ARGET ATRP AS A TOOL FOR CELLULOSE MODIFICATION

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Doctoral Thesis

Kungliga Tekniska högskolan, Stockholm 2012

AKADEMISK AVHANDLING

som med tillstånd av Kungliga Tekniska högskolan i Stockholm framlägges till offentlig granskning för avläggande av teknologie doktorsexamen fredagen den 14 december 2012, kl. 10.00 i sal K2, Teknikringen 28, KTH, Stockholm. Avhandlingen försvars på engelska. Fakultetsopponent: Dr. Steve Edmondson, Loughborough University, UK.
To my family
ABSTRACT

The importance of finding new applications for cellulose-based products has increased, especially to meet the demand for new environmentally friendly materials, but also since the digitalization of our society will eventually decrease the need for paper. To expand the application area of cellulose, modification to improve and/or introduce new properties can be a requisite. Thus, the focus of this study has been to achieve fundamental knowledge about polymer grafting of cellulose via well-controlled radical polymerization.

Cellulose, in the form of filter paper, has successfully been grafted via activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP) of the monomers: methyl methacrylate, styrene, and glycidyl methacrylate. The advantages of ARGET ATRP are that only a small amount of a copper catalyst is required and the reaction can be performed in limited amount of air; yet, providing for relatively well-controlled reactions. These benefits can render ARGET ATRP an attractive method for industrial utilization.

The contact-angle measurements of the grafted filter papers confirmed that the hydrophobicity of cellulose was significantly increased, even for shorter graft lengths. FT-IR spectroscopy established that the amount of polymer successively increased with monomer conversion. High-resolution FT-IR microscopy (FT-IRM) was proven to be a very useful technique for the analysis of cellulose substrates, displaying the spatial distribution of polymer content on cellulose fibers. The polymer was shown to be fairly homogenously distributed on the fiber.

An initiator with a reducible disulfide bond rendered cleavage of the polymer grafts possible, employing mild reaction conditions. The cleaved grafts and the free polymers – formed from a sacrificial initiator in parallel to the grafting – were shown to have similar molar masses and dispersities, confirming that the grafts can be tailored by utilizing a sacrificial initiator. Moreover, the initiator content on filter paper and microcrystalline cellulose was assessed.

A comparison between the two grafting techniques, grafting-from cellulose via ARGET ATRP and grafting-to cellulose via copper(I)-catalyzed alkyne-azide cycloaddition, was performed. To achieve a trustworthy comparison, the free polymer formed in parallel to the grafting-from reaction was employed as the pre-polymer in the grafting-to approach, resulting in nearly identical graft length on the substrates for the two grafting methods. FT-IRM analyses verified that under the selected conditions, the grafting-from technique is superior to the grafting-to approach with respect to controlling the distribution of the polymer content on the surface. The results were corroborated with X-ray photoelectron spectroscopy.
Behovet av att hitta nya tillämpningar för cellulosabaserade produkter har ökat, framförallt för att möta efterfrågan på nya miljövänliga material, men även då digitaliseringen av vårt samhälle på sikt kommer att minska pappersbehovet. För att öka cellulosans användningsområde kan modifisering, för att förbättra och/eller introducera nya egenskaper, vara en nyckelfråga. Denna studie har således fokuserat på att erhålla grundläggande kunskaper om polymera ympningsprocesser av cellulosa genom välkontrollerad radikalpolymerisation.

Cellulosa, i form av filterpapper, ympades framgångsrikt med monomeren metylmetakrylat, styren samt glycidylmetakrylat via ARGET ATRP (activators regenerated by electron transfer atom transfer radical polymerization). Fördelarna med ARGET ATRP är att endast små mängder kopparkatalysator krävs samt att reaktionen kan utföras i närvaro av begränsade mängder luft, och trots detta uppnås relativt välkontrollerade reaktioner. Dessa fördelar gör ARGET ATRP till en attraktiv metod att använda industriellt.


En initiatormed en reducerbar disulfidbinding möjliggjorde klyvningen av de ympade polymerkedjorna under milda betingelser. De klyvda kedjorna och de fria polymererna – polymeriserade från en fri initiatormed ympningen – hade liknande molmassor och dispersiteter, vilket visar att de ympade kedjor kan skräddarsys genom användandet av den fria initiatorn. Vidare uppskattades även initiatormängden på filterpapper samt på mikrokrystallin cellulosa.

En jämförelse mellan de två ympningsteknikerna, ympning från cellulosa via ARGET ATRP samt ympning till cellulosa via koppar(I)-katalyserad alkyn-azid cycloaddition utfördes. För att erhålla en relevant jämförelse användes den fria polymeren, bildad parallelt med ympning-från-reacttion, som prepolymer i ympning-till-metoden, vilket resulterade i näst intill identiska kedjelängder på substraten för de två ympningsmetoderna. FT-IRM verifierade att under de gällande reaktionsbetingelserna så är ympning-från-tekniken överlägsen ympning-till-tekniken med avseende på kontroll över polymerfördelningen på ytan. Dessa resultat bekräftades med XPS.
LIST OF PAPERS

This thesis is a summary of the following papers:


My contribution to the appended papers:

I. All of the experimental work, all of the analyses, and most of the preparation of the manuscript.

II. Most of the experimental work, all of the analyses, and most of the preparation of the manuscript.

III. All of the experimental work, most of the analyses, and most of the preparation of the manuscript.

IV. All of the experimental work, most of the analyses, and most of the preparation of the manuscript.

This thesis also contains unpublished results.
Scientific contributions not included in this thesis:


VII. “Linear vs. hyperbranched polymers in the preparation of polymer/clay nanocomposites” Linda Fogelström, Susanne Hansson, Anna Carlmark, Anders Hult, and Eva Malmström, manuscript
ABBREVIATIONS

AGU  anhydroglucose
AFM  atomic force microscopy
Al2O3 aluminum oxide
ARGET activators regenerated by electron transfer
AsAc ascorbic acid
ATR  attenuated total reflectance
ATRA atom transfer radical addition
ATRP atom transfer radical polymerization
BiB  α-bromoisobutyryl bromide
CA  contact angle
CRP  controlled radical polymerization
CuAAC copper(I)-catalyzed azide-alkyne cycloaddition
Cu(II)Br2 copper(II) bromide
CuSO4 · 5 H2O copper sulfate pentahydrate
DCM dichloromethane
DMAP 4-dimethylaminopyridine
DMF N,N-dimethylformamide
DP degree of polymerization
DS degree of substitution
DTT 1,4-dithiothreitol
DM  molar mass dispersity
EBiB ethyl 2-bromoisobutyrate
FE-SEM field-emission scanning electron microscopy
FT-IR Fourier transformation infrared
FT-IRM FT-IR microscopy
GMA glycidyl methacrylate
HDA hetero Diels-Alder
IE initiator efficiency
\( k_{act} \) rate constant of activation
\( k_{deact} \) rate constant of deactivation
\( K_\text{eq} \) equilibrium rate constant
\( k_{P,app} \) apparent rate constant of propagation
\( k_p \) rate constant of propagation
\( k_t \) rate constant of termination
MMA methyl methacrylate
MCC microcrystalline cellulose
<table>
<thead>
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<tbody>
<tr>
<td>NaAsc</td>
<td>sodium ascorbate</td>
</tr>
<tr>
<td>NaN₃</td>
<td>sodium azide</td>
</tr>
<tr>
<td>NCC</td>
<td>nanocrystalline cellulose</td>
</tr>
<tr>
<td>NFC</td>
<td>nanofibrillated cellulose</td>
</tr>
<tr>
<td>NMP</td>
<td>nitroxide mediated polymerization</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>PMDETA</td>
<td>(N,N,N',N'',N'''-pentamethyldiethylenetriamine)</td>
</tr>
<tr>
<td>RAFT</td>
<td>reversible addition fragmentation chain transfer</td>
</tr>
<tr>
<td>RDRP</td>
<td>reversible-deactivation radical polymerization</td>
</tr>
<tr>
<td>(R_p)</td>
<td>rate of polymerization</td>
</tr>
<tr>
<td>SET-LRP</td>
<td>single-electron transfer mediated living radical polymerization</td>
</tr>
<tr>
<td>SI</td>
<td>surface-initiated</td>
</tr>
<tr>
<td>Sn(EH)₂</td>
<td>tin(II) 2-ethylhexanoate</td>
</tr>
<tr>
<td>St</td>
<td>styrene</td>
</tr>
<tr>
<td>TBAF · 3 H₂O</td>
<td>tetrabutylammonium fluoride trihydrate</td>
</tr>
<tr>
<td>TEA</td>
<td>triethylamine</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>IUPAC</td>
<td>international union of pure and applied chemistry</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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1. PURPOSE OF THE STUDY

The interest in cellulose – a renewable and inexpensive resource with a stiffness almost comparable to steel – has increased significantly the last decades. Some requests are to achieving more environmentally friendly materials, as well as to increase the utilization of cellulose in more advanced applications, compared with more traditionally commodities such as paper. However, to exploit the full potential of cellulose, modification of the native resource is often a prerequisite, in order to improve the properties of cellulose and/or to introduce new functionalities. The modification in this study was performed by grafting polymers from and to cellulose; moreover, to have the possibility to tailor the surface properties, the polymerization should be performed in a well-controlled manner.

The purpose of this study was to investigate the grafting process by applying the method activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP) when grafting from cellulose substrates. Another important aim was to develop an approach to detach the grafted polymer chains under mild reaction conditions; thereby, rendering their post-characterization possible while keeping the substrate intact. The amount of available reactive sites present on the cellulose substrate was also the object of investigation, as well as the polymer distribution on the substrate surface, with the purpose of obtaining valuable knowledge about the grafting process.

Another objective was to systematically study and compare the grafting efficiency of the two grafting approaches grafting-from and grafting-to by investigating the polymeric amount on the surface, employing different graft lengths.

The ARGET ATRP process was also investigated with the purpose of making the grafting reaction more applicable in an industrial context.
2. INTRODUCTION

2.1 CELLULOSE

Cellulose – the main component in plants together with lignin and hemicelluloses – is the most abundant natural resource in the world. It is an attractive and inexpensive polymeric raw material that is renewable, biocompatible, and has excellent mechanical properties. The modulus of native cellulose is 138 GPa, which can be compared to the modulus of steel: 200 GPa.¹ Thus, the interest of utilizing cellulose has increased significantly the recent decades, especially due to environmental concerns. The focus has lately been to replace petroleum-based materials with renewable resources like cellulose, employing cellulose in a broader range of products than only in commodities such as papers and card boards. Nevertheless, the digitalization of our society will in the long term decrease the utilization of paper, increasing the importance of finding new applications for cellulose-based products. As an example, cellulose fibers can be employed as a filler or reinforcement in a polymeric matrix, forming a composite, e.g. sawdust in polypropylene². The large advantages of cellulose fibers compared to traditional fillers, such as carbon fibers or glass fibers, are lower cost and density, high specific strength, renewability, degradability, and non-toxicity.³⁻⁵ However, common drawbacks are sensitivity to moisture, bacteria, and rot, but it is especially the poor interfacial adhesion between the hydrophilic cellulose fibers and the hydrophobic polymer matrix that results in weakened material performance of the composite.⁵ ⁶ Poor compatibility between filler and matrix renders the composite inhomogeneous, causing loss of mechanical strength since it is more difficult to transfer the applied load throughout the material.³ Therefore, surface modification of cellulose is a requisite.
2.1.1 Structure of cellulose

Cellulose is composed of β-D-glucose units that are linked together with 1-4 glycosidic bonds, forming a linear polysaccharide with one primary and two secondary hydroxyl groups on each anhydroglucose unit (AGU), see Figure 1. The degree of polymerization (DP), i.e., the number of constituent AGUs, of native cellulose is dependent on its origin. The most common sources are wood or cotton, and the DP can then range from 300 to 10,000. Cellulose exhibits a fascinating hierarchical structure from a molecular to macroscopic scale, which provides for the outstanding properties of cellulose fibers, see Figure 1. In plants, the extended cellulose chains are aligned in sheets that are stabilized by intra- and intermolecular hydrogen bonds. These crystalline sheets are closely packed, with secondary forces that are holding them together, forming three-dimensional microfibrils that have both ordered and less ordered regions of cellulose. The microfibrils are arranged in bundles of microfibrils that together with the hemicelluloses and lignin build up the cell wall. The wood cell consists of several cell-wall layers with various cellulosic compositions and with the cellulose microfibrils arranged in different orientation, which is vital for the high strength of the cellulose fiber. The microfibrils and the microfibril bundles have a lateral dimension of 1.5–3.5 nm and 10–30 nm, respectively, and the length can be up to a few micrometers. The cellulose fiber has generally the width of some tens of a micrometer, and lengths of a few millimeters.

Figure 1. The idealized schematic picture of the hierarchical structure of cellulose, adopted from Isogai et al.8
2.1.2 Cellulose types

Cellulose can be extracted from wood by removing the lignin and hemicelluloses, resulting in cellulose pulp. By producing cellulose from different cellulose sources, e.g. flax, hemp, and jute, and not only wood, and by employing chemical and/or mechanical methods, it is possible to obtain many different types of products. Cellulose can also be obtained from aerobic bacteria. Recently, the focus has been to achieve nanosized cellulose components, e.g., nanofibrillated cellulose (NFC) and nanocrystalline cellulose (NCC). NFC and NCC can have rather similar widths of 5–70 nm, but the length of NFC is generally much longer, up to several micrometers, compared to the length of NCC that originates from plant cellulos: 100 to 250 nm. Furthermore, NCC consists of elongated rodlike crystals and has no amorphous regions like NFC, limiting the flexibility of NCC. Apart from nanocellulose, microcrystalline cellulose (MCC) is another interesting and commercially available substrate. It is derived from cellulose pulp by hydrolysis with mineral acids, resulting in particles in the range of 10–100 μm. Another common cellulose substrate is Whatman filter paper that is produced from high-quality cotton linters, resulting in a very pure product with high cellulose content (>98 %) and with a crystallinity of 68 %.

2.1.3 Modification of cellulose

The many hydroxyl groups along the backbone of cellulose are suitable sites for chemical modification. However, the number of available hydroxyl groups is dependent on how the cellulose substrate is pretreated. Treatment with a strong base such as NaOH (mercerization) breaks the hydrogen bonds, swelling and increasing the activity of cellulose. Nevertheless, cellulose exists in different crystalline forms and upon mercerization the crystal structure cellulose I, which is the native form, is converted to cellulose II. Cellulose II has antiparallel chains and is more thermodynamically stable than cellulose I. The functionalization of the available hydroxyl group may have a slight impact on the mechanical properties, especially if the strong hydrogen bonds that build up the cellulose structure are affected. The challenge when modifying cellulose fibers can therefore be to preserve the internal structure of the fiber.

Cellulose can be modified by grafting synthetic polymers onto its surface, an approach that has gained increasing interest for the past years. The two most common grafting approaches are the grafting-from and grafting-to techniques, see
Figure 2. In the grafting-*from* method, i.e., the surface-initiated (SI) polymerization, the polymer chains are built up through successive monomer addition from initiating sites on the surface. Comparatively, when grafting *to* the surface, a pre-formed polymer with suitable functionality is covalently or physically attached to reactive sites on the surface. The grafting-*from* method is assumed to result in a higher grafting efficiency due to less steric hindrance of diffusing small monomers, compared to the grafting-*to* approach where larger polymer chains have to diffuse to the reactive sites, which may be shielded by the already grafted polymer chains.\(^{12, 13, 16}\) In the majority of all grafting studies, grafting *from* is reported to yield higher grafting densities,\(^{12, 14, 17-22}\) although examples have been reported where grafting-*to* approaches have provided grafting densities in the same range.\(^{23-25}\)

![Grafting from vs Grafting to](image)

**Figure 2.** The schematic picture of the grafting-*from* and the grafting-*to* method.

The advantage with the grafting-*to* method is that the employed pre-formed polymer can be easily characterized, and thereby the molar mass and molar mass dispersity (\(D_M\)) can be determined prior to the grafting reaction; therefore, the grafting-*to* method is preferred from an industrial point of view.

The challenge with the grafting-*from* approach is to know the characteristics of the polymer grafts on the surface. However, this can be circumvented by utilizing a sacrificial initiator that forms an unbound, free polymer in the reaction media in parallel to the grafting process. The freely formed polymer, which easily can be characterized, has shown to have comparable characteristics to the polymer grafts,\(^{18, 26-28}\) also rendering this an applicable approach to control the polymer grafts on the surface, by employing different ratios between the monomer and the
initiator (targeted degree of polymerization \( \text{DP}_{\text{target}} = [M]_0/[I] \)). However, to evaluate the graft properties, detachment of the covalently linked polymer chains and their subsequent analysis is vital. Acidic hydrolysis of cellulose has been employed as a method to isolate the grafts for subsequent characterization,\(^{17, 21, 29, 30}\) resulting in a complete degradation of the substrate. Nevertheless, this method may not be applicable for polymers containing sensitive functional groups like esters, such as (meth)acrylate polymers.

### 2.2 REVERSIBLE-DEACTIVATION RADICAL POLYMERIZATION (RDRP)

Free-radical polymerization is the most common polymerization method applied in the industry for the production of polymers, since it is the most economically favorable approach to produce large volumes. One advantage is the facile reaction conditions that can be employed on a variety of monomers, without any specific demands for high purity. However, due to the high concentration of radicals formed during the reaction, many chain-transfer and termination reactions take place, resulting in poor control over the polymerization. To obtain more complex and well-defined polymers, it is crucial to be able to predetermine the molar mass, the molar-mass dispersity \( (D_M) \), and the chain-end functionality. Therefore, polymerization methods that suppress chain-transfer and termination reactions are required. In a living polymerization system, no irreversible transfer or termination reactions occur. The initiation is fast and quantitative and the reaction will continue until all the monomers are consumed. Reversible-deactivation radical polymerization (RDRP) techniques almost follow the concept of a true living system; however, these methods are discouraged to be referred to as ‘living’ by IUPAC.\(^{31}\) In addition, RDRP was previously called controlled radical polymerization (CRP) but the terminology RDRP is now being encouraged.

The RDRP methods can be divided into nitroxide mediated polymerization (NMP),\(^{32, 33}\) atom transfer radical polymerization (ATRP)\(^{34-36}\), and reversible addition fragmentation chain transfer (RAFT) polymerization\(^{37, 38}\). NMP and ATRP are based on a dynamic equilibrium between a large majority of dormant species and only a few active species, keeping the radical concentration low, see Scheme 1. In RAFT polymerization, the equilibrium is based on reversible chain transfer. NMP was the first method to successfully scavenge radicals by utilizing a nitroxide leaving group that reversibly terminate the propagating species. RAFT polymerization relies on a chain-transfer agent that captures and releases
propagating radicals reversibly. ATRP, discussed in more detail in the next section, is based on the transfer of an atom between a transition-metal catalyst complex and the propagating chain. The RDRP methods diverge in their applicability for different monomer systems, and all have their advantages and disadvantages.

Scheme 1. The dynamic equilibrium present in RDRP techniques.

2.2.1 Atom transfer radical polymerization (ATRP)

ATRP is the most studied RDRP method owing to its versatility and compatibility with a variety of monomers, rendering the synthesis of functional polymers with well-defined compositions possible. In 1995, ATRP was independently discovered by Sawamoto et al. and Wang and Matyjaszewski. ATRP originates from the atom transfer radical addition (ATRA), which is a modification of the Kharasch addition reaction. The reversible redox process in ATRP involves the atom transfer of a halogen atom between the active and the dormant chain, catalyzed by a transition metal/ligand complex. In the activation process, this complex abstracts the halide from the dormant chain, forming an active chain bearing a radical. The active species can then either add a monomer in a propagating step or react with the oxidized metal complex via back-transferring of the halogen atom to the propagating chain-end, which deactivates the radical. To achieve proper control, it is crucial that the initiation is fast and quantitative and that the reversible deactivation occurs rapidly. However, it is impossible to achieve a truly ‘living’ system, and termination reactions also occur, principally via radical coupling and disproportionation. Yet, just a few propagating chains undergo termination during the initial, non-stationary stage of the polymerization. During this stage, the concentration of the deactivator increases, shifting the equilibrium towards the dormant side, and thereby inhibiting the termination reactions. This phenomenon is called the persistent radical effect.
2.2.1.1 Components of ATRP

An ATRP system is generally composed of a monomer, an initiator, and a catalyst based on a transition metal/ligand complex. The choice of monomer determines which initiator and catalyst – as well as temperature and solvent – that will be utilized.\textsuperscript{43} Monomers that successfully have been polymerized \textit{via} ATRP are styrenics,\textsuperscript{35, 44} (meth)acrylates,\textsuperscript{45-47} meth(acrylamides),\textsuperscript{48, 49} and acrylonitriles,\textsuperscript{50, 51} which all are effective in stabilizing the propagating radical.\textsuperscript{43, 52} ATRP is also tolerant to several functional groups such as epoxides,\textsuperscript{53-55} hydroxyl groups, amines, and cyanides.\textsuperscript{43} Vinylpyridines can be polymerized if a strongly coordinating ligand is employed, suppressing the monomer’s ability to coordinate to the transition metal. Conversely, acidic monomers cannot be polymerized \textit{via} an ordinary ATRP system due to protonation of the ligand.\textsuperscript{43} However, Jana \textit{et al.} have recently reported a unimolecular ligand-initiator dual-functional system that renders ATRP of (meth)acrylic acids possible.\textsuperscript{56}

The initiator determines the number of propagating chains, and hence also the DP. A rapid initiation and negligible transfer and termination reactions result in that the number of propagating chains is equal to the initial initiator concentration; thus, the molar mass or DP can be estimated according to Eq. 1

\[
DP = \frac{[\text{monomer}]}{[\text{initiator}]} \cdot \text{conv.}
\]

The initiator is commonly composed of an alkyl halide, where the halide most frequently is a bromide or chloride. The homolytic cleavage of the labile bond on the initiator results in a free radical that can initiate the polymerization. The bond-dissociation energy for bromide halides is lower than for chloride halides, suggesting that bromide halides are more efficient. It can be beneficial to utilize an initiator that resembles the monomer in structure, e.g. a benzylic halide for the polymerization of styrene, but it is not necessary. Tertiary alkyl halides are better at stabilizing the radical than secondary alkyl halides, resulting in a faster initiation for the tertiary compound.\textsuperscript{43}

The catalyst has a central role in ATRP, since it determines the equilibrium between the active and dormant species. Ideally, the catalyst should be very selective for atom transfer and not participate in other reactions; furthermore, the deactivation should be extremely rapid. The transition metal must have two accessible oxidation states and affinity to the halogen atom, and the ligand should
complex to the metal relatively strongly.\textsuperscript{43} The most frequently utilized transition metal is copper, due to its low cost and applicability to several different monomers. Many other metals have also been employed: titanium, chromium, molybdenum, rhenium, iron, ruthenium, osmium, rhodium, nickel, palladium,\textsuperscript{57, 58} and cobalt.\textsuperscript{58} The catalytic activity and selectivity is strongly ligand dependent, since it controls the redox potential of the metal center. Another important role for the ligand is to solubilize the metal in the organic media. Commonly, the ligands are based on nitrogen or phosphorus. Nitrogen-based ligands are especially applicable to copper-mediated systems.\textsuperscript{39, 43, 52}

ATRP can be performed in bulk or in solution. Various organic solvents have been employed for different monomers, and it is especially essential if the polymer is insoluble in the monomer. The structure of the catalyst may be affected by different solvent, resulting in different reaction rates. ATRP can be performed in aqueous medium,\textsuperscript{59, 60} which is of interest both from an environmental as well as industrial perspective. Polar media has shown to enhance the reaction rate since it can promote the solubility of the catalyst,\textsuperscript{59, 61} which has resulted in the development of an alternative mechanism,\textsuperscript{62-64} compared with the original mechanism presented by Matyjaszewski \textit{et al.}\textsuperscript{52}. Both mechanisms will be discussed in the next section.

\textbf{2.2.1.2 Suggested mechanism of ATRP}

In free radical polymerization, the polymerization occurs in three steps: initiation, propagation, and termination. In ATRP, mainly initiation and propagation take place since the termination reactions are suppressed. The mechanism, presented in Scheme 2, is exemplified with copper(I) as catalyst. The initiation involves the homolytic cleavage of the alkyl halide (R-X), transferring the halogen radical atom to the activator Cu(I)X/L, forming the radical R• and the deactivator Cu(II)X$_2$/L, where L represent the ligand. The ATRP equilibrium rate constant of the initiation is denoted as $K_{eq}$. The active species can react with either a monomer or the deactivator by back-transfer of the halogen in the reversible redox reaction. The latter reaction must be favored, and the rate constant of deactivation ($k_{deact}$) should be higher than the propagation rate constant ($k_p$), to achieve a controlled polymerization.\textsuperscript{52} In the initial stage of the polymerization, equal amounts of radicals and Cu(II) are formed, which results in similar rates of activation and deactivation. Due to the persistent radical effect that occurs in the early stage of the polymerization, the concentration of the Cu(II)X$_2$/L complex increases and shifts the equilibrium to the dormant side, maintaining the
concentration of the active species low.\textsuperscript{39,43} If appropriate conditions are obtained, the few termination reactions that occur in the initial stage of the reaction, with the rate constant $k_t$, will not have a significant impact to the system.\textsuperscript{43}

**Initiation**

\[
\begin{align*}
R-X & \quad \overset{K'_{eq}}{\rightleftharpoons} \quad \text{Cu(I)X/L} \\
(X = \text{Cl or Br}) & \\
R^* & \quad + \quad \text{monomer} \quad \overset{k_p'}{\longrightarrow} \quad P_1^* \\
\end{align*}
\]

**Propagation**

\[
\begin{align*}
P_{n-1}X & \quad + \quad \text{Cu(I)X/L} \quad \overset{K_{eq}}{\rightleftharpoons} \quad P_n^* \quad + \quad \text{Cu(II)X}_2/L \\

P_n^* & \quad + \quad \text{monomer} \quad \overset{k_p}{\longrightarrow} \quad P_{n+1}^* \\
\end{align*}
\]

**Termination**

\[
P_n^* \quad + \quad P_m^* \quad \overset{k_t}{\longrightarrow} \quad P_{n+m}
\]

**Scheme 2.** The suggested mechanism for copper-mediated ATRP in aprotic solvents.

The ATRP process occurs with a homolytic inner-sphere electron-transfer mechanism.\textsuperscript{62} The alternative mechanism, the heterolytic outer-sphere single-electron transfer mediated living radical polymerization (SET-LRP), was reported by Percec et al.\textsuperscript{62-64} and is claimed to be valid when polar solvents, e.g., water and alcohols, polar aprotic solvents, or ionic liquids, are employed. In SET-LRP, the Cu(I)X/L species disproportionate spontaneously to Cu(0) and Cu(II)X\textsubscript{2}/L. Accordingly, the Cu(I)X/L species is inactive meanwhile the electron donor Cu(0) is extremely reactive. The deactivator Cu(II)X\textsubscript{2}/L is suggested to be formed only due to disproportionation, making the persistent radical effect unnecessary, i.e., termination reactions are essentially absent.

**2.2.1.3 Kinetics of ATRP**

The kinetics of the ATRP mechanism can be derived by assuming that the initiation is fast and quantitative and that termination reactions are absent; consequently, the concentration of radicals will be constant. The rate of polymerization, $R_p$, is dependent on the apparent rate constant, $k_{p\text{app}}$, and the concentration of the monomer [M], and hence, $R_p$ is of first order with respect to
the [M], activator [Cu(I)X], and initiator [PX], while it is of negatively first order with respect to the deactivator concentration [Cu(II)X], see Eq. 2. However, due to the persistent radical effect, some deactivators are formed in the initial period of the reaction, making the actual kinetics more complicated.

\[ R_p = k_p^{app}[M] = k_p [P^*][M] = k_p K_{eq} \frac{[PX][Cu(I)X][M]}{[Cu(II)X]} \]  

(2)

where \( K_{eq} = \frac{k_{act}}{k_{deact}} = \frac{[P^*][Cu(II)X_2]}{[PX][Cu(I)X]} \)  

(3)

According to Eq. 2, an increased initiator concentration, resulting in a higher number of propagating radicals and lower DP\(_{target}\), will increase the polymerization rate.\(^{65}\) If not all initiators initiate, the initiator efficiency (IE) will be less than 1, and the molar mass of the formed polymer will be higher than the DP\(_{target}\). The IE can be estimated by

\[ IE = \frac{DP_{target} \cdot M_{monomer} \cdot conv. + M_{initiator}}{M_n} = \frac{M_{theo}}{M_n} \]  

(4)

where \( M_n \) is the obtained by size exclusion chromatography (SEC). The IE has shown to gradually increase with reaction time for methacrylate systems, when ethyl 2-bromoisobuturate (EBiB) is utilized as the initiator and anisole as the solvent, implying that the initiation do not only occur at the initial stage of the polymerization.\(^{65, 66}\) The IE can be increased by employing a solvent that solubilize the deactivator complex better, increasing the deactivation rate. Accordingly, acetone and DMF were shown to yield higher IE than anisole.\(^{66}\)

The transfer and termination reactions, which can be complicated to completely avoid, can be suppressed by reducing the DP\(_{target}\) and limit the conversion, i.e., aim for shorter polymer chains.\(^{65}\) The rate of propagation is significantly reduced at high conversions as the monomer concentration decreases (Eq. 2). The rate of the side reactions, on the other hand, is not as affected by the monomer concentration and can thereby be essentially unchanged.\(^{43}\)
2.2.2 Activators regenerated by electron transfer (ARGET) ATRP

Although ATRP has many advantages in comparison with conventional radical polymerization, it suffers from some drawbacks. The requirement of a relatively large amount of the transition metal catalyst, which subsequently requires purification of the final product, complicates and increases the industrial productions costs. Furthermore, residual copper traces may color the product, and can further cause severe problems in some application, e.g., biological systems, due to its toxicity. Another disadvantage is the high sensitivity towards oxygen, which needs to be removed by thorough degassing, further complicating and increasing the price of the reaction process. To circumvent these drawbacks, Matyjaszewski and coworkers developed a new approach to conduct ATRP: activators regenerated by electron transfer (ARGET) ATRP. ARGET ATRP is based on the regeneration of the active species Cu(I) from the deactivator Cu(II) by the utilization of a reducing agent, see Scheme 3. The system is composed of a monomer, an initiator, the transition metal in its inactive form: Cu(II)X₂, a ligand, and a reducing agent. Owing to the reducing agent, the oxidatively stable Cu(II) complex is continuously reduced to Cu(I) throughout the polymerization, significantly reducing the amount of copper to only a few ppm.

Scheme 3. The mechanism of ARGET ATRP.

Ascorbic acid (AsAc) is frequently utilized as an environmentally friendly reducing agent. AsAc is a strong reducing agent, so to avoid a too high concentration of radicals, which would reduce the control over the polymerization, the solubility in the reaction medium can be limited by employing a heterogeneous system with for example anisole as solvent. Two
other not as strongly reducing agents that can be utilized are sodium ascorbate (NaAsc), the salt of AsAc, as well as tin(II) 2-ethylhexanoate (Sn(EH)2).\textsuperscript{67, 69} The beauty of employing a reducing agent in ARGET ATRP is that the reaction can be conducted in the presence of limited amounts of air, since the reducing agent also scavenge oxygen. Thereby, the difficulty with tedious deoxygenation procedures is reduced or avoided. Moreover, Matyjaszewski and coworkers recently presented an aqueous ARGET ATRP system, where the addition of a halide salt, e.g. NaCl, promoted an increased concentration of deactivators to improve the control over the polymerization.\textsuperscript{70}

2.3 ‘CLICK’ CHEMISTRY – POLYMER CONJUGATION REACTIONS

The ‘click’ concept that was introduced by Sharpless and coworkers\textsuperscript{71} in 2001 was firstly intended for organic chemistry, but it has also had a great impact on polymer chemistry and the synthesis of macromolecules with well-defined architectures and functionalities.\textsuperscript{72} The requirements of a ‘click’ reaction are that it must give very high yields, be modular, wide in scope, and orthogonal, and must also proceed by a single reaction trajectory. However, not too many reactions in polymer chemistry can be referred to as a true ‘click’ reaction, and the term ‘click’ is commonly misused. Therefore, Barner-Kowollik et al. introduced a modified definition adapted to polymer chemistry, including other parameters such as equimolarity and large-scale purification. Polymer-linking reactions that do not fulfill these criteria are not ‘click’ reactions but (sometimes efficient) conjugation processes.\textsuperscript{73} Examples of reactions that can be classified as ‘click’ reactions are thiol-ene reactions,\textsuperscript{74-76} hetero Diels-Alder (HDA) chemistry,\textsuperscript{77-79} and azide-alkyne cycloaddition\textsuperscript{80}.

2.3.1 Copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC)

The most frequently utilized ‘click’ reaction is the copper(I)-catalyzed azide-alkyne cycloaddition,\textsuperscript{81, 82} which is a modification of the classical Huisgen 1,3-dipolar cycloaddition between alkynes and azides\textsuperscript{83}. The 1,4-cycloaddition between an azide and alkyne, catalyzed by Cu(I), forming the 1,2,3-triazole ring, is presented in Scheme 4. A common Cu-system to employ is the Cu(II)SO\textsubscript{4} combined with NaAsc that reduces Cu(II) into Cu(I), but other systems utilizing e.g., Cu(I)Br or Cu(I)I also exist.\textsuperscript{84}
Introduction

Scheme 4. The 1,4-cycloaddition catalyzed by Cu(I) forming the 1,2,3-triazole.

2.4 GRAFTING OF CELLULOSE VIA WELL-CONTROLLED POLYMERIZATION REACTIONS

As mentioned before, an approach to expand the utilization of cellulose is by grafting polymers onto the cellulose surface. However, to understand and to tailor the surface properties for a given application, a deeper and more fundamental knowledge about chemical modifications, such as grafting, is required. If cellulose is to be applied for more sophisticated applications, e.g., superhydrophobic,\textsuperscript{85} stimuli-responsive,\textsuperscript{86-88} or antibacterial surfaces,\textsuperscript{30, 89} sensors,\textsuperscript{90, 91} and biomedical applications,\textsuperscript{88, 92-95} the demands on understanding well-controlled reactions, such as RDRP, are highly significant.

To obtain a controlled polymerization when grafting polymers from a surface, surface-initiated (SI) ATRP, NMP, and RAFT polymerization, can be employed. Among these methods SI-ATRP is the most studied one.\textsuperscript{13, 88, 96} In SI-ATRP systems, a sacrificial initiator can be employed to control the graft length, forming a free polymer in the solution, as mentioned above. The sacrificial initiator also keeps the concentration of radicals low, since the overall concentration of dormant species on the surface is too low to achieve a controlled polymerization. However, from a processing point of view, the sacrificial initiator can be a disadvantage since the freely formed polymer has to be removed. Thus, another useful approach to fine-tune the SI-ATRP can be by adding the deactivator, i.e., Cu(II), to the solution, shifting the dynamic equilibrium towards the dormant side without the formation of free polymer.\textsuperscript{16, 88, 97}

RAFT and ATRP are frequently utilized when grafting polymers from cellulose substrates.\textsuperscript{12-14} When SI-RAFT polymerization is employed, pretreatment of cellulose with NaOH, to increase the surface area, has shown to be crucial to obtain sufficient grafting efficiency.\textsuperscript{21} The first SI-ATRP from cellulose filter paper was reported in 2002 by Carlmark and Malmström.\textsuperscript{19} Since then, several reports on the grafting-from approach of various cellulose substrates employing ATRP
have been described. A problem correlated with SI-ATRP from cellulose is that it can occasionally be problematic to remove the copper catalyst, which might result in colored products despite thorough washing. However, this can be circumvented by utilizing ARGET ATRP. ARGET ATRP has proven to be a very efficient tool when grafting polymers from cellulose substrates. ARGET ATRP has been employed for grafting of nanotubes, without the presence of a sacrificial initiator, showing that the molar mass could be controlled by varying the reaction time. Furthermore, SI-ARGET ATRP has been performed from a silicon wafer without the requirement for any deoxygenation, which most certainly can increase its commercial significance.

ATRP and RAFT polymerization are frequently utilized to produce the pre-polymer for the ensuing grafting-to reaction. A great advantage of employing a RDRP is the preserved end-group functionality. For an ATRP system, the active end-group, which commonly has a bromine or chlorine functionality, can be transformed into an azide moiety. An azide or alkyn functionality can also be incorporated into the ATRP initiator prior to the polymerization, forming functionalized pre-polymers that can be grafted by conjugation via CuAAC to an alkyn- or azide-functional surface. Cellulose substrates have been modified by employing efficient conjugation reactions such as CuAAC, thiol-ene chemistry, and HDA chemistry. The assumed lower grafting efficiency connected to the grafting-to procedure may be enhanced by utilizing these highly efficient conjugation reactions.

2.5 CHARACTERIZATION OF MODIFIED CELLULOSE SUBSTRATES

A persistent challenge when modifying solid cellulose substrates is to actually know the characteristics of the grafted surfaces, i.e., polymer graft characteristics, polymer distribution, degree of substitution (DS), initiator content, and grafting density. Several surface characterization methods exist, such as: Fourier-transformation infrared (FT-IR) spectroscopy, contact angle (CA) measurement, field-emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and ellipsometry. However, the inherent surface roughness of cellulose substrates, such as filter paper, combined with its porosity renders cellulose a tricky substrate to analyze properly. Comparatively, flat surfaces such as silicon and gold wafers are more convenient substrates to characterize, especially with methods like XPS and ellipsometry.
With the latter, it is possible to determine the thickness of thin polymer layers on smooth surfaces, but not on cellulose substrates due to its roughness. On the contrary, XPS analysis, which can provide the elemental composition on the surface, can be utilized on cellulose, however, it is difficult to obtain quantitative information about modified cellulose substrates due to the inhomogeneous surface, but the success of the modification can be confirmed by the comparison of spectra from different surfaces.

2.5.1 High-resolution FT-IR microscopy (FT-IRM)

An advantageous method to employ for characterization of grafted substrates is high-resolution FT-IR microscopy (FT-IRM) imaging. It combines the benefits of IR spectroscopy and microscopy, yielding information about the chemical composition on the surface combined with the surface topography. Thereby, the spatial distribution of the grafted polymer content can be visualized. A focal plane array detector spatially resolves the incoming beam of the ATR crystal, acquiring 4096 FT-IR spectra over an area of 32 × 32 μm. The measurement only takes a few minutes and can be achieved without any requirements of special sample preparation. FT-IRM has proven to be a highly applicable technique for the characterization of modified cellulose surfaces, allowing for analysis of single cellulose fibers. The topography of the cellulose fibers can be obtained by integration of the cellulose absorption intensity from the FT-IR spectra from 950 to 1200 cm⁻¹, which originates from the C-O vibration in cellulose. If the intensity of a characteristic polymer signal is utilized, e.g., between 1700 and 1760 cm⁻¹ that corresponds to the stretching vibration of a carbonyl bond, the spatial distribution of the polymer content on the fiber can be visualized. This is presented in Figure 3, where the corresponding regions of the spectra result in two FT-IRM micrographs of a single cellulose fiber, respectively. Noteworthy, the micrographs correspond to the same fiber, but with different intensity scales of the corresponding regions.
Figure 3. The characteristic carbonyl (polymer) and cellulose region as a single FT-IR spectrum (top) and as FT-IR micrographs (bottom), where 4096 FT-IR spectra are acquired over an area of $32 \times 32 \ \mu m$ of a PMMA-grafted filter paper. The micrographs correspond to the same fiber, but with different intensity scales of the corresponding regions.
3. EXPERIMENTAL

3.1 MATERIALS

α-Bromoisobutyryl bromide (BiB, 98 %), 2-bromoethanol (95 %), copper(II) bromide (Cu(II)Br₂, 99 %), 4-dimethylaminopyridine (DMAP, 99 %), oxalyl chloride (98 %), N,N,N’N’’-pentamethyldiethylenetriamine (PMDETA, 99 %), 3-(trimethylsilyl)propargyl alcohol (99 %), and Whatman no. 1 filter paper were purchased from Sigma Aldrich. Ascorbic acid (AsAc, 99 %), sodium bisulfate (NaHSO₄), and sodium carbonate (Na₂CO₃) were purchased from Fluka. Triethylamine (TEA) and succinic anhydride (99 %) were purchased from Merck. Tetrabutylammonium fluoride trihydrate (TBAF · 3H₂O), copper sulfate pentahydrate (CuSO₄ · 5 H₂O), sodium azide (NaN₃), sodium ascorbate (NaAsc), and 1,4-dithiothreitol (DTT, 99 %) were purchased from ABCR. Methyl methacrylate (MMA, 99 %, Sigma Aldrich), styrene (St, 99 %, Fluka), and glycidyl methacrylate (GMA, 97 %, Fluka), were passed through a column of activated neutral aluminum oxide (Al₂O₃, Sigma Aldrich) prior to use in order to remove the inhibitor.

3.2 INSTRUMENTATION

¹H NMR spectra were recorded on a Bruker Avance 400 MHz NMR instrument, using CDCl₃ as solvent. The solvent residual peak was used as internal standard.

The CP/MAS ¹³C-NMR spectra were recorded in a Bruker Avance III AQS 400 SB instrument operating at 9.4 T. The filter paper was wetted with deionized water to 40–60% water content and packed uniformly in a zirconium oxide rotor. Recording spectra on wet rather than dry samples gives a higher apparent resolution. All measurements were made at 295 (±1) K with a MAS rate of 10 kHz. A 4-mm double air-bearing probe was used. Acquisition was performed.
using a CP pulse sequence, i.e., a 2.95 microseconds proton 90° pulse and a 800 microseconds ramped (100–50 %) falling contact pulse, with a 2.5 seconds delay between repetitions. A SPINAL64 pulse sequence was used for 1H decoupling. The Hartmann-Hahn matching procedure is based on glycine. The chemical shift scale was calibrated to the TMS ((CH$_3$)$_4$Si) scale by assigning the data point of maximum intensity in the glycine carbonyl signal to a shift of 176.03 ppm. A total of 4096 transients were recorded on each sample, giving an acquisition time of approximately 3 h. The software for spectral fitting was developed at Innventia AB and is based on a Levenberg-Marquardt algorithm.\textsuperscript{117} All computations are based on integrated signal intensities as obtained from the spectral fitting.\textsuperscript{118}

Size exclusion chromatography (SEC) using THF (1.0 mL min$^{-1}$) as the mobile phase (in paper I, II, and II) was performed at 35 °C using a Viscotek TDA model 301 equipped with two T5000 columns with porous styrene divinylbenzene copolymer (300 mm L × 7.8 mm ID, exclusion limit MW polystyrene: 400,000,000 Da) from Malvern (UK), a VE 2500 GPC autosampler, a VE 1121 GPC solvent pump, and a VE 5710 GPC degasser from Viscotek Corp. (the Netherlands). A conventional calibration method was created using narrow linear polystyrene standards. Corrections for the flow-rate fluctuations were made by using toluene as an internal standard. Viscotek OmniSEC version 4.0 software was used to process data.

SEC measurements were also performed using THF (1.0 mL min$^{-1}$) at 35 °C (in paper IV) on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 μm bead-size guard column (50 × 7.5 mm) followed by three PLgel 5 μm MixedC columns (300 × 7.5 mm) and a differential refractive index detector. The SEC system was calibrated using linear poly(methyl methacrylate) standards ranging from 700 to 2,000,000 g·mol$^{-1}$ (Mark-Houwink parameters $K = 12.8 \times 10^{-5}$ dL g$^{-1}$, $\alpha = 0.69$).\textsuperscript{119}

SEC measurements were performed using DMF (0.2 mL min$^{-1}$) with 0.01 M LiBr as the mobile phase at 50 °C on a TOSOH EcoSEC HLC-8320GPC system equipped with an EcoSEC RI detector and three columns (PSS PFG 5μm; Microguard, 100 Å, and 300 Å) (MW resolving range: 300 to 100,000 Da) from PSS GmbH. A conventional calibration method was created using narrow linear poly(methyl methacrylate) standards. Corrections for flow-rate fluctuations were made using toluene as an internal standard. PSS WinGPC Unity software version 7.2 was used to process data.
Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR equipped with a MKII Golden Gate™, Single Reflection ATR System (from Specac Ltd, London, UK). The ATR-crystal was a MKII heated Diamond 45° ATR Top Plate.

Field-emission scanning electron microscope (FE-SEM) images were recorded on a Hitachi S-4800 FE-SEM. The samples were mounted on a substrate with carbon tape and coated 3 s of a carbon coater (Cressington 108carbon/A) and subsequently 2 x 4 nm of a gold/palladium sputter coater (Cressington 208HR).

A Cary 100 UV/VIS spectrophotometer (Varian, Palo Alto, CA, USA) was used to record the absorbance increase at 412 nm. The cellulose substrate from which the polymer had been cleaved-off was immersed in 20 mL of a 3.0 mM DTNB phosphate buffer solution, pH 7.0, for 30 min to make sure that all thiols on the surface were accessible. 1 mL of the solution was characterized employing a 3.0 mM solution of DTNB medium as a reference (1 mL). Prior to the DTNB-treatment, each substrate was weighed (see Sample weight in Table 2), in order to assess the initiator content.

FT-IR microscopy (FT-IRM) imaging measurements of the cellulose samples have been performed using a Bruker FT-IR microscope HYPERION 3000 coupled to a research spectrometer VERTEX 80. The HYPERION 3000 microscope is equipped with two types of detectors: a single element MCT-detector (Mercury Cadmium Telluride) for the conventional mapping approach and a multi-element FPA-detector (Focal Plane Array) for imaging. The multi-element FPA-detector consists of 64 × 64 elements. This fact allows for the simultaneous acquisition of 4096 spectra covering a sample area of 32 × 32 μm (for ATR detection). For post-processing, baseline correction and atmospheric compensation were used. With the FPA-detector in combination with the 20× Germanium ATR-lens, a theoretical lateral resolution of 0.25 μm² per pixel is achieved.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a K-Alpha XPS spectrometer (ThermoFisher Scientific, East Grinstead, UK). Data acquisition and processing using the Thermo Avantage software is described elsewhere. All samples were analyzed using a microfocused, monochromated Al Kα X-ray source (400 μm spot size). The K-Alpha charge compensation system was employed during analysis, using electrons of 8 eV energy, and low-energy argon ions to prevent any localized charge build-up. The spectra were fitted with one or more Voigt profiles (BE uncertainty: ±0.2eV) and Scofield sensitivity factors were applied for quantification. All spectra were referenced to the C1s
Experimental peak assumed to originate from surface-hydrocarbon contamination at 285.0 eV binding energy controlled by means of the well-known photoelectron peaks of metallic Cu, Ag, and Au, respectively.

Contact-angle measurements were performed at 50 % relative humidity and 23 °C and conducted on a KSV instruments CAM 200 equipped with a Basler A602f camera, using 5 μL droplets of deionized water. The water contact angles were determined using the CAM software.

3.3 INITIATOR SYNTHESSES

Initiators suitable for ARGET ATRP were designed and synthesized with the aim to also hold certain functionalities to enable ensuing reactions; e.g., a disulfide-containing initiator for immobilization onto cellulose, prior to grafting, was produced, rendering post-cleavage of the polymer grafts from the surface possible. Furthermore, by introducing alkyne functionality to an ATRP initiator, the freely formed polymer will bear this functionality, and can thereby be employed in a subsequent conjugation reaction when grafting to a surface. Noteworthy, all details regarding the experimental reactions can be found in the corresponding articles.

3.3.1 Synthesis of disulfide-containing sacrificial initiator

By reacting 2,2’-dithiodiethanol with α-bromoisoobutyryl bromide (BiB) for 3 h at ambient temperature, the disulfide-containing sacrificial initiator OH-diS-Br was synthesized, see Scheme 5 and paper II.26

\[ \text{Scheme 5. The synthesis of the disulfide-containing sacrificial initiator OH-diS-Br.} \]
3.3.2 Synthesis of disulfide-containing initiator for immobilization onto cellulose substrates

The disulfide-containing sacrificial initiator Oh-diS-Br was reacted with succinic anhydride for 18 h at ambient temperature to introduce a carboxylic acid moiety that subsequently was transformed into an acid chloride, utilizing oxalyl chloride for 3 h at ambient temperature, forming Cl-diS-Br, see Scheme 6. The $^1$H NMR of Cl-diS-Br is presented in Figure 9 and paper II.26

![Scheme 6. The synthesis of the disulfide-containing initiator Cl-diS-Br for immobilization onto cellulose.](image)

3.3.3 Synthesis of silane-protected alkyne-functional sacrificial initiator

3-(Trimethylsilyl)propargyl alcohol and BiB were reacted for 18 h at ambient temperature to form the silane-protected alkyne-functional sacrificial initiator Si-Alk-Br, see Scheme 7 and paper IV.115
3.3.4 Synthesis of bromine-functional initiator for immobilization onto cellulose substrates

A bromine-functional initiator was produced by reacting 2-bromoethanol and succinic anhydride for 18 h at ambient temperature. The carboxylic acid was subsequently reacted with oxalyl chloride for 3 h at ambient temperature, forming Cl-R-Br (R = CO-(CH₂)₂-COO-(CH₂)₃), see Scheme 8 and paper IV.¹¹⁵

3.4 IMMOBILIZATION OF INITIATORS ONTO CELLULOSE

Whatman no. 1 filter papers of various sizes (2 x 3 cm, 1 x 1 cm, or Ø = 4 cm) were washed with ethanol, acetone, and THF and ultrasonicated for 2 min in each solvent, prior to the immobilization of the initiator. The available hydroxyl groups on the surface were converted into ARGET ATRP initiators by the reaction with an initiator holding either an acid-bromide or acid-chloride moiety:
BiB, Cl-diS-Br, or Cl-R-Br. The reactions were allowed to proceed for 0.25 - 18 h in THF at ambient temperature on a shaking device. Scheme 9 shows the immobilization of Cl-R-Br and the post-transformation of the bromines into azides employing NaN₃ (see also paper IV).¹¹⁵ Scheme 10 depicts BiB (as in paper I and III)¹⁰², ¹¹₄ and Cl-diS-Br (as in paper II and IV)²⁶, ¹¹₅ immobilized onto the cellulose substrate.

![Scheme 9](image)

**Scheme 9.** Immobilization of bromine-functional initiator Cl-R-Br onto cellulose and post-transformation of the bromines into azides.

### 3.5 GRAFTING OF VARIOUS MONOMERS FROM CELLULOSE VIA ARGET ATRP

The general polymerization system employed when grafting MMA (in paper I, II, III, and IV),²⁶, ¹⁰², ¹¹₄, ¹¹₅ styrene (in paper I),¹⁰² or GMA (in paper I)¹⁰² from initiator-functionalized cellulose consisted of a sacrificial initiator (EBiB, OH-diS-Br, or Si-Alk-Br), PMDETA, Cu(II)Br₂, AsAc or NaAsc, and anisole, in an inert atmosphere, see Scheme 10 for further details. Different ratios of initiator to monomer were utilized obtain different DPₜarget, and the other employed ratios were: [MMA] : [I] : [Cu(II)Br₂] : [PMDETA] : [AsAc/NaAsc] = DPₜarget : 1 : 0.1 : 1 : 1, except for PGMA where the ratio of AsAc was 0.5. The reaction was monitored by ¹H NMR and terminated when the desired conversion was reached or after a predetermined time. The polymer was precipitated and the grafted cellulose substrate was thoroughly washed.
Experimental

Scheme 10. The surface-initiated ARGET ATRP of MMA, St, or GMA from initiator-functionalized cellulose substrate (Cel-BiB or Cel-diS-Br) in parallel to the polymerization initiated from a sacrificial initiator (EBiB, OH-diS-Br, or Si-Alk-Br).

In addition, grafting of MMA from BiB-functionalized filter paper (2 × 3 cm) without any deoxygenation was also investigated (unpublished results). The same ratios as above were employed, except that the amount of AsAc was changed for some polymerization systems. The reaction took place in either a round-bottom flask capsuled with a rubber septum or in a glass jar with a screw lid, both with and without the addition of solvent. Experiments with the addition of a small amount of H₂O (≤ 0.1 mL to 25 g MMA) to the bulk reactions were also performed.

3.6 CLEAVAGE OF PMMA GRAFTS FROM MODIFIED CELLULOSE

The PMMA grafts, which had been grafted from the cellulose substrate functionalized with the disulfide-containing initiator, were cleaved off by employing 1,4-dithiothreitol (DTT) for five days at ambient temperature, see Scheme 11 and paper II.²⁶,¹¹⁵
3.7 GRAFTING OF ALKYNE-FUNCTIONAL PMMA TO CELLULOSE VIA CUAAC

The PMMA polymer Si-Alk-PMMAx-Br (where x denotes the DP calculated from $^1$H NMR), formed from the sacrificial initiator Si-Alk-Br in parallel to the grafting from cellulose, was utilized as the pre-polymer for the grafting-to reaction. Prior to the grafting reaction, the silane-protected PMMA has to be deprotected.

3.7.1 Activation of alkyne-functional PMMA

The silane-protected PMMA was deprotected by subjecting it to tetrabutylammonium fluoride trihydrate (TBAF · 3 H2O) under inert atmosphere, see Scheme 12 and paper IV.\textsuperscript{115}
**Scheme 12.** Deprotection of silane-protected PMMA, forming Alk-PMMA\textsubscript{x}-Br.

### 3.7.2 Grafting to cellulose

The grafting-to reaction was conducted by immersing the azide-functionalized cellulose substrate into a solution containing the alkyne-functional PMMA, copper sulfate pentahydrate (Cu(II)SO\textsubscript{4} \cdot 5 H\textsubscript{2}O), NaAsc, a small amount of H\textsubscript{2}O, and DMF, employing an inert atmosphere, see Scheme 13 and paper IV.\textsuperscript{115}

**Scheme 13.** The grafting of alkyne-functional PMMA to an azide-functionalized cellulose substrate via CuAAC.
4. RESULTS AND DISCUSSION

Cellulose is a fascinating natural resource in many perspectives. By modifying the available hydroxyl groups on cellulose via grafting of polymer, the applicability of cellulose can be enhanced. To truly tailor the surface characteristics, it is crucial to obtain knowledge about the grafting properties; furthermore, certain control over the reaction mechanism is essential. However, due to the inherent surface roughness of cellulose substrates, such as filter paper, it is challenging to characterize the grafted substrate quantitatively. Nevertheless, to be able to apply the modification industrially, simple and not too harsh reaction conditions are a prerequisite. Therefore, the development of straightforward surface-initiated ARGET ATRP grafting systems, with low amount of copper combined with low sensitivity towards oxygen, can be of great importance.

4.1 GRAFTING OF VARIOUS MONOMERS FROM CELLULOSE VIA ARGET ATRP

ARGET ATRP was employed for surface-initiated polymerization of cellulose substrates, utilizing the various monomers: MMA, St, and GMA. Commonly, fine-tuning of ATRP systems for different monomers is required for the polymerization to succeed, but only minor adjustments to the reaction conditions for these three rather different monomers were performed. The changes in between the systems were the reaction temperature as well as the choice of reducing agent (see Scheme 10). Furthermore, the grafting procedure is performed straightforwardly by just immersing the initiator-functionalized substrate in the reaction mixture, followed by a few minutes of purging with inert gas. The graft length was controlled by employing a sacrificial initiator, also allowing for the monitoring of the kinetics by $^1$H NMR and SEC. Noteworthy, parallel grafting experiments were conducted and quenched after a
predetermined time, since the withdrawal of aliquots may affect the kinetics. The unbound polymer, freely formed from the sacrificial initiator, was visually colorless after precipitation, without the requirement for removal of the Cu salt by passing the polymer solution through an Al₂O₃ column; nevertheless, small amounts of Cu can be remaining. Therefore, the polymer was purified from copper when being employed in subsequent reactions.

The free polymer formed simultaneously in the solution showed first-order kinetics with respect to monomer conversion up to at least 20 % monomer conversion for all three systems; e.g., see Figure 4 for the kinetic plot of the PMMA system, targeting two different DPs. For the PS system, a distinct induction period in the beginning of the reaction, when the Cu(II) species is transformed to Cu(I) species, could be observed. For the PMMA – and PGMA – systems this effect was not as clearly observed, which can be due to that the stronger reducing agent AsAc was employed instead of NaAsc as for PS. Moreover, the propagation rate constant \( k_p \) is much larger for MMA than for styrene.³⁹,⁴³

![Figure 4. Kinetic plot for ARGET ATRP of PMMA. Experimental conditions: \( T = 40 ^\circ \text{C}, \text{anisole (50 wt%)} \), @\([\text{MMA}]:[\text{EBiB}]:[\text{Cu(II)Br}_2]:[\text{PMDETA}]:[\text{AsAc}] = 400:1:0.1:1:1\) and ■\([\text{MMA}]:[\text{EBiB}]:[\text{Cu(II)Br}_2]:[\text{PMDETA}]:[\text{AsAc}] = 800:1:0.1:1:1\).¹⁰²](image)

Figure 5 illustrates the molar mass and dispersity of crude samples of PMMA (DP_{target} = 800) as a function of monomer conversion. At low conversions, the molar masses obtained from SEC are higher than the theoretical values calculated from \(^1\text{H} \text{NMR} \) (see Eq. 4), suggesting that the initiator efficiency is below 1. The incomplete initiation and the fact that the end-group of a PMMA chain has an
activation rate constant \((k_{\text{act}})\) that is approximately eight times higher compared with \(k'_{\text{act}}\) of EBiB,\textsuperscript{66, 122, 123} see Scheme 2 and Eq. 3, explains why the molar mass is higher at low monomer conversion. At higher monomer conversions, the molar mass is lower than the theoretical value, which we previously explained to be due to that the surface propagation contributes to the consumption of monomers to large extent, when aiming for higher \(DP_{\text{target}}\).\textsuperscript{102} However, at that time, we did not know that on the cellulose substrate employed (filter paper: 2 \times 3 cm) approximately 1.1 \(\mu\)mol initiators are present\textsuperscript{26} (discussed in detail in section 4.3). In the same system, the \(DP_{\text{target}}\) of 800 with a monomer amount of 10 g corresponds to 125 \(\mu\)mol of EBiB; thus, the sacrificial initiator is in large excess compared with the initiator on the surface. Therefore, the monomer consumed by the cellulose substrate cannot be the only explanation, also suggesting the occurrence of transfer reactions, such as intra- and intermolecular chain-transfer as well as transfer to monomer or solvent. Transfer reaction results in an increased number of total chains. The chain transfer to polymer results in branching\textsuperscript{124, 125}, which decreases the hydrodynamic volume of the polymer, and thereby lowering the obtained \(M_n\) since the SEC separates molecules according to the hydrodynamic volume.\textsuperscript{125}

Figure 5. Molar mass and dispersity (PDI) of PMMA as a function of monomer conversion. The continuous line represents the theoretical values that were calculated from the monomer conversion determined by \(^1\text{H} NMR. Experimental conditions: } T = 40 ^\circ\text{C, anisole (50 wt\%), } [\text{MMA}]:[\text{EBiB}]:[\text{Cu(II)Br}_2]:[\text{PMDETA}]:[\text{AcAs}] = 800:1:0.1:1:1.\textsuperscript{102}

Another possibility can be that as the reaction proceeds, the initiator efficiency increases as reported previously,\textsuperscript{65, 66} forming more propagating species which will lower the molar mass. Matyjaszewski et al. have reported the same
phenomenon seen in Figure 5 for MMA with EBiB as an initiator, also suggesting that the reason is transfer reactions and slower initiation. A schematic graph of how the different features affect the molar mass as a function of the monomer conversion is presented in Figure 6. Nevertheless, the same deviation of $M_n$ from $M_{\text{theo}}$ was observed for PS and PGMA, but the difference at higher conversion was not as pronounced as for the PMMA system. Figure 5 also demonstrates that the $D_M$ (named here as PDI) slightly decreases with increasing monomer conversion, which is contradictory to the presence of chain-transfer reactions which would increase the dispersity.

![Schematic Graph](image)

**Figure 6.** A schematic graph to illustrate how $M_n$ varies as a function of the conversion, for different reaction features in the polymerization system.

The cellulose substrates grafted with PMMA, PS, or PGMA were characterized with FT-IR to verify the successful grafting. It could be concluded that the amount of polymer successively increased with monomer conversion. As an example, Figure 7 depicts the increase in the carbonyl region for the PMMA-grafted cellulose substrates with increasing reaction time. However, it is important to keep in mind that the method is semi-quantitative, since the spectra are normalized against the noise arising from the ATR crystal ($2300$–$1950 \text{ cm}^{-1}$). Furthermore, when analyzing a rough substrate such as cellulose filter paper, the absorbance can vary slightly depending on which point on the surface that is being examined. This effect can also be due to that the polymer layer may not be completely homogenous. Nevertheless, FT-IR is a versatile method to prove a successful grafting, but it does not give the spatial distribution of the polymer grafts on the surface.
Figure 7. FT-IR spectra of PMMA-grafted cellulose at different reaction times (DP_{target} = 800), showing the increase of carbonyl peak at 1732 cm\(^{-1}\) as well as the bound water in cellulose (approx. 1600–1700 cm\(^{-1}\)).

To determine the spatial distribution of the polymer content on the surface, high-resolution FT-IRM was employed. Figure 8 depicts the FT-IRM micrographs of the grafted cellulose substrates with increasing graft length for PMMA\(_x\) (where \(x\) denotes the DP calculated from \(^1\)H NMR). The six upper images correspond to the same substrates as in Figure 7, except that the substrate modified for 0.5 h is excluded. As can be seen, the polymer distribution is relatively uniform, especially as the graft length increases. However, a tendency to form smaller regions with higher polymer concentration can also be observed. These smaller inhomogeneities may be a result of the surface roughness. Still, FT-IRM was proven to be a very useful method for the characterization of cellulose substrates.
Figure 8. False color high-resolution FT-IR micrographs (4 cm⁻¹ spectral resolution with a 0.25 μm² theoretical spatial pixel resolution and an optical resolution of close to 1 μm) of initiator-functionalized cellulose (with BiB) and PMMA-x-grafted cellulose (where x denotes the DP calculated from ¹H NMR), displaying the carbonyl region by integration of the C=O stretching vibration (between 1700–1760 cm⁻¹). Regions with dark blue color represent low intensity and pink color depicts high intensity regions.¹¹⁴

The hydrophobicity of the cellulose surface was investigated utilizing CA measurements. The CA is affected by the chemical composition of the surface as well as the surface roughness. Due to the inherent surface roughness of filter paper, it is difficult to determine absolute values; hence, the CAs are only approximations. An applied water droplet is immediately absorbed by an unmodified filter paper due to the hydrophilic character of cellulose. Upon the grafting of a hydrophobic polymer, the CA is significantly increased, even for cellulose substrates with shorter polymer grafts; e.g., a DP of around 50 results in CAs of 109°±3° for PMMA-grafted and 137°±3° for PS-grafted cellulose. In fact, shorter polymer chains may result in a higher CA due to a rougher surface,¹²⁸ since longer polymer grafts tend to smoothen the surface (see Figure 10b in section 4.2), which is also corroborated by the FT-IRM results that suggest a more homogeneous topography for longer polymer grafts. The CAs of the cellulose substrates grafted with higher DPs, e.g., DP = 384 for PMMA and DP = 288 for PS,
were essentially the same as for those with shorter grafts: 112°±2° and 132°±3°, respectively.

4.2 SELECTIVE CLEAVAGE OF POLYMER GRAFTS

An initiator, employed for immobilization onto cellulose prior to the grafting reaction, was designed with a disulfide linker (Scheme 6) to allow for cleavage of polymer grafts, as well as for an estimation of the initiator content. Mild conditions of the cleavage reaction were a prerequisite, in order to avoid degradation of a sensitive substrate like cellulose, and also to be able to perform the subsequent surface analysis. The 1H NMR of the initiator Cl-diS-Br is presented in Figure 9. The initiator was immobilized for 0.25, 0.50, 1.0, and 15 h at ambient temperature, prior to the grafting of MMA via ARGET ATRP. A sacrificial initiator (OH-diS-Br) was employed to be able to compare the characteristics of the grafted polymers with the free polymer. The grafted substrates were subjected to DTT to cleave the disulfide bond at ambient temperature for five days (see Scheme 11). FT-IR analyses of the cleaved substrates showed that most polymer chains were cleaved off after only 18 h, suggesting that the disulfide bonds are readily accessible. However, to obtain complete cleavage, which is crucial for the following analysis, longer reaction times combined with a larger amount of DTT were required.

![Figure 9. 1H NMR spectrum of the disulfide-containing initiator Cl-diS-Br employed for immobilization onto cellulose in CDCl₃.](image)

The amount of the obtained polymer grafts was insufficient for precipitation, why crude samples were analyzed by SEC. The molar masses of the free and the cleaved polymers are in good agreement – Table 1 – suggesting that the polymerization occurs at similar rate from the surface as from the sacrificial initiator, corroborating the hypothesis that grafts can be tailored by employing a
sacrificial initiator. The free polymers have slightly higher molar masses which are probably due to removal of low molar-mass molecules during precipitation, resulting in an overall higher average molar mass and lower $\bar{M}_w$.

Table 1. Properties of the free polymer and the cleaved grafts, $D_{P_{\text{target}}} = 800$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Free polymer</th>
<th>Cleaved grafts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_n$</td>
<td>$D_M$</td>
</tr>
<tr>
<td>PMMA$_{240}$</td>
<td>20 900</td>
<td>1.14</td>
</tr>
<tr>
<td>PMMA$_{432}$</td>
<td>47 000</td>
<td>1.18</td>
</tr>
</tbody>
</table>

<sup>a</sup> PMMA$_x$ where $x$ represents the DP calculated from the conversion obtained from $^1$H NMR.<sup>b</sup> Obtained from THF-SEC (PS standards).<sup>c</sup> SEC of a crude sample.

FE-SEM was employed to study the surface topography of the modified substrates. The initiator-functionalized cellulose substrate displays the typical fine structure of an unmodified cellulose substrate, Figure 10a. On the contrary, the PMMA-grafted cellulose substrate in Figure 10b gives rise to a smoother surface. After cleavage of the PMMA-grafts, the fine structure of cellulose can be perceived again (Figure 10c), indicating that the grafts have been successfully removed. The initiator-functionalized and DTT-treated cellulose structures are very similar to the unmodified substrate, establishing that both treatments are essentially non-destructive.

**Figure 10.** FE-SEM micrographs of cellulose substrate a) initiator-functionalized, b) PMMA-grafted, and c) after cleavage, magnified 10 000x.<sup>26</sup>

### 4.3 ASSESSING INITIATOR CONTENT

After the reduction of the disulfide bonds, thiol moieties are present on the surface, which can readily be quantified by Ellman’s reagent (5,5’-dithiobis-2-nitrobenzoic acid (DTNB)).<sup>129-132</sup> The reaction between DTNB and a thiol generates the chromophore 5-thio-2-nitrobenzoic acid (TNB), which absorbs strongly at 412
nm, providing for the possibility to assess the initiator content of the substrate via UV analysis. The measured absorbance was utilized to calculate the number of moles of thiols present on the substrate, see Table 2. To evaluate the initiator content, the number of moles of thiols was normalized to the sample weight (Table 2), resulting in a value of approximately 21 μmol initiators per gram of cellulose. As a comparison, the initiator content of silica nanoparticles with various sizes has been reported to be in the range of 35 to 260 μmol/g.\textsuperscript{28, 133} suggesting that the values are reasonable. To further verify the versatility of this method, microcrystalline cellulose (MCC) – with an average diameter of 20 μm – was utilized as an additional substrate. The initiator content was found to be roughly twice as high as for filter papers, see Table 2. Comparatively, silica particles in the same size as MCC, where the OH-groups were reacted with a monofunctional silyl chloride to immobilize the initiator, have initiator contents of 135 μmol/g\textsuperscript{134} and 260 μmol/g\textsuperscript{27}.

The initiator density of the filter paper was estimated by employing the specific surface area of cellulose, which is 0.59 m\textsuperscript{2}/g according to BET measurements reported in the literature.\textsuperscript{135} Thus, the number of moles initiator per square centimeter of cellulose can be assessed, see Table 2.

The results in Table 2 also demonstrate that the immobilization of the initiator onto the surface is a fast reaction when a large surplus of the immobilized initiator was utilized: 1.33 mmol of Cl-diS-Br to approximately 1 μmol reacted hydroxyl groups. After 30 min of immobilization, the initiator content on the surface was essentially the same as after 15 h.

Table 2. Data assessed from UV analysis of the cleaved cellulose substrates.

<table>
<thead>
<tr>
<th>Sample\textsuperscript{a}</th>
<th>Immob. [h]</th>
<th>Abs. (λ=412 nm)</th>
<th>n thiols [μmol]</th>
<th>Sample weight [mg]</th>
<th>Initiator content [μmol/g]</th>
<th>Initiator density\textsuperscript{b} [nmol/cm\textsuperscript{2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiator\textsubscript{0.25}</td>
<td>0.25</td>
<td>0.653±0.003</td>
<td>1.005±0.004</td>
<td>53.9</td>
<td>18.6±0.1</td>
<td>3.4</td>
</tr>
<tr>
<td>Initiator\textsubscript{0.5}</td>
<td>0.50</td>
<td>0.686±0.002</td>
<td>1.055±0.003</td>
<td>51.2</td>
<td>20.6±0.1</td>
<td>3.5</td>
</tr>
<tr>
<td>Initiator\textsubscript{1.0}</td>
<td>1.0</td>
<td>0.681±0.003</td>
<td>1.048±0.005</td>
<td>52.0</td>
<td>20.2±0.1</td>
<td>3.5</td>
</tr>
<tr>
<td>PMMA\textsubscript{240}</td>
<td>15</td>
<td>0.685±0.001</td>
<td>1.053±0.001</td>
<td>51.1</td>
<td>20.6±0.1</td>
<td>3.5</td>
</tr>
<tr>
<td>PMMA\textsubscript{432}</td>
<td>15</td>
<td>0.701±0.005</td>
<td>1.078±0.008</td>
<td>51.3</td>
<td>21.0±0.2</td>
<td>3.6</td>
</tr>
<tr>
<td>MCC</td>
<td>3.5</td>
<td>0.661±0.003</td>
<td>1.017±0.004</td>
<td>25.6</td>
<td>39.7±0.2</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Initiator\textsubscript{y} where \textit{y} represent the immobilization time of the initiator. \textsuperscript{b} Calculation based on the specific surface area of cellulose filter paper: 0.59 m\textsuperscript{2}/g.\textsuperscript{135}
To determine the number of available hydroxyl group on filter paper, solid-state NMR (CP/MAS $^{13}$C NMR) was employed, suggesting that filter paper has 7.1 (± 0.4) % of available OH-groups when it is swelled in water. The molar mass of the AGU of cellulose ($C_6H_{10}O_5$) is $162.2 \text{ g/mol}$. Thus, 1.0 g of cellulose contains 18.5 mmol of hydroxyl groups, where 1.31 mmol of these are active, according to the NMR analysis. Upon immobilization of the initiator onto cellulose, THF was employed as a solvent; thus, the cellulose is not as swollen as in water, resulting in fewer available hydroxyl groups. However, if the higher value of active OH-groups is utilized, the initiator content of approximately 20 $\mu \text{mol/g}$ corresponds to 1.5 % of the available hydroxyl groups having reacted.

## 4.4 COMPARISON BETWEEN GRAFTING-FROM AND GRAFTING-TO CELLULOSE

The grafting-from and the grafting-to approaches both have their pros and cons, but the general comprehension is that the surface-initiated polymerization, i.e., the grafting-from reaction, results in a higher grafting density. However, to the best of our knowledge, a comparative study investigating this has not been conducted until now. The difference in grafting efficiency – when grafting from cellulose via ARGET ATRP and grafting to cellulose via CuAAC – was evaluated by FT-IRM and XPS. The grafting-from reaction was performed in parallel to the in-situ polymerization from a sacrificial initiator with a protected alkynefunctionality. Owing to the alkyn-functional initiator, the free polymer, bearing this functionality, can subsequently be utilized in the grafting-to reaction via conjugation to an azide-functionalized cellulose substrate. Thus, the polymers grafted from and to the surface were essentially identical, in terms of molar mass and dispersity. This was further validated by employing the disulfide-containing initiator for immobilization onto the cellulose surface, rendering cleavage and ensuing characterization of the grafted polymers possible. See Scheme 14 for the schematic synthetic pathway.
Scheme 14. The schematic synthetic pathway of the grafting strategy, where the freely formed PMMA in the grafting-from reaction was employed as the pre-polymer in the grafting-to reaction after the deprotection of the protected alkyne-functional initiator.115

4.4.1 Grafting from and grafting to cellulose

The grafting from cellulose and the in-situ formation of the free polymer were performed by ARGET ATRP of MMA, targeting the final DP of 1200 (Scheme 10). Four polymerizations were conducted at 50 °C to different conversions: 11, 39, 51, and 80 %, in order to obtain different graft lengths. The silane-protected alkyne-functional initiator Si-Alk-Br, see Scheme 7, was utilized as a sacrificial initiator. The free polymer Si-Alk-PMMAx-Br (where x denotes the DP calculated from 1H NMR) was precipitated and characterized with SEC to verify that well-controlled reactions were obtained, see Table 3. The slightly higher dispersity ($D_M$) for Si-Alk-PMMA$_{860}$-Br can be explained by the high conversion, which probably led to a higher degree of termination, compared to the other reactions; still, the $D_M$ is below 1.3.
Table 3. Characteristics of the free polymers and the cleaved polymer grafts obtained in the grafting-from reactions.

<table>
<thead>
<tr>
<th>Name(^a)</th>
<th>(p^b) (%)</th>
<th>(M_{\text{theo}}^c) (g/mol)</th>
<th>(M_{n}^d) (g/mol)</th>
<th>(D_M^d)</th>
<th>Name(^e)</th>
<th>(M_{n}^d) (g/mol)</th>
<th>(D_M^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-alk-PMMA(132)-Br</td>
<td>11</td>
<td>13 100</td>
<td>21 000</td>
<td>1.07</td>
<td>SH-PMMA(132)-Br</td>
<td>23 200</td>
<td>1.08</td>
</tr>
<tr>
<td>Si-alk-PMMA(612)-Br</td>
<td>39</td>
<td>47 500</td>
<td>53 300</td>
<td>1.09</td>
<td>SH-PMMA(612)-Br</td>
<td>45 600</td>
<td>1.10</td>
</tr>
<tr>
<td>Si-alk-PMMA(960)-Br</td>
<td>51</td>
<td>61 200</td>
<td>69 400</td>
<td>1.12</td>
<td>SH-PMMA(960)-Br</td>
<td>66 700</td>
<td>1.23</td>
</tr>
<tr>
<td>Si-alk-PMMA(960)-Br</td>
<td>80</td>
<td>96 600</td>
<td>100 800</td>
<td>1.26</td>
<td>SH-PMMA(960)-Br</td>
<td>87 400</td>
<td>1.31</td>
</tr>
</tbody>
</table>

\(^a\) PMMA\(_x\) where \(x\) represents the DP calculated from the conversion obtained from \(^1\)H NMR. \(^b\) Conversion calculated from \(^1\)H NMR. \(^c\) \(M_{\text{theo}} = DP_{\text{target}} \times p \times M_{\text{MMA}} + M_{\text{Si-alk-Br}}\) based on \(^1\)H NMR conversion. \(^d\) Obtained from THF-SEC (PMMA standards).

The PMMA-grafts (SH-PMMA\(_x\)-Br) were cleaved off the surface (Scheme 11), and subsequently precipitated and isolated by centrifugation, due to very small obtained amounts (a few mg). The dried polymer was characterized by SEC, and the results compared to those of the free polymer formed from the sacrificial initiator, see Table 3. As can be seen, the molar masses and the dispersities were in good agreement, which also has been suggested by others\(^{18,26-28}\) proposing that the graft length can be tailored by the utilization of a sacrificial initiator.

The silane-protecting group of the free polymers (Si-alk-PMMA\(_x\)-Br) was removed utilizing TBAF, resulting in the alkyne-functional polymers Alk-PMMA\(_x\)-Br (Scheme 12). The polymers were precipitated and characterized with SEC, see Table 4. The molar masses for these pre-formed grafts for the grafting-to reaction were in the same range as the cleaved grafts from the grafting-from surfaces, presented in Table 3, which are of utmost importance to obtain a systematic comparison of the grafting techniques.

To conjugate these polymers onto cellulose substrates \textit{via} CuAAC, the initiator Cl-R-Br was first immobilized onto cellulose prior to the transformation of the bromines to azides, forming azide-functionalized cellulose: Cel-Az, see Scheme 9. The same conditions were employed as when immobilizing Cl-diS-Br to the surface, most likely resulting in the same amount of initiator on the cellulose substrate. The grafting-to reaction was performed by utilizing Cu(II)SO\(_4\)·5 H\(_2\)O and NaAsc in DMF (Scheme 13); furthermore, a small amount of H\(_2\)O was added to the solution to facilitate the dissolution of the catalyst. The polymer concentration was kept constant (1.5 mM) to obtain the same number of moles of
alkyne end-groups for the four different polymer lengths (Table 4). The resulting cellulose substrates Cel-Az-PMMAₓ-Br were thoroughly rinsed and ultrasonicated to remove any polymer residues that were not covalently conjugated to the substrate.

Table 4. The polymer characteristics after deprotection of the silane-protecting group of the free polymers.

<table>
<thead>
<tr>
<th>Name</th>
<th>( M_n ) (g/mol)</th>
<th>( D_M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alk-PMMA₁₃₂-Br</td>
<td>18 500</td>
<td>1.07</td>
</tr>
<tr>
<td>Alk-PMMA₄₆₈-Br</td>
<td>51 800</td>
<td>1.07</td>
</tr>
<tr>
<td>Alk-PMMA₆₆₂-Br</td>
<td>66 700</td>
<td>1.06</td>
</tr>
<tr>
<td>Alk-PMMA₉₆₀-Br</td>
<td>89 400</td>
<td>1.26</td>
</tr>
</tbody>
</table>

*PMMAₓ where x represents the DP calculated from the conversion obtained from \(^1\)H NMR. *Obtained from THF-SEC (PMMA standards).

4.4.2 XPS analysis of modified cellulose substrates

The modified cellulose substrates were analyzed by XPS to confirm the successful reactions. In Figure 11A, the C 1s spectra of pure Whatman no. 1 filter paper is depicted, showing mainly the three characteristics peaks: the C-H and C-C bonds at 285.0 eV, the C-O bond of alcohol (C-OH) and ether (C-O-C) groups at 286.8 eV, and the O-C-O bond of acetals (and/or C=O) bonds at 288.3 eV. However, a fourth peak at 289.5 eV can often be detected, corresponding to oxidation and impurities of cellulose.¹¹² Upon immobilization of the initiator Cl-diS-Br the atomic percentages of C-C and C-H bonds increase, and the peak at 289.4 eV, corresponding to the ester bonds¹³⁷ (O-C=O) that have been introduced to the substrate, is also enhanced, see Figure 11B. Additionally, the successful grafting of PMMA from the cellulose surfaces can also be confirmed, as the characteristic polymer peaks at 285.0 (C-C and C-H) and 289.4 (O-C=O) eV significantly increase, which is seen in Figure 11C and 11D for the Cel-diS-PMMA₁₃₂-Br and for Cel-diS-PMMA₉₆₀-Br, respectively. Comparatively, upon cleavage of the polymer graft, the characteristic polymer peaks at 285.0 and 289.3 eV have clearly decreased, confirming the detachment of the grafts, see Figure 11E.
Results and Discussion

**Figure 11.** C 1s XPS spectra for the cellulose substrates modified *via* the grafting-*from* approach: (A) Pure cellulose, (B) Cel-diS-Br, (C) Cel-diS-PMMA\textsubscript{132}-Br, (D) Cel-diS-PMMA\textsubscript{132}-Br, and (E) Cel-SH\textsubscript{132}. The spectra were normalized to the peak with the highest intensity.\textsuperscript{115}

XPS was also performed on the cellulose substrates modified *via* the grafting-*to* approach. The C 1s spectra in Figure 12 show that the peak corresponding to O-C=O is enhanced upon immobilization of the initiator Cl-R-Br and the post-transformation of the bromines into azides (Figure 12B), as for the immobilization of the initiator Cl-diS-Br for the grafting-*from* reaction (Figure 11B). Figures 12C and 12D depict the spectra after the conjugation reaction between the substrate Cel-Az and the polymers Alk-PMMA\textsubscript{132}-Br and Alk-PMMA\textsubscript{960}-Br, respectively. As can be seen, the characteristic polymer peaks at 285.0 and 289.3 eV are increased, confirming that the polymers have been grafted to the initiator-functionalized cellulose substrate. However, the spectrum shows a high intensity of the signal attributed to the C-O bonds from the cellulose substrate for Cel-Az-PMMA\textsubscript{132}-Br, suggesting that the coverage of the polymer grafts are rather inhomogeneous and low. In comparison, for Cel-Az-PMMA\textsubscript{960}-Br the polymer signal becomes higher than the cellulose signal, suggesting a more homogeneous polymer layer.
The ratio between the characteristic cellulose signal (C-O) and the ester signal (O-C=O) acquired from XPS is presented in Table 5. The expected theoretical ratio of 1, given by the structure of the repeating unit MMA (C-O/O-C=O = 1/1), corresponds to that only the polymer layer is being measured. As can be seen, upon immobilization of the initiators Cel-diS-Br and Cel-Az the ratios are greatly decreased compared to the pure cellulose substrate. As PMMA is grafted \textit{from} the substrate, this ratio is further reduced with increasing graft length. The ratio of 1.9 for Cel-diS-PMMA$_{132}$-Br suggested that the grafted polymer chains do not cover the cellulose surface completely. For the longer polymer grafts (Cel-diS-PMMA$_{468}$-Br and Cel-diS-PMMA$_{960}$-Br) the ratio is 1.2, implying that the cellulose substrate has not influenced the measurement significantly and mainly the polymer layer was analyzed.

Upon cleavage, the cellulose/polymer ratio (Table 5) was increased and the values are in the same range as for the initiator-functionalized surface Cel-diS-Br, clearly
proving that the polymer grafts have been cleaved off the substrates. Yet, the slightly lower ratio for Cel-SH\textsubscript{960} may suggest the presence of polymeric residues.

For the cellulose substrates grafted \textit{via} the CuAAC, the ratios are not as low as for the grafting-\textit{from} substrates, i.e. not only the polymer layer was measured but also the cellulose substrate to certain extent. For Cel-Az-PMMA\textsubscript{132}-Br, the ratio is almost twice as large as for Cel-Az-PMMA\textsubscript{960}-Br (Table 5), suggesting that the polymer coverage is larger for the substrate with the longer grafts than for the shorter grafts. The ratio of Cel-Az-PMMA\textsubscript{468}-Br is in between the ratio of the other grafted substrates. Thus, according to XPS, the polymer content varies slightly between the substrates grafted \textit{via} the grafting-\textit{to} approach.

\textbf{Table 5.} The ratios between the characteristic peaks of cellulose (C-O) and PMMA (O-C=O), as obtained by XPS analysis.

<table>
<thead>
<tr>
<th>Modification</th>
<th>Name</th>
<th>C-O/O-C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure cellulose</td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>\textit{Grafting from}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cel-diS-I</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>Cel-diS-PMMA\textsubscript{132}-Br</td>
<td></td>
<td>1.9</td>
</tr>
<tr>
<td>Cel-diS-PMMA\textsubscript{468}-Br</td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>Cel-diS-PMMA\textsubscript{960}-Br</td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>\textit{After cleavage}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cel-SH\textsubscript{132}</td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>Cel-SH\textsubscript{468}</td>
<td></td>
<td>22</td>
</tr>
<tr>
<td>Cel-SH\textsubscript{960}</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>\textit{Grafting to}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cel-Az</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>Cel-Az-PMMA\textsubscript{132}-Br</td>
<td></td>
<td>2.6</td>
</tr>
<tr>
<td>Cel-Az-PMMA\textsubscript{468}-Br</td>
<td></td>
<td>1.8</td>
</tr>
<tr>
<td>Cel-Az-PMMA\textsubscript{960}-Br</td>
<td></td>
<td>1.5</td>
</tr>
</tbody>
</table>
4.4.3 FT-IRM of modified cellulose substrates

The modified substrates were characterized with FT-IRM to determine the differences in the spatial distribution of the polymer content on the cellulose fibers. Figure 13 depicts the FT-IR micrographs of the cellulose substrates after modification via the grafting-from approach (Figure 13A), after the cleavage of the polymer grafts (Figure 13B), and after modification via the grafting-to method (Figure 13C). The same intensity scales for the cellulose region, 0 to 52, and the carbonyl signal, -0.3 to 1.5, are employed for all the micrographs to ensure comparability. The micrographs of Cel-diS-PMMA-Br in Figure 13A clearly show an increased polymer signal with increasing monomer conversion, confirming that the cellulose substrates were grafted with different graft lengths; hence, different polymeric amounts on the cellulose substrates were attained. As the conversion increases above 11%, the polymer becomes more evenly distributed over the whole fiber; however, the polymer grafts are not completely uniformly distributed.

The detachment of the polymer grafts from the grafted cellulose substrates was confirmed by FT-IRM. The polymer signals present in Figure 13A have disappeared for the cleaved substrates Cel-SH, see Figure 13B. However, for Cel-diS-PMMA-Br there appears to be a minor polymeric residue on the cellulose substrate, which also the XPS results suggest, see Table 5.

The micrographs of the cellulose substrates Cel-Az-PMMA-Br modified via the grafting-to approach are presented in Figure 13C, confirming that the conjugation reaction occurred. However, the increased graft length of the pre-polymer does not result in an increased content of polymer on the surface as the intensity of the carbonyl signals is essentially identical for the four substrates. Although, for Cel-Az-PMMABr, having the longest grafts, a slightly thicker and more evenly distributed polymer layer was obtained compared to the other grafted substrates. This indicates that the surface with the shortest chains has higher grafting density compared to the substrates with the longer grafts, since the total amount of grafted polymer on the surfaces is similar for all surfaces. The reactive sites on the surface are probably not as shielded when polymers with shorter graft lengths are used compared to when larger polymers are utilized. The higher accessibility probably yields a better diffusion of the chain ends to the reactive sites on the surface. As a comparison, the grafting-from technique clearly results in an increased amount of polymer with increasing graft length, Figure 13A. The much smaller monomer units, in comparison to polymer grafts, have a much better
accessibility to the reactive sites on the surface throughout the reaction; thus, the steric hindrance becomes much lower when grafting from the surface, resulting in higher grafting efficiency. Accordingly, the obtained results suggest that the grafting-from approach is superior over the grafting-to technique, with respect to controlling the polymer content on the surface. All the same, the results are valid under these conditions and it may be hard to generalize them to other grafting systems, i.e., the reaction methodology and the substrate employed can have an impact. However, the obtained result support the suggested theory with higher grafting efficiency for the grafting-from reaction compared to the grafting-to.
### Results

| (A) Grafting from | Cel-diS-PMMA\textsubscript{132}-Br | Cel-diS-PMMA\textsubscript{589}-Br | Cel-diS-PMMA\textsubscript{132}-Br | Cel-diS-PMMA\textsubscript{589}-Br |
| | Cellulose region: 950-1200 cm\(^{-1}\) | Cellulose region: 950-1200 cm\(^{-1}\) | Cellulose region: 950-1200 cm\(^{-1}\) | Cellulose region: 950-1200 cm\(^{-1}\) |
| | Carbonyl region: 1700-1760 cm\(^{-1}\) | Carbonyl region: 1700-1760 cm\(^{-1}\) | Carbonyl region: 1700-1760 cm\(^{-1}\) | Carbonyl region: 1700-1760 cm\(^{-1}\) |

| (B) After cleavage | Cel-SH\textsubscript{132} | Cel-SH\textsubscript{589} | Cel-SH\textsubscript{132} | Cel-SH\textsubscript{589} |
| | Cellulose region: 950-1200 cm\(^{-1}\) | Cellulose region: 950-1200 cm\(^{-1}\) | Cellulose region: 950-1200 cm\(^{-1}\) | Cellulose region: 950-1200 cm\(^{-1}\) |
| | Carbonyl region: 1700-1760 cm\(^{-1}\) | Carbonyl region: 1700-1760 cm\(^{-1}\) | Carbonyl region: 1700-1760 cm\(^{-1}\) | Carbonyl region: 1700-1760 cm\(^{-1}\) |

| (C) Grafting to | Cel-Az-PMMA\textsubscript{132}-Br | Cel-Az-PMMA\textsubscript{589}-Br | Cel-Az-PMMA\textsubscript{132}-Br | Cel-Az-PMMA\textsubscript{589}-Br |
| | Cellulose region: 950-1200 cm\(^{-1}\) | Cellulose region: 950-1200 cm\(^{-1}\) | Cellulose region: 950-1200 cm\(^{-1}\) | Cellulose region: 950-1200 cm\(^{-1}\) |
| | Carbonyl region: 1700-1760 cm\(^{-1}\) | Carbonyl region: 1700-1760 cm\(^{-1}\) | Carbonyl region: 1700-1760 cm\(^{-1}\) | Carbonyl region: 1700-1760 cm\(^{-1}\) |

**Intensity - cellulose region:**

**Intensity - carbonyl region:**

**Figure 13.** False color high-resolution FT-IR micrographs (4 cm\(^{-1}\) spectral resolution with a 0.25 μm\(^2\) theoretical spatial pixel resolution and an optical resolution of close to 1 μm) of (A) Cel-diS-PMMA\textsubscript{Br} modified via the grafting-from approach, (B) Cel-SH\textsubscript{Br} after cleavage of the grafted polymers, and (C) Cel-Az-PMMA\textsubscript{Br} modified via the grafting-to approach, displaying the cellulose region by integration of the C-O vibrations (between 950–1200 cm\(^{-1}\)) and the carbonyl region by integration of the C=O stretching vibration (between 1700–1760 cm\(^{-1}\)). Regions with dark blue color represent low intensity and pink color depicts high intensity regions. The images corresponding to the same sample (e.g. Cel-diS-PMMA\textsubscript{132}-Br) represent the same fiber region (32 × 32 μm).\textsuperscript{115}
4.5 TOWARDS INDUSTRIAL GRAFTING OF CELLULOSE

ARGET ATRP has proven to be an efficient and straightforward approach to employ when grafting cellulose. Moreover, the low amounts of the copper catalyst that is required result in that the free polymer formed in solution is colorless after precipitation, see Figure 14A, without the demand for tedious removal of copper. The grafted cellulose substrates are also visually free from copper traces after thorough washing. To further demonstrate the advantages of ARGET ATRP, with the ambition to enable its applicability in the industry, the polymerization was performed without any deoxygenation and with simple reaction setups. The reactions were performed either in flasks sealed with a septum or in conventional crème jars with screw lids, the latter exemplified in Figure 14B. All the reactants were simply added to the reaction vessel before sealing the system; besides, the vessel was almost completely filled with the reaction mixture to keep the volume of free air low. The polymerizations were performed in anisole or in bulk, where the latter can be preferable form an industrial point of view. The various polymerization systems, employing BiB-functionalized cellulose and EBiB as a sacrificial initiator, are shown in Table 6. The first polymerization (PMMA\textsubscript{208}), performed in anisole, showed that even with the presence of limited amounts of air, ARGET ATRP can be performed in a controlled manner, see Table 6. The exclusion of anisole resulted in a polymer (PMMA\textsubscript{160}) with slightly higher dispersity, but still with retained control ($D_M < 1.3$). When a large excess of AsAc to CuBr\textsubscript{2} was utilized, the polymerization rate increased significantly. The formed PMMA glass (Figure 14B) was difficult to dissolve, resulting in that the conversion could not be trustworthy measured. However, it was possible to run SEC (see Table 6, sample PMMA\textsubscript{Ex}), showing that the reaction was not as well-controlled. The molar mass is higher than the theoretical maximum of 80 300 g/mol, suggesting that the initiator efficiency was poor and that termination \textit{via} radical coupling may have occurred (see Figure 6), also giving rise to a broad dispersity. However, a shorter reaction time might reduce the termination reactions, establishing better control over the system.

In addition, to facilitate the solubility of the CuBr\textsubscript{2} and AsAc when performing the reaction in bulk, a small amount of H\textsubscript{2}O was added; thus, the reaction rate was greatly increased, see Table 6 for the reaction times and conversions. The addition of 0.1 mL water resulted in a conversion of 67 % after only 2.2 h and a broad $D_M$ of 2.42. When the water amount was decreased to 0.05 mL, no reaction was observed after 2.2 h, but after 15 h the conversion was as high as 89 %.
Despite a higher conversion, the reaction resulted in a polymer with lower $D_M$ (< 2.0), suggesting a slightly more controlled reaction with lower amount of H$_2$O.

![Image](image_url)

**Figure 14.** The image of A) precipitated PMMA after ARGET ATRP without copper removal and B) ARGET ATRP polymerization performed in a crème jar.

**Table 6.** ARGET ATRP systems performed without deoxygenation.

<table>
<thead>
<tr>
<th>Sample $^a$</th>
<th>System $^b$</th>
<th>[AsAc]/[CuBr$_2$]</th>
<th>Time (h)</th>
<th>p $^c$ (%)</th>
<th>$M_{\text{theo}}$ $^d$ (g/mol)</th>
<th>$M_\text{ef}$ (g/mol)</th>
<th>$D_M$ $^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA$_{208}$ + cellulose</td>
<td>20 g MMA</td>
<td>8</td>
<td>26</td>
<td>26</td>
<td>21 000</td>
<td>27 900</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>8 ml Anisole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25 mL Flask</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMMA$_{160}$ + cellulose</td>
<td>25 g MMA</td>
<td>10</td>
<td>22</td>
<td>20</td>
<td>16 200</td>
<td>23 800</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>Bulk</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25 mL Flask</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMMA$_{Ex}$ + cellulose</td>
<td>25 g MMA</td>
<td>80</td>
<td>22</td>
<td>-</td>
<td>-</td>
<td>137 800</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>Bulk</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 mL Crème Jar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMMA$_{536}$ no cellulose</td>
<td>25 g MMA</td>
<td>10</td>
<td>2.2 h</td>
<td>67</td>
<td>53 900</td>
<td>88 000</td>
<td>2.42</td>
</tr>
<tr>
<td></td>
<td>0.1 mL H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25 ml Flask</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMMA$_{712}$ + cellulose</td>
<td>25 g MMA</td>
<td>10</td>
<td>15 h</td>
<td>89</td>
<td>71 500</td>
<td>105 000</td>
<td>1.93</td>
</tr>
<tr>
<td></td>
<td>0.05 μL H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 mL Crème Jar</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

$^a$ PMMA$_x$ where $x$ represents the DP calculated from the conversion obtained from $^1$H NMR. $^b$ System: [MMA]:[EBiB]:[Cu(II)Br$_2$]:[PMDETA] = 800:1:0.1:1, 40 °C. $^c$ Conversion calculated from $^1$H NMR. $^d$ $M_{\text{theo}} = \text{DP}_{\text{target}} \times p \times M_{\text{MMA}} + M_{\text{EBiB}}$ based on $^1$H NMR conversion. $^e$ Obtained from DMF-SEC (PMMA standards).
Results and Discussion

FT-IR measurements verified the successful grafting reaction and showed that the polymeric amount of PMMA_{208} and PMMA_{160} on filter paper was very similar, whereas it was much larger for PMMA_{712} and even larger for PMMA_{Ex}. For PMMA_{536} with the higher water amount, no cellulose substrate was added.

To conclude, further developments to improve the straightforward systems need to be conducted, however, the first trial that were performed suggested that ARGET ATRP can indeed be an interesting method to employ industrially. Noteworthy, from an industrial point of view, simple and straightforward systems can be more important to achieve than well-controlled reactions.
5. CONCLUSIONS

To expand the application area of cellulose and to meet the demand for new environmentally friendly materials, modification of cellulose is a prerequisite. The focus of this study has therefore been to achieve valid fundamental knowledge about the cellulose modification via well-controlled grafting processes. Moreover, experiments have been conducted with the aim to facilitate the employment of ARGET ATRP industrially.

Cellulose has successfully been grafted via surface-initiated ARGET ATRP of various monomers: MMA, St, and GMA, confirmed by FT-IR. CA measurements suggested that the length of the polymer grafts does not significantly affect the value of the contact angles, and even short graft lengths greatly enhance the hydrophobicity of cellulose.

High-resolution FT-IRM imaging was demonstrated to be a very useful method for studying the spatial distribution of the polymer content on the cellulose substrate. The polymer content increased with increasing graft length, and the distribution of the polymer on the cellulose fiber was shown to be rather homogenous, even though some smaller areas contained more polymer.

An initiator with a cleavable disulfide linker was successfully synthesized and immobilized onto cellulose, rendering the ensuing cleavage of the polymer grafts possible. The molar masses and dispersities of the grafts were comparable to values of the free polymers formed in parallel to the grafting, suggesting that the polymerization from the surface and in the solution proceeded with similar kinetics, confirming that the grafts can be tailored by utilizing a sacrificial initiator. Moreover, FE-SEM results confirmed that the cleavage was accomplished in a non-destructive manner, keeping the cellulose substrate intact, rendering the characterization of the initiator content possible by employing Ellman’s reagent. Thus, the initiator content (in μmol/g cellulose) on filter paper
as well as on MCC was efficiently assessed, also demonstrating that the immobilization of the initiator to the surface is a fast reaction. The number of active OH-groups of water-swelled cellulose was also determined by solid-state NMR.

The two grafting techniques, grafting-from via ARGET ATRP and grafting-to via CuAAC, were systematically compared by ensuring that the graft lengths were in the same range for the two methods. The successful grafting via ARGET ATRP and CuACC was confirmed by XPS and FT-IRM analyses. Under the selected condition, it was verified that the grafting-from technique is superior to the grafting-to approach with respect to controlling the polymeric amount on the surface. At the same time, it is important to note that the present results should not be generalized to all grafting-to vs. grafting-from comparisons.

ARGET ATRP has the advantages of requiring only small amounts of the copper catalyst and no deoxygenation step; yet, providing for well-controlled reactions. The straightforward system was performed with reduced requirements of advanced reactions vessels and of organic solvents. Furthermore, the reaction rate was increased by the addition of a small amount of water to the bulk system of the water-insoluble monomer, aiding the dissolution of the copper complex. These advantages can render ARGET ATRP to an industrially acceptable method.
6. FUTURE WORK

Grafting of polymers has the potential to be an applicable method for the modification of cellulose, with the purpose of utilizing cellulose in a wider range of products, including more advanced applications. To facilitate the industrial scale-up, certain improvements of the reaction conditions can be of importance, such as the immobilization of reactive sites prior to the grafting. A milder immobilization reaction, compared to the employment of an acid halide, that preferable can be performed in water is something to strive for and to investigate more thoroughly, as well as the ARGET ATRP grafting system, where more trials and fine-tuning need to be performed.

Modified cellulose is, as discussed, a complicated substrate to characterize due to the surface roughness. Therefore, it could be significant to perform the grafting and cleavage of polymer grafts via the disulfide linker from well-studied, less complex, and flat substrates like silicon wafers. Moreover, the comparative study of the grafting-from and grafting-to methods could also be interesting to investigate when employing these types of surfaces.

The versatility of surface modification can be explored by introducing more specific functionalities to the cellulose substrates, aiming for the employment of cellulose in more advanced applications, such as sensors and biomedical applications.

It is also worth to investigate the production of (bio-)composite materials with modified and tailored cellulose fibers as fillers, aiming towards large-scale production of better materials containing less petroleum-based components.
7. ACKNOWLEDGEMENTS

First of all, I want to express my sincere gratitude to my supervisor Prof. Eva Malmström for accepting me as her Ph.D. student. Thank you for your endless support and for always taking your time despite your fully-booked calendar. Your passion about science has always inspired me and helped me. I also appreciate your friendship, the nice atmosphere you create in “Ympgruppen”, and all the pleasant summer dinners. My second supervisor Ass. Prof. Anna Carlmark Malkoch is sincerely acknowledged for all the help and encourage she has given me throughout the years. Your positive energy and friendliness can brighten up a bad day in the lab. Thanks also for sharing the hotel room with me in Denver and for laughing at all the crèmes that I had brought with me. Dr. Emma Östmark is also greatly thanked for her supervision of my first years and for all the help after that. You are a genuinely friendly person and devoted to whatever you are working with. Thanks also for the interpretation of the “NMR forest” of isosorbide. Dr. Linda Fogelström is acknowledged for all her supervision, ever since I was a master student. You have really taught me much, especially how reports shall be written, and corrected! You have been a significant support during my time as a Ph.D. student (especially the last weeks). Thanks for your sweet friendship, your thoughtfulness, and for always being in such a good mood.

Prof. Anders Hult is thanked for creating the great working atmosphere in “Ytgruppen” and for understanding the importance of a high EQ vs. a high IQ. Prof. Mats Johansson is acknowledged for scientific discussions and for his enthusiasm about winning over me in Wordfeud. Ass. Prof. Michael Malkoch is thanked for your great knowledge about organic chemistry, and the coffee machine.

Wilhelm Beckers Jubileumsfond and the Swedish Research Council (Vetenskapsrådet) are greatly acknowledged for financial support. The VINN Excellence Centre BiMaC Innovation is thanked for contributing to scientific knowledge and discussions, allowing for the opportunity to find new collaborations. The Karlsruhe House of Young Scientists (KHYS) and KTH travel grants are thanked for financing my KIT visit. KTH Travel grants are also acknowledged for financing conference trips.

Prof. Christopher Barner-Kowollik is acknowledged for letting me work in his group, for all the support and discussions, and for the very fruitful collaborations. My co-authors and friends Anja, Thomas, and Vanessa are greatly thanked for their effort and friendliness. I would also like to acknowledge Michael (and Ronja), Corinna, Elise, Kim, Jan, Bernhard, Lukas, Natalie, Andrew, Guillaume, Christiane, Elena, Alex H, Alex Q, Anna, Kristina,
Acknowledgements

Nicolas, Mathias, Özcan, and all the other people in the Macroarc group for making my KA visit not only scientifically productive but also so fabulous and fun. Jawohl!

Assoc. Prof. Tomas Larsson, at Innventia and WWSC, is sincerely thanked for help with solid-state NMR measurements and valuable discussions.

All former and present friends and members of “Ytgruppen” are thanked for creating a great team spirit and supportive climate combined with a lot of fun at, and after, work. I will really miss this amazing working place! Thanks to Linn for being an extraordinary friend, for the songwriting, and for loving “valleken” as much as me; Sara O. for your dear friendship, for you-know-what, and for our cozy tapas nights; Yvonne for your kindness, all the laughter, and for turning me into a true “Friluftsnörd”; Jan for being sweeter than sugar, for how you express your love, and for all “gosigos”; Robert for all the hugging, your funny stories, and for being truly awesome; Camilla for being so sweet and friendly and for all the fun ppt-presentations; Pontus for everything you trusted me with (SEC, forskarskolan…), for being sexy-smart, and for our great future plans; Hanna Lö. for proving that you can be both blond and smart and for all the dancing in the lab, Maribel for being so lovely and for the Swedish-Spanish word-exchange that I will not mention here; Lina E. for having the guts of following your heart and for the great time we had; Markus for our raw but tender humor, our nice chats, and for your special kicking “skills”; Kim for our Pershagen-connection, for appreciating my modesty, and for flexing your twins, Christian for being my excellent master student, for talking more and faster than me, and for your social skills; Emma L. for all the time we spent with the SEC and for eating, and enjoying, the white part of the clementine; Carl for the close-to-death-by-laughter experience in the elevator and for all the great recipes; Assya for being a sweet, funny, and very “wood” girl, and for letting me know that you actually can be angry sometimes; Alireza for being a great roommate and for being – the thoughtful – Alibubu; Ting for literally flushing down my problems in the toilet and for saying so many funny things; Martin for coming back to KTH and for being positive and happy all the time; Kristina for your smiling and for understanding the fun about finding a horse in the storage room for bikes; Marie for being smart and for loving hearing me say “sacre bleu”; Emelie for being neat and for taking over my legendary fume hood; Mauro for poring sugar on my already sweet cinnamon buns; Hui for lending me her fume hood the last weeks; Daniel for introducing me to the wonderful world of ATRP; Pelle for the nice collaboration; Helena – almost a member of Ytgruppen – for helping me with the calibration curves; Stacy for helping me with Ellman’s regent; Petra for being so nice, calm, and cool; Sara K. for her occasionally but very pleasant visits; Niklas for your characteristic click sounds; Mange for being Mange; Kattis for the nicely coated metal roof you left behind; Josefina for paving the way for my project; Susana for joining the hiking; Oliver for helping me with computer issues; Carmen for you enthusiasm, and Eric for the nice Spanish breakfast. Former members and diploma and project workers are also thanked, especially, Amanda, Anna A., Axel, Chung, Dahlia, Hanna L., Jocke, Jesper, and Tobias, for contributing to the great atmosphere. The former and present PF-people Bella, Kristin, Jonas, and Shams are thanked for your important and pleasant presence here.

All seniors, employees, and friends at the department of Fiber and Polymer Technology are acknowledged, especially Prof. Lars W., Assoc. Prof. Anna F. W., Inger, Inga, Mia,
Acknowledgements


Många tack går även till mina underbara vänner ute i den stora vida världen för att ni alltid finns där för mig. Ålskade Viveka, vad vore livet utan våra gemylta promenader, allt tedrickande och alla loppisfynd?! Dötrist! Lisa, min käraste partypingla, tack för allt roligt och mys vi haft och för att du sådde fröet till min kärlek till havet! Elli – “mammas lilla hjärtegull” – vi har upplevt många studier i livet tillsammans, tack för att du alltid funnits vid min sida i vått och torrt. Lina, min barndomsvän, du har betytt mycket under min uppväxt och det gör du fortfarande, tack för allt! Frida, tack för att vi kan dela alla fantastiska och roliga minnen från en av de bästa upplevelserna jag haft. Åsa, tack för att du förgyllde mina första 4.5 år på KTH med alla bra samarbeten och allt kul. Söitis-Tomas, tack bl.a. för allt mys med ”koppis” och ”arkis”. Tack goaste papi Henrik och favoritbarnet Adriana för allt roligt vi haft under och efter forskarsholan. Tack även till ej nämnnda men icke glömda vänner!


Sist men inte minst, jag har mycket att tacka forskarsholan för… Rickard, jag är så glad att vi träffades. Du gör mig så glad och lycklig!!! Tack för att du är så underbar på alla sätt och vis, för alla skratt, för att du kan få mig att koppla av (vilket är en stor bedrift) samt för allt kul som du vill göra ihop med mig! Någon gång ska vara den första, så varför inte här… Jag älskar dig!!!
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Figure adopted from the homepage of The Matyjaszewski Polymer Group: http://www.cmu.edu/maty/crp/feature-development-crp/features.html (accessed 2012-11-09).


