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Atom Transfer Radical Polymerization from Cellulose Fibers at Ambient Temperature

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Surface properties play an increasingly important role in our society's need for polymeric materials with tailored properties. Essentially all devices contain many different materials which have to be compatible. For instance, there is an ambition today to fabricate plastic composites where the reinforcing fiber is made from renewable resources, i.e., cellulose. This has sparked off the strive to control properties such as wettability, hydrophobicity, and adhesion of the cellulose fibers.[1] Composite failures are most often due to weak boundary layers between the fiber and the matrix. One approach to overcome this is to surface modify the fiber to improve the adhesion.[2,3]

Atom transfer radical polymerization (ATRP) is a robust and versatile technique to accurately control chain length and polydispersity.[4−6] ATRP has previously been utilized for "grafting from" processes from silicon,[7−11] gold[12,13] and silica[14] surfaces, and porous substrates.[15,16]

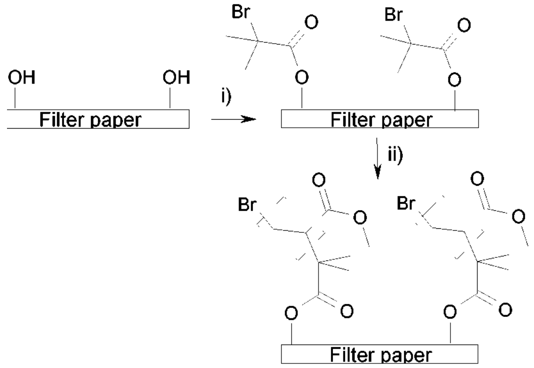
This paper reports on the ATRP of methyl acrylate from initiators immobilized on cellulose fibers. The grafted filter papers were analyzed by contact angle measurements, FT-IR and DSC. To our knowledge, this is the first time an organic substrate has been employed for surface grafting by controlled radical techniques.

A filter paper was chosen for this introductory study as an appropriate cellulose substrate, mainly to circumvent the practical problems impaired by using free fibers. The filter paper of choice was Whatman 1 since it has high cellulose content and contains only a minor amount of impurities.[17] The size of the papers used in the experiments was 1 × 1 cm. The hydroxyl groups on the cellulose were converted into tertiary bromoester groups, which are known to be efficient ATRP initiators for acrylates.[18] In a recent study, the experimental conditions for ATRP of methyl acrylate from a multifunctional hyperbranched initiator were elaborated.[19] Essentially the same conditions were utilized here for the polymerization from the paper-immobilized initiator. Baker et al. have utilized a similar system for initiators immobilized on gold.[13]

Scheme 1 outlines the synthetic pathway for the preparation of the PMA-grafted filter papers.

The initiator was immobilized by reacting 2-bromoisobutyryl-bromide with the hydroxyl groups on the filter paper for 24 h at room temperature. The filter paper was thereafter thoroughly washed with dichloromethane. The grafting was accomplished by immersing the initiator-modified paper into the reaction mixture[20] containing methyl acrylate (MA), Cu(I)Br, tris(2-(dimethylamino)ethyl)amine (Me_6-TREN),[21,22] sacrificial initiator, and ethyl acetate. The polymerization was conducted in ethyl acetate to simplify the workup of the product. A sacrificial initiator, ethyl 2-bromoisobutyrate, was used to control the length of the PMA-grafts, as the ratio between the free initiator and monomer determines the degree of polymerization. All polymerizations were carried out at room temperature for 18 h. The nonimmobilized polymers were analyzed by size exclusion chromatography (SEC) with respect to molecular weight and polydispersity, Table 1. After completed polymerization the papers were subjected to intense washing: THF, THF:water, water, and dichloromethane. Ultrasonication was used in combination with all four solvents. No washing by solvent reflux was conducted to avoid heat treatment of the fibers.

Scheme 1 [a]



[a] Conditions: (i) 2-bromoisobutyryl bromide, triethylamine, DMAP, CH_2Cl_2; (ii) methyl acrylate, ethyl 2-bromoisobutyrate, Cu(I)Br, Me_6-TREN, ethyl acetate.

Table 1. Results from SEC and Contact Angles Measurements

sample (DP aim)	MW theoretical	MW	DP[a]	PDI	contact angle $(\theta)_a$, deg
blank[b]	17 212	14 830	172	1.05	*c*
DP-100	8 609	6 430	75	1.10	*d*
DP-200	17 212	12 810	149	1.06	128 ± 10
DP-300	25 818	25 630	298	1.05	133 ± 5

[a] The degree of polymerization was calculated from SEC data. [b] The filter paper was not reacted with initiator but subjected to polymerization conditions. [c] Wets such as untreated filter paper, water is rapidly adsorbed. [d] Not measurable since water is continuously adsorbed into the paper.

To verify the success of the "grafting from"-reaction a blind test was performed (denoted blank). This sample was treated identically with the samples subjected to polymerization with the exception that no initiator was immobilized on its surface. The aimed DP for this sample was 200.

The SEC data for the nonimmobilized polymer are presented in Table 1. As can be seen, all polydispersities are low, below 1.1. However, the targeted degree of polymerization (DP) and the observed DP values deviate somewhat. This is probably due to imperfect reaction conditions since no optimization with respect to stirring and degassing has been performed. All polymerizations have been conducted having the paper hanging in the flask to enable stirring without destroying the filter paper.

Surface characterization of a rough filter paper is not straightforward. Ellipsometry is impossible and contact angle measurements very difficult, both due to the surface roughness and the adsorbing nature of the filter paper. Therefore, contact angle measurements

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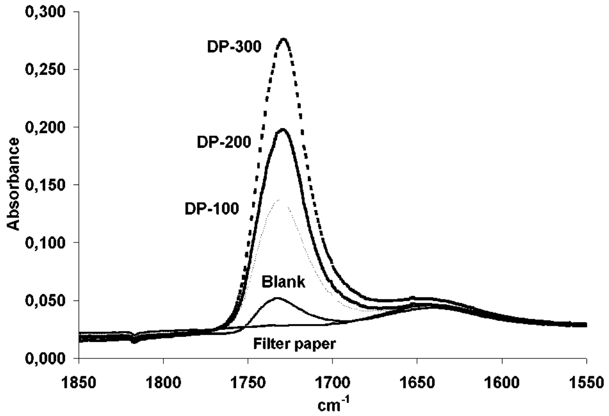

Figure 1. FT-IR of the grafted and ungrafted papers.

can only be considered as rough estimates of the surface properties. Due to the same reasons, only the advancing angle, θ_a, has been measured. Water was used for the measurements since hydrophobicity is the main interest at present. The virgin filter paper was found to be extremely hydrophilic and adsorbed all water immediately while no contact angle could be measured. The initiator-modified paper wets similarly to the neat paper. However, papers having grafts became increasingly hydrophobic with increasing graft lengths, Table 1. For sample DP-300, a $\theta_a = 133°$ was measured that is consistent with a very hydrophobic surface. No water adsorption could be detected for samples DP-200 and DP-300. Sample DP-100, however, very slowly adsorbed water. The blank sample behaved just like the virgin paper with respect to water adsorption.

FT-IR[23] and DSC were also used to verify the success of the surface grafting. Figure 1 displays the FT-IR spectra for the grafted and ungrafted filter papers.

All samples were compared to the blank sample and to a filter paper subjected only to solvents and MA (cf. filter paper in Figure 1).

It is clearly seen that the carbonyl peak at 1730 cm^{-1} increases almost proportionally with the length of the PMA grafts. This indicates that the thickness of the grafted layer can be tailored by altering the monomer-to-initiator ratio. Furthermore, this is suggesting the control of the polymer graft lengths on the surface through the ATRP technique. The FT-IR spectrum of the initiator-modified filter paper is identical with that of the unmodified filter paper.

FT-IR analysis of the blank filter paper revealed a small carbonyl peak that is attributed to physiosorbed PMA. This implies that the washing procedure was not completely successful. Most likely, all grafted surfaces contain some physiosorbed PMA. However, the difference between the grafted samples and the blank is still evident.

DSC[24] analysis of the grafted papers corroborated the results obtained by FT-IR, Figure 2. The glass transition for samples DP-200 and DP-300 is clearly seen close to 20 °C. For sample DP-100, no T_g is observed, which is attributed to the restricted motion of the surface-immobilized, rather short PMA-grafts.

It would be desirable to cleave off the PMA-grafts and analyze them separately. However, due to the small amount of polymer grafted from the paper it is not possible under the conditions used to isolate the PMA cleaved off by hydrolysis (KOH/MeOH). The small amount of grafted polymer also renders gravimetric monitoring impossible.

In conclusion, cellulose fibers have been successfully grafted with PMA using ATRP, mediated by Me_6-TREN and Cu(I)Br. The initially hydrophilic cellulose was first modified by reacting the hydroxyl groups with 2-bromoisobutyryl bromide whereupon methyl acrylate was grafted from the surface. The resulting polymer-grafted papers were extremely hydrophobic, $\theta_a = 133°$. FT-IR analysis indicates that the grafted amount can be controlled.

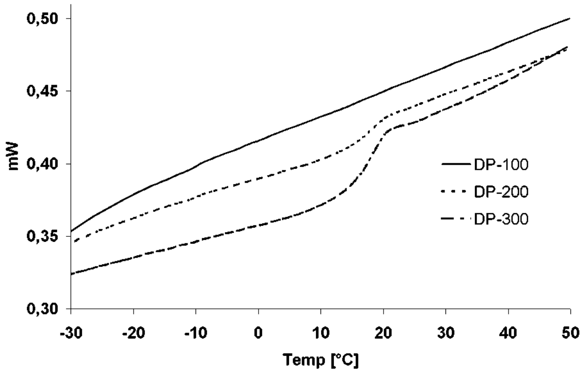

Figure 2. DSC traces for samples DP 100, 200, and 300. (First heating, 10 °C min^{-1}.)

At present, we are optimizing the reaction conditions to investigate the degree of control of the PMA-grafts. To successfully accomplish this larger substrates are required. The versatility of the grafting process will be further investigated by the use of various monomers. Ideally, the surface properties of the fibers can be tailored by the appropriate choice of monomers. Eventually, surface-modified fibers will be evaluated in composites.

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(24) Differential Scanning Calorimetry was performed on a Mettler DSC 820 calibrated with use of standard procedures. Heating and cooling were performed at 10 K min^{-1}.

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