

Toward Industrial Grafting of Cellulosic Substrates via ARGET ATRP

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ABSTRACT: For the past decade, the interest in controlled grafting of cellulose has increased immensely. Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP) has attracted the most interest; however, the sensitivity of this system has so far hindered its utilization in industry. In this study, filter paper, dissolving pulp, bleached and unbleached Kraft-pulp, and chemi-thermomechanical pulp papers were grafted with methyl methacrylate, employing activators regenerated by electron transfer (ARGET) ATRP. The reactions were performed in bulk or with small amounts of aqueous solutions, with no deoxygenation performed. To further demonstrate the robustness of this method towards simpler and more industry-friendly processes, the polymerizations were conducted in glass jars with screw lids. The possibility of recycling the reaction solution was also explored. We believe this thorough study to be an important step towards industrializing the “grafting-from” concept, and the results herein can most likely be extended to other surfaces and monomers. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41434.

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INTRODUCTION

Cellulose is one of the most important natural resources in the world, providing a broad range of important products such as construction material (e.g., wood), paper, cardboards, and hygiene articles, to mention a few.¹ However, the utilization of cellulose could be extended far beyond traditional uses through the modification of the fiber surface with polymer grafts.^{2–4} If hydrophobic polymers are grafted from the surface of the fibers, it has been shown that this compatibilizes the fibers, enabling them to be utilized as reinforcing agent in composite materials with a polymeric matrix.^{5–7} Grafting can be performed either via grafting-from or via grafting-to, where grafting-from has proved to be a superior method in terms of grafting density.^{8,9} Grafting from cellulose via free radical (co)-polymerization can be performed by employing various redox-systems, typically forming active radicals on the cellulosic backbone, which subsequently react with suitable vinyl monomers.^{4,10} Although this approach can be sufficient, it suffers from drawbacks such as the need for inert atmosphere, as well as the formation of unbound polymers, which tends to be the predominating reaction in these systems. Furthermore, the molar mass and distribution of the polymer brushes cannot be controlled or predicted, nor can more complex architectures, such as block copolymers, be obtained.¹⁰ Hence, to achieve a more controlled

grafting reaction, where the molar mass more easily can be predetermined and controlled, a reversible deactivation radical polymerization (RDRP) is preferred.¹¹ RDRP techniques provide control over molar mass, molar mass dispersity (\mathcal{D}_M), and preserved end-group functionality. One of the most common RDRP methods is atom transfer radical polymerization (ATRP).^{12–15} Previous work by our group has shown that surface-initiated ATRP (SI-ATRP) is a versatile method to control the “grafting-from” reaction on cellulose fibers.^{16–18} However, from an industrial point of view, SI-ATRP is not particularly applicable since it is a sensitive system requiring deoxygenation procedures. Furthermore, the amount of catalyst employed, which often is a Cu(I) halide, can be relatively high. Another drawback is that the catalyst requires removal from the end-product since it is toxic, and the removal, or perhaps the recycling, will be both time- and cost-consuming.^{19,20} With the intention to lower the amount of Cu-salts, Matyjaszewski and coworkers developed a refined version of ATRP called activators regenerated by electron transfer (ARGET) ATRP, where a reducing agent is employed to reduce Cu(II) into Cu(I) *in situ*, implicating that that just a few ppm of Cu(II) is required for the reaction.²⁰ Effectively, the ARGET ATRP system becomes less sensitive since the added Cu(II) salt is in the higher oxidation state. An even greater advantage is that the reducing agent

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employed can also scavenge oxygen, rendering it possible to run the reaction in limited amounts of air.^{20,21} Our foregoing studies have shown that cellulose fibers can be efficiently grafted with various monomers using ARGET ATRP.²² In previous studies by Matyjaszewski and coworkers, ARGET ATRP was performed in aqueous solution using the environment-friendly ascorbic acid as reducing agent.²³ It was shown that by the addition of NaCl to the reaction, better control was achieved. Furthermore, the same group has shown that surfaces can be grafted straightforwardly by ARGET ATRP in the presence of a small amount of oxygen.²⁴

Inspired by these results, the aim of this study was to develop a system where cellulose surfaces could be grafted with hydrophobic polymers in a controlled manner, without using the stringent conditions often employed in the laboratory, but rather reaction conditions that are more applicable in industry, that is, low catalyst amounts, no deoxygenation, either in bulk or in aqueous solutions and with limited washing steps. Herein, cellulose in the form of filter paper, dissolving pulp, bleached and unbleached Kraft-pulp and chemi-thermomechanical pulp (CTMP) papers were grafted with methyl methacrylate (MMA) by ARGET ATRP, in bulk or in bulk with small amount of aqueous solutions (deionized water or NaCl-solutions), with no deoxygenation performed. To demonstrate the robustness of this method towards simpler and more industry-friendly reaction conditions and equipment's, the polymerizations were conducted in glass jars with screw lids, employing different reaction temperatures and times. The grafting reactions were performed with and without the addition of a free, sacrificial initiator. Furthermore, the possibility of recycling of the reaction solution was also explored. We believe this thorough study to be an important step toward industrializing the "grafting-from" concept, and the results herein can most probably be extended to other surfaces and monomers.

EXPERIMENTAL

Materials

α -Bromoisobutyryl bromide (BiB, 98%), ethyl 2-bromoisobutyrate (EBiB, 98%), 4-(dimethylamino)pyridine (DMAP, 99%), copper(II) bromide (Cu(II)Br₂, 99%), N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA, 99%), and Whatman 1 filter paper were purchased from Aldrich. Sodium ascorbate (NaAsc) was purchased from Sigma. Ascorbic acid (AsAc, 99%) was purchased from Fluka. Triethylamine (TEA) was purchased from Merck. The monomer, MMA (99%, Aldrich), was passed through a column of neutral aluminum oxide prior to use to remove the inhibitor.

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. Size exclusion chromatography were performed on a TOSOH EcoSEC HLC-8320GPC system equipped with an EcoSEC RI detector and three columns (PSS PFG 5 μ m; Microguard, 100 \AA , and 300 \AA ; MW resolving range: 100–300,000 g mol⁻¹) from PSS GmbH, using DMF (0.2 mL min⁻¹) with 0.01M LiBr as the mobile phase at 50°C. 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.²⁵

Fourier transform infrared spectroscopy (FT-IR) was collected using a Perkin-Elmer Spectrum 2000 FT-IR equipped with a MKII Golden Gate, single reflection ATR System from Specac, (London, UK). The ATR-crystal used was a MKII heated Diamond 45° ATR Top Plate. For each spectrum, 32 scans were recorded.

Contact angle (CA) 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 μ L droplets of deionized water. The water CAs were determined using the CAM software. Prior to the measurements, the substrates were conditioned at 50% relative humidity and 23°C for 3 h.

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 by a carbon coater (Cressington 108 carbon/A) and subsequently coated 2 \times 4 nm by a gold/palladium sputter coater (Cressington 208HR).

Paper Sheet Manufacturing

Wood fibers (3 g) of dissolving pulp, bleached and unbleached Kraft pulp, and bleached and unbleached CTMP were used to form paper sheets. The pulps were dispersed in deionized water and sheets were prepared using a Rapid Köthen sheet-forming device (PTI, Vorchdorf, Austria). The sheets were dried at 93°C and 0.95 bars for 12 min.

Immobilization of BiB onto Cellulose Substrates

Whatman no. 1 filter papers, dissolving pulp, bleached and unbleached Kraft-pulp, and CTMP papers (2 \times 3 cm) were washed with ethanol and subsequently dried in an oven at 100°C for 1 h, prior to the immobilization of the initiator. The available hydroxyl groups on the surface were converted into ARGET ATRP initiators by immersing five substrates in a solution containing BiB (126 mg, 0.550 mmol), TEA (61.2 mg, 0.605 mmol), and a catalytic amount of DMAP in tetrahydrofuran (THF, 30 ml). The reaction was allowed to proceed on a shaking device for 8 h at ambient temperature. Thereafter, the papers were thoroughly washed in THF and ethanol, and finally dried in a vacuum oven at 50°C.

Grafting of BiB-Functionalized Cellulose via ARGET ATRP in Bulk

The general grafting procedure was performed by immersing the initiator-functionalized paper into a 30 mL glass jar containing MMA (25 g, 0.25 mol), sacrificial initiator EBiB (60.9 mg, 0.31 mmol), Cu(II)Br₂ (7.0 mg, 31.2 μ mol), PMDETA (54.1 mg, 0.31 mmol), and AsAc (55.0 mg, 0.31 mmol), targeting a final DP of 800. DP_{targets} of 200 and 1200 were also used. The glass jar was sealed with a screw lid and placed in a thermostated oil bath at 40 or 80°C. For some experiments, a small amount of deionized water (50.0–100 μ L) or a NaCl-solution (aq) of various concentrations and volumes

Table I. Reaction Conditions and SEC Results from the Free-Forming Polymer for the Grafting of MMA ([MMA] : [EBiB] : [PMDETA] : [Cu(II)] : [AsAs] = [800] : [1] : [1] : [0.1] : [1] in bulk) from Cellulose at Various Temperatures and Times

Sample ^a	Cellulose substrate ^b	T (°C)	Time (h)	M _n ^d (g/mol)	Đ _M ^d
P-40C-10h	C-40C-10h	40	10	–	–
P-40C-15h	C-40C-15h	40	15	56,900	1.34
P-60C-8h	C-60C-8h	60	8	–	–
P-80C-2h	C-80C-2h	80	2	28,000	1.17
P-80C-3h-1	C-80C-3h-1	80	3	46,600	1.19
P-80C-3h-2	C-80C-3h-2	80	3	40,200	1.21
P-80C-3h-Blank	C-80C-3h-Blank	80	3	49,900	1.22
P-80C-8h-DP1200 ^c	C-80C-3h-DP1200	80	8	107,400	1.67

^aP-xC-yh, where P represent free polymer, x the reaction temperature, and y the reaction time.

^bC-xC-yh.

^cDP_{target} was 1200.

^dDetermined by DMF-SEC.

(10.0–4000 mM and 75.0–100 μL, respectively) were added before closing the system. For these experiments, the temperature was set to 40°C. The grafting was also performed without the addition of the sacrificial initiator, at both 40 and 80°C, and with water addition. The grafting reaction was terminated by exposing the solution to air after a predetermined time. The grafted filter paper was washed in dichloromethane (DCM) combined with ultrasonication, and also in THF, THF : water (50 : 50), and ethanol. For the experiments without sacrificial initiator, the washing procedure was performed without DCM. The free polymer was precipitated in cold methanol and thereafter dried at ambient temperature and denoted in the form of P-xC-yh, as explained in Table I. The grafted papers are denoted in the form of C-xC-yh.

Grafting of BiB-Functionalized Cellulose by Recycling the Reaction Mixture

The polymerization was performed from an initiator-functionalized filter paper at 80°C for 8 h without the addition of a sacrificial initiator aiming for a DP_{target} of 800, as described above. The grafting reaction was terminated by opening the screw lid and removing the grafted filter paper (denoted C-No I-80C-8h-Rec.first), which was replaced by another initiator-functionalized filter paper combined with the addition of 55 mg of AsAc. This reaction was allowed to proceed for 16 h, resulting in substrate C-No I-80 C-16h-Rec.second. The papers were washed as described above.

RESULTS AND DISCUSSION

Cellulose substrates were grafted employing ARGET ATRP, attempting to demonstrate the versatility of this method, and its possible applicability in industry. No deoxygenation was performed prior to the polymerizations and no organic solvents were used which is beneficial both from an environmental- as well as economical aspect. The grafting reactions were conducted in glass jars into which all the reagents were transferred and the jar was sealed with a screw lid. This set-up was chosen to investigate a simple reaction set-up, thus eliminating the need for common laboratory equipment, such as round-bottom

flasks and rubber septa which may not be applicable in industry. Several polymerizations of MMA were performed and the parameters that were varied were: polymerization temperature, time, amount added water or NaCl-solution, and the utilization of a sacrificial initiator. The molar ratios generally employed were: [EBiB] : [PMDETA] : [Cu(II)] : [AsAs] = [1] : [1] : [0.1] : [1]. The targeted DP, that is, the ratio between the monomer and sacrificial initiator ([MMA] : [EBiB]), was generally 800, but DP_{targets} of 200 or 1200 were also investigated. Furthermore, efforts were made to adapt the washing of grafted papers to more industry-friendly processes, utilizing a procedure which was fast and demanded little energy consumption. Hence, no Soxhlet extractions were performed on the grafted papers, just simple washing with few repetitive steps and ultrasonication.

Grafting of Cellulose at Different Temperatures

The initial investigated polymerization temperature was 40°C which resulted in a slow reaction where virtually no polymer had formed after 10 h. However, after 15 h the viscosity had increased significantly, indicating that polymer had formed, Table I, sample P-40C-15h. These results suggest that the induction period—when the reducing agent is consuming oxygen as well as reducing Cu(II) into Cu(I)—was long, but once the reaction started it was relatively fast and after <5 h the molar mass was almost 60,000 g/mol according to SEC. The resulting molar mass was higher than the targeted one, most likely due to low initiator efficiency. The extended induction period is probably due to low solubility of the reducing agent as well as of the catalyst complex, since no solvent was used.

Prolonged reaction times are not desirable for an industrial process, wherefore the maximum reaction time was set to 8 h in this study. Thus, grafting at 40°C for 15 h is not feasible. The temperature was therefore increased to 60°C in an attempt to increase the rate of polymerization; yet, no polymer was formed after 8 h. However, when the temperature was increased to 80°C, the induction time was <2 hours and after 3 h a viscous liquid was formed (Table I, P-80C-2h or –3h). The increased polymerization rate at 80°C is probably not only attributed to the fact that the propagation rate constant, *k_p*, is increased, but

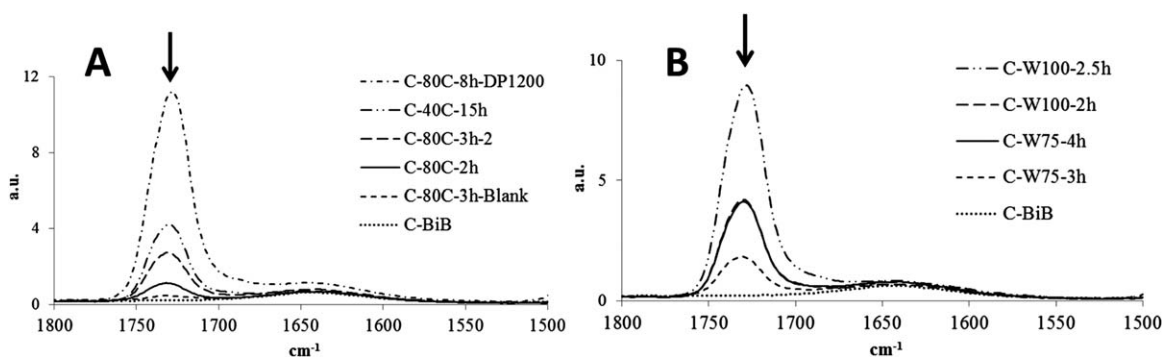


Figure 1. A: FT-IR spectra of initiator-functionalized filter paper, a native filter paper subjected to a polymerization of MMA at 80°C for 3 h (blank), and PMMA-grafted filter paper at 40 or 80°C for different reaction times. Arrow indicating the signal corresponding to the carbonyl group in PMMA. B: FT-IR spectra of initiator-functionalized filter paper and PMMA-grafted filter paper with the addition of 75.0 or 100 μ L of water to the reaction performed at 40°C for different reaction times.

also due to increased solubility of the ascorbic acid as well as the catalyst complex, significantly decreasing the induction period of ARGET ATRP. The polymerizations were shown to be well-controlled (Table I, $D_M < 1.23$), especially considering that the reaction was performed in bulk without degassing. All of the reactions run for 3 h have molar masses in the same range, signifying that the reaction at 80°C is reproducible.

With the aim to achieve grafts of high molar mass, the grafting at 80°C was performed with a DP_{target} of 1200 and for 8 h. As seen in Table I, sample P-80C-8h-DP1200, a high molar mass and a rather broad D_M was obtained, but considering that the reaction was performed without solvent and to a high conversion, a broader D_M is, however, acceptable.

In this study, a blank reference was prepared in which native filter paper was immersed into a polymerization solution at 80°C for 3 h (Table I) and subsequently washed in the same manner as the grafted surfaces. This reference was performed in order to investigate if any PMMA was physisorbed to the cellulose surface under the adapted polymerization and washing conditions.

The PMMA-modified substrates grafted at 40 and 80°C, an initiator-functionalized paper (C-BiB), and the blank reference (C-80h-3h-blank) were characterized with FT-IR, see Figure 1(A), where the arrow shows the peaks corresponding to the stretching of the carbonyl group in the PMMA side chain. As cellulose contains no carbonyl peak at 1730 cm^{-1} , a peak at this wavenumber originates from the stretching of the carbonyl group in PMMA. The immobilization of the initiator cannot be detected by FT-IR since the amount is below the detection limit for this method. For the blank substrate, no polymer should be detected since covalent grafting cannot occur from the surface; nonetheless, as can be seen in Figure 1(A), a minor amount of free polymer have been physically attached to the surface as a small carbonyl peak is present in this sample. Effectively, all of the grafted samples most probably contain small amounts of physisorbed polymer; however, the aim of the present study was to investigate industrially applicable conditions, wherefore the washing procedures were not altered herein as the complete removal of physisorbed polymer most likely would require

tedious, time and energy-consuming, Soxhlet extractions. Since the amount of physisorbed polymer appears to be very small, this was considered a minor issue in this study. For the grafted samples, a clear trend with increasing polymer content with increasing molar mass of the free polymer can be seen. For sample C-80C-3h-1, the absorbance was unreasonably high, in the proximity of the peak for C-80C-8h-DP1200. The reason for this could be due to insufficient washing of this sample, implying large amounts of physically attached polymers, and the FTIR spectrum was therefore excluded from Figure 1(A).

CA measurements were performed to investigate the hydrophobicity of the modified cellulose surfaces, see Supporting Information Table S1 in ESI. As shown in previous studies, the grafting of PMMA clearly has a large impact on the hydrophobicity, and the CA increases for all the grafted samples. In accordance with the FT-IR results, the CA measurements confirm that the blank reference sample contains small amounts of physically adsorbed polymer on the surface; the water droplet is not instantly absorbed as it would be on pure filter paper and a low CA can be measured after 10 s. After 22 s, the droplet is completely absorbed, suggesting the presence of only small polymeric residues. For the other substrates, the droplets were stable over a long period of time (several minutes).

In Figure 2, the FE-SEM images of grafted cellulose surfaces are shown for cellulose samples C-80C-2h (B1 and B2) and C-80C-8h-DP1200 (C1 and C2), which are compared with neat filter paper (A1 and A2) at two magnifications. Similar to previous studies,^{3,22} the grafting with PMMA covers the surface of filter paper, as the fibrillar structure of cellulose becomes less prominent in the more grafted samples. In C1 and C2, the filter paper with the longest grafts, the surface of the fibrils are clearly covered by the PMMA, showing the efficiency of the grafting reaction also under these reaction conditions.

Grafting of Cellulose with Addition of Water

Elevated reaction temperatures are generally not an industrial problem; nevertheless, an alternative approach to increasing the reaction rate was investigated. ATRP reactions performed in aqueous media are characterized by high reactivity combined with loss of control, since the catalyst complex is highly soluble

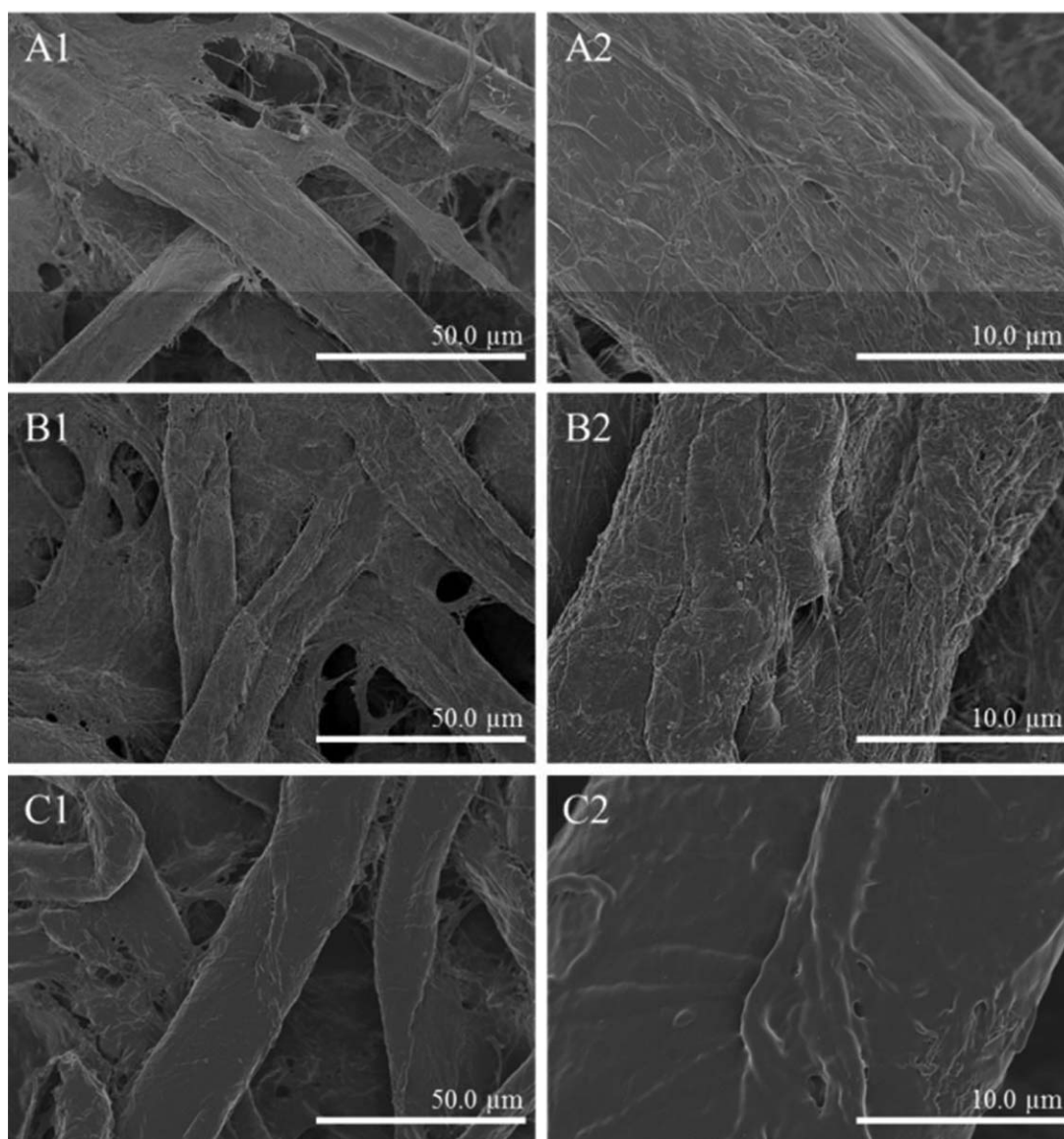


Figure 2. SEM pictures of the grafted cellulose: (A) Pure filter paper, (B) Filter paper grafted with PMMA at 80°C for 2 h with a DP_{target} of 800 and (C) Filter paper grafted with PMMA at 80°C for 8 h DP_{target} of 1200.

in polar media.^{26–28} Normally, water-soluble monomers are polymerized in such media, but since the aim is to make cellulose more hydrophobic, this type of monomer is not of interest in this study. The strategy was, therefore, to only add a small amount of water (0.3–0.4 wt % to monomer) to increase the solubility of the catalyst complex. Furthermore, the solubility of ascorbic acid is also increased, which should decrease the induction period.

To the knowledge of the authors, there are no previous reports of ARGET ATRP performed with water addition in this manner. As can be seen from our results, the reaction rate at 40°C greatly increased upon addition of only 100 μL deionized water to 25 g MMA, Table II. After 2 h, the reaction mixture had turned into a viscous liquid and after additional 30 min, a hard glass of PMMA was formed, suggesting that a high molar mass polymer could form rapidly. It is likely, however, that this reac-

tion window is too narrow if aiming for a specific molar mass, due to the apparent loss in control as can be observed by the increased D_M . Nonetheless, no polymer was formed during the first hour, implying that there still exists an induction period, during which oxygen is consumed.

Since the addition of only 100 μL of water significantly increased the reaction rate of the bulk reaction, the amount of water was decreased to 75 μL with the intention to obtain a better control over the reaction. Accordingly, the reaction time was increased to 3 and 4 h without forming a PMMA glass and the resulting dispersities for these reactions are below 1.5 (Table II), suggesting reasonably controlled reactions. However, when performing duplicates of the reaction at 3 h (not included in Table II), the reaction was uncontrolled and the molar mass became as high as 84,100 g/mol and the D_M 1.82, suggesting lost control. Attempts with addition of smaller volumes of water (10.0

Table II. Reaction Conditions and SEC Results from the Free forming Polymer for the Grafting of MMA ([MMA] : [EBiB] : [PMDETA] : [Cu(II)] : [AsAs] = [800] : [1] : [1] : [0.1] : [1]) from Cellulose at 40°C, with Small Amounts of Added Water

Sample ^a	Cellulose substrate	Time (h)	H ₂ O ^b (μL)	M _n ^c (g/mol)	Đ _M ^c
P-W100-1h	C-W100-1h	1	100	–	–
P-W100-2h	C-W100-2h	2	100	45,800	1.41
P-W100-2.5h	CP-W100-2.5h	2.5	100	73,000	1.94
P-W75-3h	C-W75-3h	3	75.0	47,400	1.47
P-W75-4h	C-W75-4h	4	75.0	57,600	1.44
P-W50-8h	C-W50-8h	8	50.0	–	–

^aP-Wx-yh, where P represents free polymer, W represents the presence of water, x the volume of added water, and y the reaction time.

^bAdded to 25.2 ml MMA mixture.

^cDetermined by DMF-SEC.

and 50.0 μL) were performed, but no polymerization had occurred after 8 h.

The grafted substrates were characterized with FT-IR, see Figure 1(B), and as for the grafted filter papers in Figure 1(A), the same trend with increasing amount of polymer on the substrate with increasing molar mass of the free polymer can be observed. The contact angles of the grafted substrates ranged from 107 to 115° and were all stable (Supporting Information Table S2 in the ESI).

Grafting of Cellulose with Addition of NaCl-Solution (aq)

The addition of water significantly increased the reaction rate at 40°C, but the reaction became less controlled. To circumvent this drawback, we also attempted the use of a small amount of NaCl-solution as an excess of chloride ions can stimulate the reformation of the deactivator.²³ Furthermore, the carbon-chlorine bond is more hydrolytically stable, and the chlorine chain-end is less reactive compared to the bromine-capped polymer. The concentrations of NaCl employed were 100, 400, and 4000 mM, and 75.0 or 100 μL of these solutions were utilized, Table III. The amount of Cu(II) employed in the polymerizations was 31.5 μmol, and since the molar amount of chlorine do not exceed this for the first four reactions in Table III, not all the bromines will be replaced, resulting in differences in reactivity of the catalyst complex. Consequently, the molar mass distribution becomes larger for the lower amounts of NaCl. Furthermore, for the lower amounts of chlorine atoms in the solution, the reformation of deactivators is probably not as pronounced as for the higher NaCl concentrations (> 100 mM), also leading to a poorer control over the reaction. For the concentration of 100 mM, the dispersity was lower for the added volume of 75.0 μL compared with 100 μL, showing that the volume of the NaCl-solution, that is, the amount of water, has a larger impact on Đ_M than the molar amount of NaCl (7.50 compared with 10.0 μmol) for low concentrations. Furthermore, the same condition as for P-Cl10-W100 was employed except that the CuBr₂ catalyst was replaced with CuCl₂, ensuring that all activators carry chlorine atoms, Table III, sample P-Cl10-W100-CuCl₂-3h. Owing to this, the control over the reaction was greatly enhanced; the molar mass was lowered from 66,700 to 41,700 g/mol and the dispersity from

1.67 to 1.30. Additionally, CuCl₂ was employed in combination with an increased concentration of the NaCl-solution—from 100 to 400 mM—but with a decreased volume to 75 μL, resulting in higher amount of chlorine chain ends (Table III, sample P-Cl30-W75-CuCl₂-3h). Consequently, the reaction rate was decreased, but no impact on the dispersity could be observed. Nonetheless, better control was achieved when performing the reaction at 80°C without any addition of water, but in certain cases, it could be more preferable to employ 40°C to save energy than obtaining a low dispersity. Furthermore, investigating different reaction conditions show the great potential of tailoring the reaction.

For the samples with CuBr₂ and 75 μL addition of NaCl-solution (aq) of different concentrations, the reaction rates and dispersities were decreased as the molar amount of NaCl increased from 7.5 to 30 μmol. However, for the duplicates of 30 μmol NaCl-addition (P-Cl30-W75-1 and -2), the molar mass and dispersity for P-Cl30-W75-1 were higher, suggesting that for this reaction the control was slightly lost and that this system may not be completely stable. Yet, the dispersity is reasonable low and some deviations between experiments are expected since the amount of oxygen can be different, and therefore also the induction period. Furthermore, an industrial set-up often monitors a polymerization reaction through *in situ* viscosity measurement, which renders it possible to terminate the reaction at the requested molar mass.

To have a large excess of the salt, 400 μmol of NaCl was added to the monomer mixture, in two different concentrations (4.16 and 4.0M, 75 and 100 μL respectively). When 75.0 μL of NaCl solution was employed, no reaction occurred after 4.3 h, implying that the reaction rate was greatly affected. The reaction time was increased to 8 h—the determined time limit—and still no reaction occurred. An increased volume of the NaCl-solution (100 μL), but with the number of moles NaCl kept constant, resulted in a M_n of 36 700 g/mol in 3 h, P-Cl400-W100-3h, Table III. The reaction was also run for 4.3 h, and a rather high molar mass of 57,500 g/mol was achieved combined with a low dispersity, confirming an increased control of the reaction for larger concentrations of salt.

Table III. Reaction Conditions and SEC Results from the Free-Forming Polymer for the Grafting of MMA ([MMA] : [EBiB] : [PMDETA] : [Cu(II)] : [AsAs] = [800] : [1] : [1] : [0.1] : [1]) from Cellulose at 40°C, with Small Amounts of Added NaCl-Solution

Sample ^a	Time (h)	H ₂ O ^b (μL)	NaCl (mM)	NaCl (μmol)	M _n ^c (g/mol)	Đ _M ^c
P-Cl7.5-W75-3h	3	75.0	100	7.50	63,400	1.57
P-Cl10-W100-3h	3	100	100	10.0	66,700	1.67
P-Cl10-W100-CuCl ₂ -3h ^d	3	100	100	10.0	41,700	1.30
P-Cl30-W75-CuCl ₂ -3h ^d	3	75.0	400	30.0	28,500	1.32
P-Cl30-W75-4.3h-1	4.3	75.0	400	30.0	58,300	1.45
P-Cl30-W75-4.3h-2	4.3	75.0	400	30.0	42,300	1.33
P-Cl400-W75-4.3h	4.3	75.0	4160	400	-	-
P-Cl400-W75-8h	8	75.0	4160	400	-	-
P-Cl400-W100-3h	3	100	4000	400	36,700	1.29
P-Cl400-W100-4.3h	4.3	100	4000	400	57,500	1.27

^aP-Clz-Wx-yh, where P represents free polymer, Cl represents the addition of NaCl-solution, x the amount of added NaCl-solution (aq), y the reaction time, and z the number of μmoles added NaCl.

^bAdded to 25.2 ml of MMA.

^cDetermined by DMF-SEC.

^dCuCl₂ (4.2 mg) was used instead of CuBr₂.

The filter papers modified under the influence of NaCl-solutions were characterized with FT-IR, all showing significant increase in the carbonyl region compared to initiator-functionalized filter paper. Supporting Information Figure S1 in the ESI depicts five of the substrates, and as before, the higher peaks correspond to samples with higher molar masses and vice versa, and the length of the graft can be correlated relatively well to the absorbance in the carbonyl region. The PMMA-grafted substrates characterized with FT-IR were also analyzed with CA measurements, and the values obtained after 10 s are presented in Supporting Information Table S3 in the ESI, all showing relatively high CAs over a period of time. For the other substrates, the CAs are in the same range.

Grafting of Cellulose Without Sacrificial Initiator

The length of the grafted polymers on the surface is generally controlled by the utilization of a sacrificial initiator, since it has been shown that the polymer formed in parallel to the grafting reactions has essentially the same molar mass as the grafts.^{29–32} However, from a processing point of view the presence of

unbound polymers can be problematic, since removal of the physisorbed polymers requires an additional purification step, most probably also involving organic solvents. To circumvent this, the grafting was performed without sacrificial initiator. The polymerizations were performed at either 40 or 80°C combined with the addition of water (75.0 μL), using the same amounts of PMDETA, Cu(II)Br₂, and AsAc as when adding a sacrificial initiator and aiming for DP_{target} of 800, Table IV. The grafting was also performed with the addition of Cu(I) and with increased amounts of the reaction components, corresponding to DP_{target} of 200.

Since no free polymer is formed, no indirect measurement of the molar mass of the grafts could be performed by SEC; hence, FT-IR analysis becomes more significant to confirm the successful grafting. Figure 3(A) depicts the FT-IR spectra of filter papers grafted without addition of sacrificial initiator. The amount of polymer seems to slightly increase with reaction time, but the differences are small, especially for the reactions performed for 8 and 16 h, respectively. Overall, the amount of polymer on the surface is very low, and hence, no stable CA measurements were achieved. This may be due to the fact that the number of initiating species is low why the dynamic equilibrium between active and dormant species cannot be adjusted appropriately. In a conventional ATRP reaction, the difficulty when grafting without the sacrificial initiator is that the initiating sites on the surface are too few to produce a sufficient concentration of the deactivator. Therefore, Cu(II) is generally added to the reaction together with Cu(I) to achieve a well-controlled reaction. In ARGET ATRP, Cu(I) is only formed by the reduction of Cu(II) and not added to the reaction. With the purpose to support the formation of the dynamic equilibrium, and to achieve a higher grafted amount, Cu(I)Br was also added to the reaction mixture. As can be seen in Figure 3(A), the amount of polymer on the surface was increased by the addition of Cu(I), suggesting that an increased amount of the activator is required. Therefore, another trial was performed, but

Table IV. Reaction Conditions and CAs for the Grafting of MMA ([MMA] : [PMDETA] : [Cu(II)] : [AsAs] = [800] : [1] : [0.1] : [1]) from Cellulose with no Addition of Sacrificial Initiator

Sample ^a	T (°C)	Time (h)	Water (μL)	CA 1 s (°)
C-No I-3h	80	3	-	-
C-No I-8h	80	8	-	83
C-No I-16h	80	16	-	75
C-No I-W75-8h	40	8	75.0	68
C-No I-Cu(I)-8h ^b	80	8	-	65
C-No I-DP200-4h ^c	80	4	-	120

^aC-No I-Wx-yh, where C represent cellulose, x the amount of added water, and y the reaction time.

^bAddition of 1.5 mg Cu(I)Br.

^cThe DP_{target} was 200.

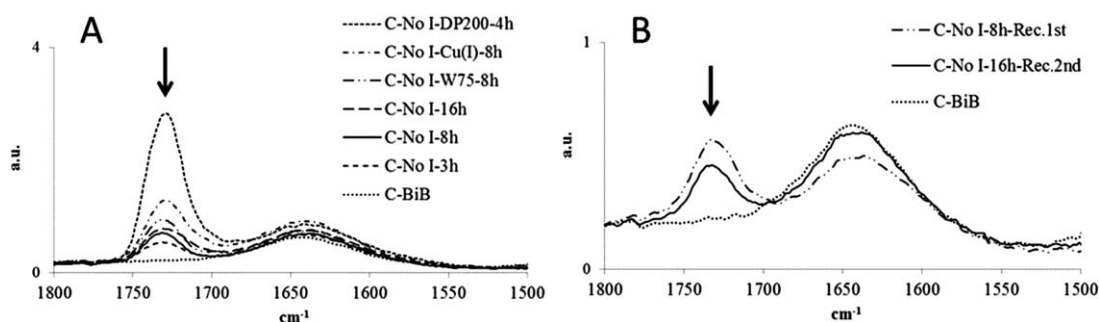


Figure 3. A: FT-IR spectra of initiator-functionalized filter paper and PMMA-grafted filter paper without the addition of a sacrificial initiator, performed for different reaction times and conditions. B: FT-IR spectra of initiator-functionalized filter paper and PMMA-grafted filter paper, for the first and second cycle of recycled catalyst-solution.

this time no Cu(I) was added, instead the amounts of Cu(II)Br₂, PMDETA, and AsAc were increased, corresponding to an aimed DP_{target} of 200. As can be seen in Figure 3(A) (C-No I-DP200-4h), the amount of polymer is increased. Furthermore, a stable CA was achieved (Table IV), confirming a sufficient amount of polymer grafts on the surface.

Since no free polymer is formed, the composition and viscosity of the reaction mixture are not significantly affected during the reaction. This brings about another great advantage of not using a sacrificial initiator: the reaction mixture can be recycled. This was investigated by first grafting an initiator-functionalized filter paper for 8 h at 80°C with DP_{target} of 800 (Sample C-No I-8h-Rec.first). Subsequently, the screw lid was opened, exposing the mixture to air, and the grafted paper was replaced with another, initiator-functionalized paper. The same amount of the reducing agent as before was also added to scavenge the new oxygen that was introduced to the system, restarting the polymerization. The second cycle of the recycling was performed for 16 h (Sample C-No I-16h-Rec.second). The FT-IR spectra in Figure 3(B) show that the recycling was successful, further proving the stability of the ARGET ATRP system. However, the amount of grafted polymer on the surface is low. Consequently, no stable CA could therefore be measured. The FT-IR results also suggest that, for the second cycle, the polymeric amount is slightly lower despite a doubled reaction time. A reason for this can be that parts of the Cu catalyst adhere to the substrate when the first paper is withdrawn. However, this system can be improved by employing a larger

catalytic amount, which also can result in less difference between the first and second cycle.

Grafting of Cellulose Wood-Fibers

ARGET ATRP has proven to be a successful polymerization method when grafting filter papers, that is, cotton-based substrates with high degrees of cellulose content (98%) and low amounts of noncellulose compounds, such as lignin and hemicellulose.^{22,29,33–35} To explore the applicability of ARGET ATRP, other cellulosic substrates based on wood fibers were used: dissolving pulp (Dis P), bleached and unbleached Kraft pulp (Ble KP and Unble KP, respectively), and bleached and unbleached CTMP (Ble CTMP and Unble CTMP, respectively). These substrates have a higher degree of noncellulose content which in turn could have an impact on the grafting. The dissolving pulp has the highest content of cellulose, with low amounts of lignin and hemicellulose. The bleached Kraft pulp contains only a few percentages of lignin but a higher degree of hemicellulose and in increasing order of lignin- and hemicellulose content are unbleached Kraft pulp, bleached CTMP and unbleached CTMP.

Paper sheets were produced from the different fibers and the surface area of the resulting sheets were measured, Supporting Information Table S4 in ESI. The bleached KP resulted in the highest surface area and the unbleached CTMP in the lowest. The sheets were cut into 2 × 3 cm² pieces and immobilized with initiator according to identical procedures as for filter paper and subsequently grafted at 80°C for 3 h, Table V. However, the dissolving pulp disintegrated in solution under these conditions, so the temperature was lowered to 40°C and 100 μL

Table V. Reaction Conditions and SEC Results from the Free-Forming Polymer for the Grafting of MMA ([MMA] : [EBiB] : [PMDETA] : [Cu(II)] : [AsAs] = [800] : [1] : [1] : [0.1] : [1]) from Wood Pulp

Sample ^a	Cellulose substrate	T (°C)	Time (h)	M _n ^b (g/mol)	Đ _M ^b
P-Dis P-CI400-3h	C-Dis P-CI400-3h	40	3	35,000	1.35
P-Ble KP-3h	C-Ble KP-3h	80	3	29,400	1.11
P-Unble KP-3h	C-Unble KP-3h	80	3	33,000	1.12
P-Ble CTMP-3h	C-Ble CTMP-3 h	80	3	28,600	1.11
P-Unble CTMP-3h	C-Unble CTMP-3h	80	3	30,700	1.10

^aP-x-yh, where P represent polymer, x the substrate, and y the reaction time.

^bDetermined by DMF-SEC.

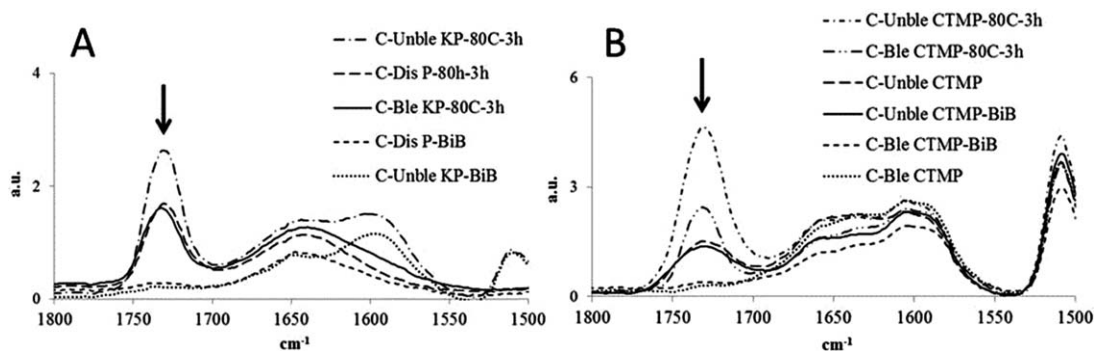


Figure 4. A: FT-IR spectra of initiator-functionalized wood pulps and PMMA-grafted wood pulps, at 80°C and 3 h reaction. B: FT-IR spectra of native CTMP (bleached and unbleached), initiator-functionalized CTMP (bleached and unbleached), as well as PMMA-grafted CTMP (bleached and unbleached).

of the 4.0M NaCl-solution was employed to increase the reaction rate while retaining a good control. Yet, the substrate was not intact as a sheet as can be seen in Supporting Information Figure S2 in the ESI.

The molar masses of the grafts were in the range of 30 kg/mol for all the different substrates, according to SEC analysis of the freely formed polymer, Table V. The dispersity of the polymer formed in parallel to the grafting of the dissolving pulp—the pulp with the highest cellulosic content—is higher than for the other substrates, which probably is due to the NaCl-solution employed for this reaction. However, when comparing the wood-fiber substrates with the cotton-based filter papers in Table I, the D_M is slightly lower for all the wood fiber-based samples.

The native and modified wood fiber-based substrates were characterized with FT-IR. The spectra of the dissolving pulp and the bleached Kraft pulp appears similar to that of filter paper, due to low quantities of lignin in these substrates. Upon immobilization of the initiator no differences can be seen, as expected, therefore, the BiB-functionalized bleached Kraft pulp was excluded from Figure 4(A). The unbleached Kraft pulp shows signals that arise from the residual lignin components around 1600 and 1510 cm^{-1} . Upon grafting, the carbonyl peak increases to the same extent as for the bleached Kraft pulp and the dissolving pulp, whereas there seems to be a larger amount of polymer on the grafted unbleached Kraft Pulp, although the molar masses of the grafts should be in the same range according to SEC measurements of the free-forming polymers. This indicates that the number of grafted chains is higher for the unbleached Kraft pulp. This is most likely attributed to a higher availability of the OH-groups in this substrate.

FT-IR spectra of the CTMP substrates are presented in Figure 4(B). The native unbleached CTMP (C-Unble CTMP) has an absorbance in the carbonyl region, most likely attributed to the acetyl groups or of the possible presence of ferulic acid present in hemicellulose. Furthermore, for both the bleached and the unbleached CTMP substrates the peak at 1510 cm^{-1} , corresponding to aromatic skeletal vibrations of lignin, gives rise to a stronger signal than for the unbleached Kraft pulp, confirming a larger presence of lignin in CTMP. Furthermore, the region

1550–1700 cm^{-1} has a slightly different profile all together most probably due to the higher presence of lignin and hemicelluloses in these samples. Upon immobilization of the initiator, no changes can be detected, which is in accordance with the other substrates. The CTMP substrates were successfully grafted, and for the unbleached CTMP the carbonyl peak is larger due to the overlapping signals from the paper. However, by comparing C-Ble CTMP-80C-3h in Figure 4(B) with C-Unble KP-80C-3h in Figure 4(A), the polymeric amounts seem to be in similar range.

The CAs of the initiator-functionalized wood-fiber substrates, presented in Supporting Information Table S5 in the ESI, showed stable values above 100° for all substrates except the dissolving pulp and the bleached Kraft pulp, that is, for the substrates containing the lowest amounts of residual lignin and hemicellulose, suggesting that the lignin and hemicelluloses render the substrates more hydrophobic or that more OH-groups are accessible for the reaction with BiB in these substrates. The latter explanation can be corroborated with the FT-IR results that showed a higher amount of polymer on the unbleached Kraft pulp. The grafted samples of dissolving pulp and bleached kraft pulp showed stable CA s, but they were below 100°.

CONCLUSIONS

It has been shown that heterogeneous grafting of cellulose by ARGET ATRP can be performed utilizing a more industrially friendly method while maintaining sufficient control over the reaction. Our study show that no deoxygenation was necessary prior to polymerization and that the addition of miniscule amounts of water or NaCl-solution significantly increases the reaction rate while upholding satisfactory control. The washing procedure was kept to a minimum, resulting in only small amounts of physisorbed polymer on the substrate. However, the amount of grafted polymer could be governed by adjusting the ratio of monomer-to-free initiator. When no free initiator was added, the polymeric amount could be varied by increasing the reaction time. In this case, it was possible to recycle the polymerization solution, although this gave rise to a decreased amount of grafted polymer on the surface for the second cycle with a subsequently less hydrophobic paper. Several sources of

cellulose were successfully grafted, such as filter paper, dissolving pulp papers, bleached and unbleached Kraft-pulp and CTMP papers. This study is an important step towards industrializing the “grafting-from” of cellulose fibers.

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