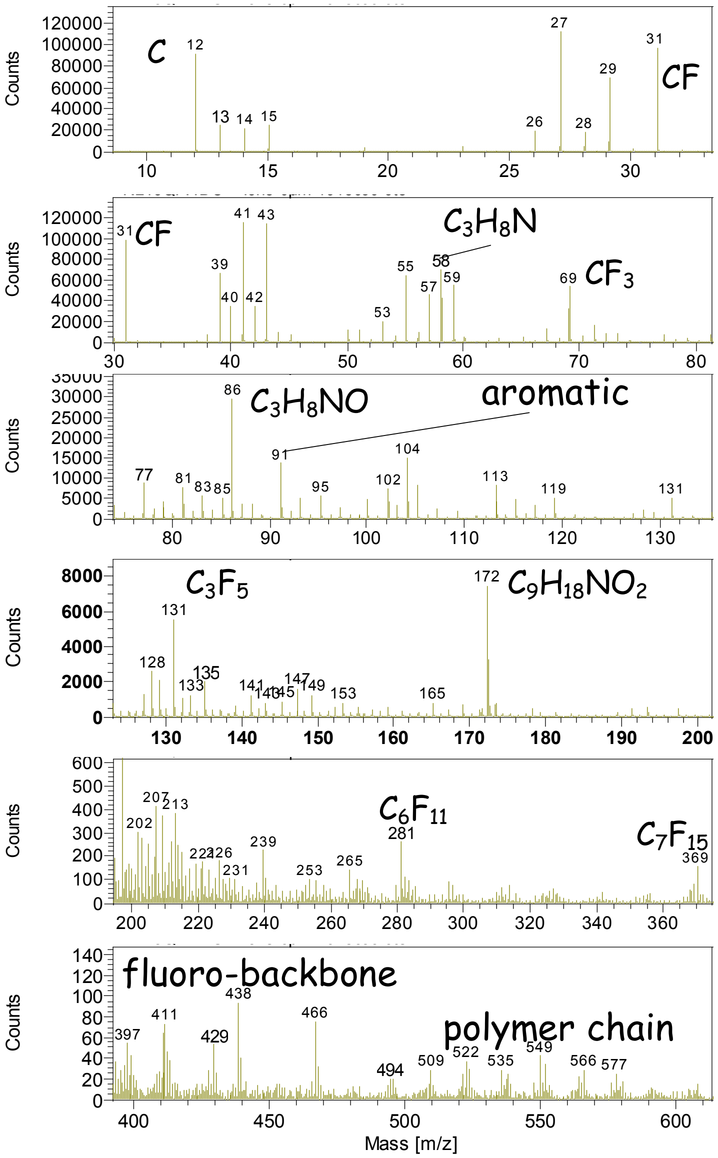


Figure 10 An example of a mass spectrum of fine paper base coated with PFMA9Q. [V]

The relative amounts of the most representative mass signals are listed in Table 10. The amount of CF increases with the increasing molar amount of the fluoro-containing segment in the methacrylate co-polymer. The presence of fluorine can also be seen in the increase in the amount of C on the surface. At the same time, the amount of C_3H_8N decreases along with the increasing content of CF. [V]

Table 10 The relative intensities of representative ions on blade coated surfaces. [V]

Copolymer	Hydrophobic segment	Ions detected in ToF-SIMS Intensity, a.u.					
	mol-%	C_3H_8N	CF	C	CH_3	C_2H_3	C_3H_5
PFMA5Q	4.9	85.6	15.9	16.6	10.6	42.0	4.6
PFMA9Q	9.1	58.2	48.4	49.5	14.8	59.4	4.2
PFMA16Q	16.3	53.0	84.1	69.9	15.8	53.6	3.1
PSMA5Q	4.9	64.8	0.3	1.9	12.5	59.8	8.2
PSMA9Q	9.1	51.3	0.2	2.8	15.5	85.7	7.3

Nonlinear increases in intensities were observed, but were most likely not due to molecular orientation. These polymers do not form dynamic structures in a water solution but aggregates, [III] and molecular orientation requires external energy, such as a temperature treatment. [86] The explanation for this behaviour lies in differences in the chemical environment between the samples. Fluorine has the highest tendency to form ionic segments and it is possible that the fluorine signal is strengthened for that reason. [52] The effect of fluorine can also be seen when PSMAQ and PFMAQ are compared. A difference between the samples was found, as the C_3H_8N signal was much stronger for the FMA samples than the SMA samples, even though the amount of C_3H_8N should be equal in each. The strong tendency of fluorine to form ions may also strengthen the C_3H_8N signal and cause non-quantitative intensities when different PFMAQ samples are compared. Therefore, a quantitative comparison of the samples is excluded.

ToF-SIMS, with an imaging tool, was used to study copolymer spreading on a paper surface. In Figure 11, the presence of nitrogen and fluorine on the surface of coated paper is visualized based on their characteristic signals. Nitrogen and fluorine compounds are evenly distributed on the surface, whereas calcium is an example of an uneven distribution. The variation observed in the surfaces is characteristic of the fiber structure originating from the paper surface. Therefore, the small amount of polymer applied to the surface spread out and then distributed on the surface evenly, without forming clusters. The approximate layer thickness of 0.16 g/m^2 polymer would be 160 nm as evenly distributed, and it could be stated that a nanolayer coating was achieved. [V]

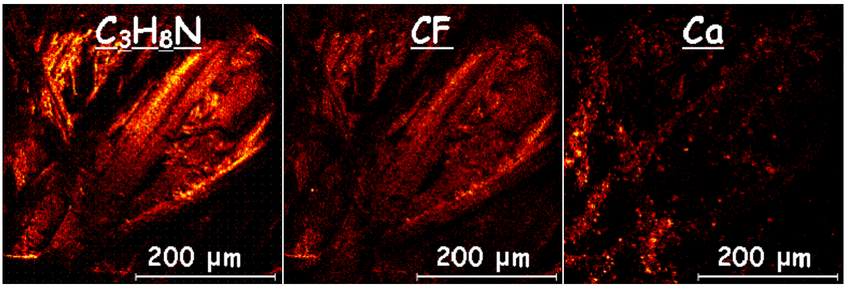


Figure 11 The distribution of PFMA9Q on FP base surfaces, shown as C_3H_8N, CF and Ca by ToF-SIMS chemical imaging. [V]

5.2 Pilot scale coating of the fine paper base with belt calendaring

In belt calendaring, the aim was to increase the surface hydrophobicity, using a polymer containing the highest possible content of hydrophobic segment that could be achieved without losing water solubility. The amount of the water that was applied on the paper surface should be rather low, usually less than 10 g/m^2, [50] in order to avoid a weakening of the paper and web breaks. The salt addition as a viscosity reducing agent was not an option due to a spray coating method in a pilot scale, and one of the polymers, containing a hydrophobic stearyl side group, was tailored to be used on a pilot scale in belt calendaring. (PSMA13Q solution; Table 8) The polymer was applied on the surface with spray coating from a 4 % solution followed by calendering. [V]

The purpose of the belt calendaring was to study the possibility of an industrial application of this particular polymer. The belt calendaring system also offered a practical tool to study the effect of the amount of coating polymer on surface properties but also to study the effect of temperature treatment by varying the calendaring temperature. In this study, the amount of coating polymer was varied with the running speed of the calendaring roll and two different amounts of solution were transferred to the surface. The higher amount of polymer solution used as moistening water was at the upper limit that can be applied on the surface without web breaks, but the PSMA13Q copolymer solution did not cause a breakage or sticking in the coating process. [V]

The aim was to obtain less wetting paper surface with chemical modification with a very small amount of the co-polymer, without physically modifying the surface characteristics. Coating with pure water was done as a reference, because water itself can change the surface chemistry of a paper sheet. Additionally, the effect of heat treatment on the coated surface was examined by using two calendaring temperatures at 120 °C and 170 °C. [V]

5.2.1 The effect of the temperature and the coating amount

A change in the hydrophobicity of the paper was estimated with contact angle measurements, and the results are presented in Table 12. The water contact angle is much higher with a polymer coating compared with the uncoated reference, but increasing the amount of coating did not further increase the water contact angle. The most effective modification was achieved when the polymer coating was combined with heat treatment. [V]

Table 12 Contact angle and TOF-SIMS quantification of PSMA13Q in belt calendaring. [V]

	PSMA13Q	Ions in ToF-SIMS				Contact Angle			
T	Mass					Water	Surface Energy		
°C	g/m²	C_3H_8N	C_3H_8NO	CH_3	CH_3O	(°)	F_{tot}	F_{disp}	F_{pol}
120	0	8.52	0.93	5.28	7.67	34	58	33	25
120	0	9.78	1.13	5.05	8.05	45	54	35	19
120	0.14	24.11	5.82	6.75	2.96	60	48	38	9
120	0.65	20.95	5.16	4.56	3.69	53	49	35	14
170	0	9.69	1.12	4.34	6.55	38	57	33	23
170	0	10.38	1.36	5.41	7.26	48	53	35	17
170	0.14	33.07	5.76	6.98	2.39	79	45	42	3
170	0.65	33.66	6.92	7.06	2.46	85	44	42	2

The effect of the polymer coating was analysed further by calculating the surface energy based on a set of different solvents. The surface energy in Table 12 is reported as total energy (F_{tot}), polar component (F_{pol}) and dispersive component (F_{disp}). The dispersive component is considered to describe the Van der Waals forces, whereas the polar component describes acid base interactions. [110] The most significant effect was seen in the polar component, F_{pol}, where the polymer coating decreased the energy by half and the temperature treatment further decreased this component to close to zero. [V]

The effect seen in contact angle values was compared with ToF-SIMS. The results are presented in Table 12 and, even in mass signals, there w no correlation between the coating amount and the strength of the nitrogen signal. Additionally, the intensities of high-temperature calendared samples are strengthened by 40%, compared to paper calendared at a lower temperature. It is very interesting that in the same samples where the contact angle was increased, the nitrogen signal is strengthened, even though an ammonium ion has a hydrophilic nature. The chosen calendaring temperatures were rather moderate, and the surface temperature of the coated paper was well below the softening temperature of the chemical components present in the paper sheet. [49] It is obvious that the possible mobile components in the polymer are the stearyl group (T_m = 40°C), in contrast to the cationic ammonium group, which is a salt. Due to the increase of water contact angle, strengthening of the stearyl signals in ToF-SIMS would have been expected. Surprisingly, the situation was opposite as amount of the ammonium groups on the surface was increased. It is possible in these samples that the polymer molecules are just flattened and no molecular orientation occurs. [V]

Spreading on the C_3H_8N on the surface can be seen in Figure 12 as chemical imaging produced from ToF-SIMS. As previously reported for surface energies, there was only a minor difference in the relative intensities of the nitrogen signals when the coating amounts were compared, but a clear increase in intensity is observed when the calendaring temperature is increased from 120 °C to 170 °C, which can be seen as a brightening of the nitrogen signal (Figure 12). It seems that even the lowest coating amount would be enough to hydrophobize the paper surface by chemical modification, and the formed polymer layer is of a nanometric scale. [V]

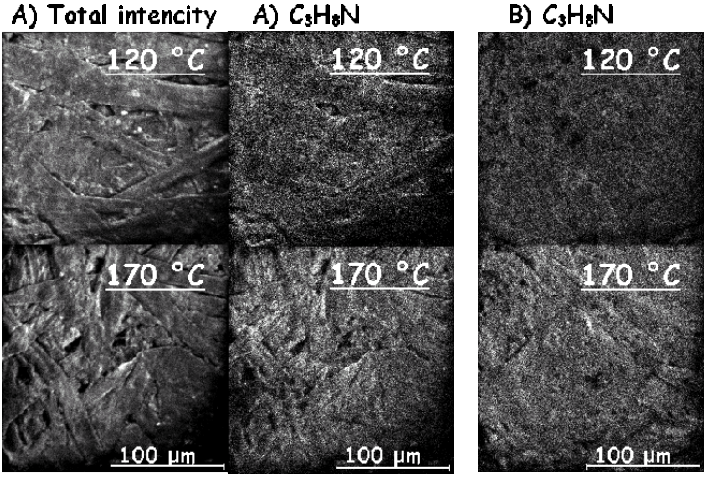


Figure 12. Chemical imaging of ToF-SIMS, visualized as total ions and C_3H_8N from paper surface calendared at 120 °C (top) and 170 °C (bottom) and with two amounts of polymer coating: A) 0.64 g/m^2 and B) 0.14 g/m^2. [V]

6. CONCLUSIONS

The aim of the research was to prepare co-polymers having a tailored structure for cellulose fiber applications. An amphiphilic nature was introduced into the polymers through block formation or with a long side group. The challenge of introducing highly hydrophobic and highly hydrophilic segments in the same polymer is the formation of a heterophase from these two components, and it was addressed in this thesis through post-modification. Cationic water soluble methacrylate co-polymers were synthesized with oxyanionic polymerization and radical polymerization. Radical polymerization was highly applicable to produce large amounts of polymer and it enabled a higher variety of monomers to be used, whereas oxyanionic polymerization required controlled conditions, producing more precise structures.

The water solubility of polymers containing a highly hydrophobic segment rapidly decreased with the increasing hydrophobicity. Polymers containing less hydrophobic poly(ethylene oxide) and poly(propylene oxide) segments form a dynamic structure with a clear critical micelle concentration in a water solution, but polymers containing a stearyl segment appear as aggregates and they do not change conformation in water solution on their own. The solution viscosity of polymers containing hydrophobic and hydrophilic segments is strongly dependent on the molecular weight, but, most importantly, on the polymer composition. At a low concentration, the polymers exhibit low viscosity, but a rapid increase in viscosity is seen at a transition concentration. The concentration dependence is stronger than what is typical for polyelectrolytes, and the phenomenon is strengthened by increasing hydrophobicity. The rheological behaviour indicates that the hydrophobic segment is strong enough to form both inter and intra molecular association in a water solution.

Quartz crystal microbalance shows that cationic polymers form an adhesion on an anionic surface with strong bondings, whereas non-ionic polymers can be rinsed off. An indication of a strong adhesion was also seen in the rheological behavior of a microfibrillar cellulose suspension, as well as in the mechanical properties of a cellulose fiber sheet. Strain hardening behavior was observed in fiber polymer systems, where no strong ionic bondings were formed. It could be stated that fluidic behaviour in a suspension indicates strain hardening behaviour in paper sheets.

A highly cationic form of block co-polymer improves the strength of a paper sheet more than a comparable weakly cationic form, but a minimum hydrodynamic radius of about 30 nm was required in order to obtain any strength enhancing properties. Polymers containing a highly hydrophobic graft also strengthened cellulose fiber sheets, but the strength was decreased when the amount of the hydrophobic graft was increased.

Finally, paper sheets were coated with a polymer containing both cationic and highly hydrophobic segments. Already a very small polymer amount (0.14 g/m^2) was enough for the chemical modification of the paper surface, and the influence was further enhanced by heat treatment.

As a conclusion, it can be stated that the properties of amphiphilic polymethacrylates can be tailored through choice of an appropriate polymerization method, choice of the segments of the copolymers, and with postmodification in order to obtain cationic polymers. This thesis increases fundamental understanding of polymer properties and polymer-cellulose interactions, and enables modification of the properties of different cellulose fiber applications.

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In this thesis a set of amphiphilic cationic co-polymers were synthesized and characterized. The synthesis was up-scaled to be tested in applications. Suitability of the prepared polymers on cellulose fiber systems was studied. The polymers containing a cationic segment formed permanent adhesion on the anionic surface, and strong bonding between the cellulose fibers. The mechanical strength of the cellulose fiber sheets was increased more with polymers containing cationic segments than the ones with corresponding nonionic segments. Strain hardening behaviour was introduced into the fiber-polymer sheets that did not contain cationic segments. A mechanically strong cellulose fiber network could also be prepared with a hydrophobic cationic polymer. The polymers containing a highly hydrophobic segment formed a thin layer coating on the paper surface. A small amount of polymer was enough for complete thin layer coverage of the surface, which supported the assumption of a nanolayer formation.

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