Graft Polymerization: Grafting Poly(styrene) from Cellulose via Reversible Addition−Fragmentation Chain Transfer (RAFT) Polymerization

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ABSTRACT: Reversible addition−fragmentation chain transfer (RAFT) polymerization was used to control the grafting of styrene from a cellulose substrate. The hydroxyl groups of the cellulose fiber were converted into thiocarbonyl-thio chain transfer agent, and were further used to mediate the RAFT polymerization of styrene. The graft copolymers were analyzed by gravimetry, attenuated total reflectance Fourier transform infrared spectroscopy, contact angle measurements, scanning electron microscopy, differential scanning calorimetry, and thermogravimetry. The results obtained from these analytical techniques confirm that grafting occurred from the surface of the cellulose fibers. The poly(styrene) chains were also cleaved from the cellulose backbone and analyzed by size exclusion chromatography and showed narrow polydispersity.

Introduction

The synthesis of cellulosic graft copolymers with tailored surface properties is of great interest due to their wide range of potential applications. For instance, graft copolymers can be used as antibacterial surfaces,[1] thermoresponsive smart materials,[2] membrane materials,[3] controlled drug delivery vehicles,[4] ion-exchange materials,[5] sorption agents for the removal of heavy metals,[6] and reinforcing agents in composite materials.[7] The interest in using natural cellulose fibers in composite materials is constantly growing due to their availability as renewable natural resources, ease of fiber surface modification, low cost, good mechanical properties, low density compared with their inorganic counterparts, and recyclability.[7−10] However, the high moisture absorption of hydrophilic cellulose fibers can lead to composite failure due to the formation of weak interfacial interactions between the natural fibers and the polymer matrix.[11] The most efficient way to reduce the hydrophilicity of cellulose fibers and to improve their compatibility and adhesion to other hydrophobic composite material components is to modify the cellulose surface by controlled grafting with hydrophobic monomers.

The grafting of hydrophobic monomers such as methyl methacrylate, styrene, acrylonitrile, butadiene, and vinyl acetate onto cellulose substrates can enhance the adhesion of the grafted materials to hydrophobic fibers.[12] Tsubokawa et al.[13] reported that the controlled grafting of hydrophobic isobutyl vinyl ether onto cellulose surface can alter the wettability of the surface from its hydrophilic nature to a truly hydrophobic nature. Narayan et al.[14] reported that well-defined, tailored cellulose−poly(styrene) graft copolymers can function effectively as compatibilizers or interfacial agents to bond a hydrophobic plastic material to a cellulosic material with a view to making new types of composites.

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To date, most of the techniques that are used to synthesize cellulosic graft copolymers are based on free radical polymerization methods. Here, free radical sites are produced along the cellulose backbone either by chemical means or by irradiation.[15−17] In the presence of vinyl monomers, the polymeric chain grows from these radical sites through a "grafting-from" approach. The major drawbacks[18−22] of these methods are (a) chain degradation of the cellulose backbone during the formation of free radical grafting sites, (b) the presence of a considerable amount of ungrafted cellulose in the product, (c) relatively few and very long (high molecular weight) grafted side chains, (d) little control over the grafting process, yields, molecular weights, molecular weight distributions, properties, and other features of the graft copolymers, (e) large amounts of homopolymer formation and the difficulties associated with their removal, and (f) that the preparation of grafted block copolymers is almost impossible due to the unreactive end groups of the polymeric chains. Therefore, ill-defined and poorly characterized cellulose graft copolymers, synthesized by conventional free radical polymerization methods, may not improve to a great extent the compatibility and interfacial activity of cellulose for composite use.[14]

Living polymerization methods could be attractive alternatives to overcome some of the above-mentioned drawbacks of conventional polymerization systems. These methods permit the synthesis of well-defined graft polymers of predetermined molecular weight and narrow polydispersity, thus giving the opportunity to tailor the surface properties of cellulose toward the required properties. The controlled grafting of cellulose using anionic or cationic polymerization methods has been reported previously.[13,20,21] These methods are based on the "grafting-to" technique, in which preformed polymer is coupled to the cellulose backbone. However, this technique suffers from limitations due to steric hindrance, as the preformed polymers have limited diffusion to the surface of cellulose, due to the overcrowding of the graft chains. As a result, the rate and

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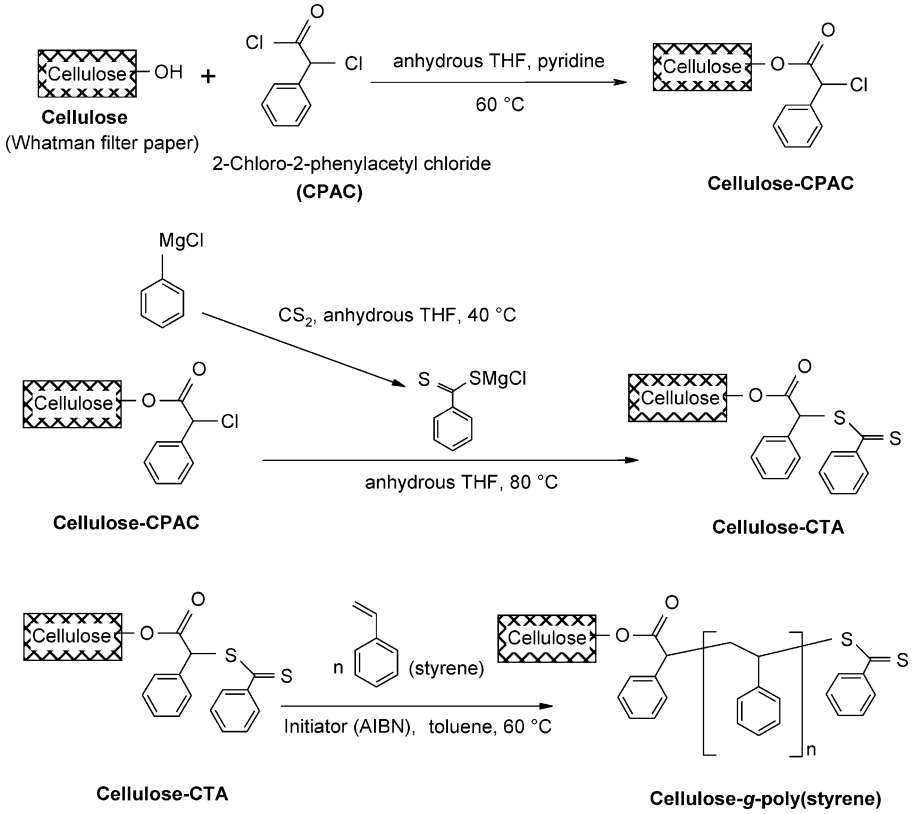
Scheme 1. Synthesis of Cellulose Chain Transfer Agent for Reversible Addition−Fragmentation Chain Transfer Polymerization and Their Use To Mediate Styrene Polymerization



extent of grafting are usually very low.[23] Moreover, the experimental conditions required to perform ionic polymerization are very demanding (e.g., low temperature, highly pure reagents, inert atmosphere, and anhydrous condition).[24] Recently, living radical polymerization techniques such as nitroxide-mediated polymerization (NMP)[25] and atom transfer radical polymerization (ATRP)[1,22,23,26,27] have been used for polymer grafting onto cellulose surfaces in a controlled manner. Although both methods have many positive aspects with respect to the synthesis of well-defined graft copolymers, the general disadvantages are high reaction temperatures and limited range of available polymerizable monomers in the case of NMP[28] and contamination of the final polymeric product with a highly colored ligand/metal complex in the case of ATRP.[29]

Reversible addition−fragmentation chain transfer (RAFT) polymerization is another promising living radical method for synthesizing well-defined graft polymers.[30,31] The major attractions of the RAFT process, over other living radical polymerization techniques, include the ability to polymerize, in a controlled manner, a wide range of vinyl monomers and the less-demanding reaction conditions that are involved.[32,33] In recent years, RAFT polymerization has been successfully used for the grafting of various monomers onto a wide range of solid supports such as silica particles,[34] silicon wafers,[35] carbon nanotubes,[36] rigid poly(propylene),[37] gold nanoparticles,[38,39] and core−shell microspheres.[40] Recently, our group reported the use of the RAFT procedure to control the grafting of different vinyl monomers onto cotton fabric surfaces.[41−43] In the present study, a hydrophobic cellulose surface was prepared by grafting poly(styrene) onto a cellulose substrate (Whatman No. 1 filter paper) via the RAFT polymerization method with a view to using the hydrophobic cellulose fibers in composites. Scheme 1 illustrates the outline of the synthesis of the cellulose-based RAFT agent and of cellulose-*g*-poly(styrene) copolymer, mediated by the RAFT process.

Experimental Section

Materials. All solvents, monomers, and other chemicals were purchased from Aldrich (Gillingham, Dorset, UK) at the highest purity available unless otherwise stated. Styrene (99+%,) was filtered before use through an activated basic alumina (Brockmann I) column. 2, 2′-Azobis(isobutyronitrile) (AIBN, 97%) was purified by recrystallization from ethanol and dried at room temperature in a vacuum oven and, finally, stored in a freezer. Tetrahydrofuran (THF), pyridine, and toluene were dried over molecular sieves (4 Å) before use. 2-Chloro-2-phenylacetyl chloride (CPAC, 90%) carbon disulfide (99.9+%), and phenylmagnesium chloride (2 M solution in THF) were used as received. The *S*-methoxycarbonylphenylmethyl dithiobenzoate (MCPDB) RAFT agent and homopoly(styrene) (M_n = 12 800 g/mol, PDI = 1.10) (size exclusion chromatography, poly(styrene) (PS) calibration) were synthesized following a procedure available in the literature.[41] A filter paper, Whatman No. 1, was used as cellulose substrate due to its high cellulose content (98% α-cellulose), lesser amount of impurities, and ease of chemical modification.[23] All other chemicals and solvents were used as received.

Elemental Analyses (EA). The cellulose samples were analyzed for C, H, N, Cl, and S contents at the Laboratory of Microanalysis, Chemistry Department, University of Leeds, UK. The C, H, and N contents were determined by combustion followed by chromatographic separation and thermal conductivity detection using a Carlo Erba EA 1108 Elemental Analyzer. The degrees of substitution (DS) of cellulose-CPAC and cellulose-CTA were calculated from their chlorine and sulfur contents, respectively.

Chlorine Analysis. The completely dried test samples (5−10 mg) were combusted by the Schöniger oxygen flask combustion method.[44] The combusted products were washed into a

flask with 5−10 mL of water. One drop of bromophenol blue (0.1% in ethanol) was added. Nitric acid solution was added dropwise until yellow, and 0.5 mL excess nitric acid was added. Then 50 mL of ethanol and diphenyl carbazone indicator (0.1% in ethanol) was added. Finally, chlorine was determined as chloride anion by titration using 0.05 M mercuric nitrate (in water) to a purple end point. A blank determination was also carried out and subtracted from the sample titration.

Sulfur Analysis. The completely dried test sample (5−10 mg) was combusted by the Schöniger oxygen flask combustion method.[44] The combusted products were washed into a flask with 5−10 mL of propan-2-ol, and 30 mL of propan-2-ol was added to the flask. Then 0.2 mL of thorin solution (0.2% in water) and 0.25 mL of methylene blue solution (0.02% in water) were added. Finally, sulfur was analyzed as sulfate anion by titration using 0.05 M barium perchlorate solution (in 95% propan-2-ol) until a definite end point (from green to pink). A blank determination was also carried out and subtracted from the sample titration.

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FT-IR). ATR FT-IR spectra of the modified and unmodified cellulose samples were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer using a single reflection horizontal ATR accessory. It has a diamond ATR crystal fixed at an incident angle of 45°. For the measurement of ATR FT-IR spectra, each sample piece (2.5 cm × 2.5 cm) was mounted on the top of the ATR crystal and a premounted sample clamp was then lightly pressed on the sample. Each spectrum was collected in the range of 4000−400 cm^{-1} by cumulating 100 scans at a resolution of 4 cm^{-1}. The scan speed was set at 0.5 cm/s. Baseline was corrected for all spectra using the Perkin-Elmer Spectrum software.

Fourier Transform Raman Spectroscopy (FT-Raman). Raman spectra of modified and unmodified cellulose samples (2.5 cm × 2.5 cm) were recorded using a Perkin-Elmer system 2000 NIR FT Raman spectrometer. The laser source was a Nd:YAG with diode pumping. The scan speed was set at 0.2 cm/s for 100 scans. Baseline was corrected for all spectra using the Perkin-Elmer Spectrum software.

Differential Scanning Calorimetry (DSC). The thermal properties of the cellulose-*g*-poly(styrene) copolymers were studied by differential scanning calorimetry (DSC) using a TA Instrument DSC 2010 thermal analyzer under a nitrogen atmosphere (200 cm^3 min^{-1}). For measurement of the glass transition temperature (T_g), about 5−10 mg samples in an aluminum holder were heated from 25 to 140 °C, then cooled to 20 °C, and reheated to 140 °C. The heating and cooling rate was set to 10 °C min^{-1}. An empty aluminum pan was used as a reference material. The T_g value was determined from the onset, end, and inflection of a step transition using the TA Instruments Thermal Advantage Universal Analysis software. DSC measurements of the unmodified cellulose, cellulose-CTA, homopoly(styrene), physical mixture of cellulose-CTA and homopoly(styrene), MCPDB RAFT agent, and graft copolymers were also performed between room temperature and 500 °C at a rate of 10 °C min^{-1}. The sample size in this case was in the range of 3−5 mg. All samples were dried under vacuum at 40 °C for 24 h prior to DSC measurements.

Thermogravimetric Analyses (TGA). Thermogravimetric analyses on unmodified cellulose, cellulose-CTA, cellulose-*g*-poly(styrene) copolymers, and homopoly(styrene) were carried out using a TA Instrument TGA 2050 Thermogravimetric Analyzer under a nitrogen atmosphere. The samples (5−10 mg) were heated from room temperature to 500 °C at a rate of 10 °C min^{-1}. The TA Instruments Thermal Advantage Universal Analysis software was used for calculating the onset temperature, end decomposition temperature, and residual mass. All samples were dried under vacuum at 40 °C for 24 h prior to TGA measurements.

Contact Angle Measurements. A Livereel Contact-θ-Meter was used to assessment the degree of hydrophobicity of cellulose-*g*-poly(styrene) copolymer surfaces. A drop of selected fluid (e.g., water) was placed on the copolymer surface, and the contact angle was determined at 20 °C.

Scanning Electron Microscopy (SEM). The surface morphology of the cellulose samples before and after the grafting was observed by SEM using a JEOL JSM-820 scanning microscope operated at an accelerating voltage of 10 kV. The dried cellulose samples were coated with a 30 nm gold layer using a Bio-Rad diode sputter coating unit. Electron micrographs of each sample were recorded at a magnification of ×1200.

Size Exclusion Chromatography (SEC). The number-average molecular weight (M_n) and polydispersity index (M_w/M_n)) of cleaved poly(styrene) grafts were determined using SEC equipped with a LC 1120 HPLC pump ((Polymer Laboratories, UK), a MIDAS (Type 830) autosampler (Spark Holland, Netherlands), a differential refractive index (DRI) detector (Shodex, RI-101), a 5.0 μm bead size guard column (50 × 7.5 mm), and two PLgel 5.0 μm MIXED-C columns (300 × 7.5 mm) in series (Polymer Laboratories, UK). THF was used as the eluent at a flow rate of 1 mL min^{-1} at ambient temperature, and toluene was used as a flow rate marker. The SEC system was calibrated with poly(styrene) standards (Polymer Laboratories, UK) with molecular weights ranging from 580 to 7 500 000 g mol^{-1}.

Pretreatment of Cellulose. Whatman No. 1 filter paper was cut into pieces (2.5 cm × 2.5 cm) and washed with ethanol. Filter paper pieces (3.3 g, number of moles of active hydroxyl group = 0.06 mol) were then immersed into an aqueous solution (500 mL) of 8 wt % NaOH for 16 h at ambient temperature. The swollen cellulose samples were repeatedly washed with absolute ethanol until neutral. Ethanol in the cellulose samples was then displaced by THF (10 × 250 mL), and the cellulose samples were directly transferred into the next step (esterification) without any drying.

Synthesis of Cellulose Ester (Cellulose-CPAC) Using 2-Chloro-2-phenylacetyl Chloride (CPAC). The pre-treated and more accessible cellulose samples were immersed into a three-neck round-bottom flask, containing anhydrous THF solution (250 mL) and an excess of pyridine (34 mL, 0.42 mol), used as proton scavenger. An excess of CPAC (30 mL, 0.20 mol) was then added dropwise to the flask. The approximate molar ratio of cellulose hydroxyl group, CPAC, and pyridine was 1:3:6. The reaction was warmed to 60 °C and allowed to proceed for 24 h. The cellulose samples were covered in a black/brown precipitate. The samples were thoroughly washed with THF, dichloromethane, THF:water (1:1), water, and methanol. A Soxhlet extraction with THF and methanol was also carried out to complete removal of any unreacted CPAC and pyridinium chloride (salt). The chlorine and nitrogen contents of the cellulosic solid product were checked (by elemental analysis) before further processing. Extra washings of the cellulose sample were carried out until constant percent Cl content and negligible percent N content were obtained. Finally, the yellowish products were placed in a vacuum oven at 60 °C to dry overnight. The modified cellulosic product is termed cellulose-CPAC in the rest of this paper.

The analytical details for this product are as follows:

Gravimetry: Weight of dry cellulose-CPAC = 8.0 g; mass increase due to esterification = 4.7 g; % mass increase = 142.4%.

EA: C, 56.3%; H, 4.6%; N, trace or nil (<0.3%), Cl: 11.88%. Average loading of CPAC (functionality) on cellulose substrates = 3.35 mmol g^{-1}; average degree of substitution (DS) at the esterification stage = 1.1 (37% substitution).

Synthesis of *S*-Methoxycarbonylphenylmethyl Dithiobenzoate (MCPDB) RAFT Agent onto Cellulose (Cellulose-CTA). Phenylmagnesium chloride (20 mL, 0.15 mol) was added to a three-neck round-bottom flask containing anhydrous THF solution (100 mL) under nitrogen. An excess of carbon disulfide (45 mL, 0.75 mol) was then added dropwise to the flask, creating a dark brown solution. The reaction mixture was heated to 40 °C for 3 h. The resultant dark brown solution was then transferred to another flask containing cellulose-CPAC (7.8 g). The reaction was warmed to 80 °C and allowed to proceed for 24 h. The samples were thereafter thoroughly washed with THF. A Soxhlet extraction with THF and methanol was also carried out to complete removal of any

unreacted RAFT agent. The resulting orange product was then oven-dried under vacuum at 60 °C. The modified cellulosic product is termed cellulose-CTA in the rest of this paper.

The analytical details for this product are as follows:

Gravimetry: Weight of dry cellulose-CTA =10.4 g; mass increase due to second dramatization = 2.6 g; % mass increase = 33.3%.

EA: C, 60.3%; H, 4.6%; Cl, 2.15%; S, 12.15%. Average loading of RAFT agent on the cellulose substrates = 1.90 mmol g^{-1}; percent conversion of CPAC functional group to RAFT agent (Cl to S) = 57%; overall average DS (conversion of OH group to RAFT agent) = 0.63 (21% substitution).

Synthesis of Cellulose-*g*-poly(styrene) Graft Copolymers by RAFT Polymerization. In a typical graft polymerization reaction, the cellulose-CTA sample (0.16 g, 0.30 mmol) was first pretreated with dry toluene (12 mL) in a 50 mL Erlenmeyer flask for 24 h. Monomer (styrene) (18 mL, 154.70 mmol) and initiator (AIBN) (0.005 g, 0.03 mmol, previously dissolved in 6 mL of dry toluene) were then added into the flask. The molar ratio of monomer, cellulose-CTA, and initiator was 500:1:0.1. The reaction was performed in toluene (50% (v/v) to monomer). The flask was sealed with a rubber septum. The reaction mixture was then degassed with nitrogen for 15 min and placed immediately in a preheated oil bath at 60 °C. The reaction was stopped after 4 h, by cooling the reaction flask in an ice−water bath, and the polymerization flask was open to air. The crude cellulose-*g*-poly(styrene) solid sample was thereafter repeatedly washed with toluene (5 × 150 mL) and THF (5 × 150 mL) to remove surface contaminations such as unreacted monomer, nonattached (free) homopolymer, and initiator. Ultrasonication was also used in THF (50 mL) for 5 min. The sample was then extracted in THF (2 × 250 mL) using the Soxhlet apparatus for 36 h to ensure the complete removal of loosely attached (not covalently bound) free homopoly(styrene). An aliquot of Soxhlet-extracted solution (50 mL) was also analyzed by SEC (after complete evaporation of solvent) to confirm that there was no more extractable homopoly(styrene) present in the cellulose-*g*-poly(styrene) sample. Finally, the cellulose-*g*-poly(styrene) sample was dried to a constant weight under vacuum at 60 °C. To calculate the graft ratio, the cellulose-CTA samples were weighed before and after polymerization with poly(styrene). The graft ratio (G, wt %) was calculated using the following formula:

$$G = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

Here, W_1 (g) is the dry weight of the cellulose-CTA sample and W_2 (g) is the dry weight of the cellulose-*g*-poly(styrene) sample.

Cleaving of PS Chain from Cellulose Backbone. Poly(styrene) chains were cleaved from the cellulose surface under acidic conditions. In a typical acid hydrolysis experiment, 0.15 g of cellulose-*g*-poly(styrene) (28 wt % graft ratio) sample was immersed into a round-bottom flask containing 10 mL of 37% HCl and 25 mL of THF. The flask was stirred at 80 °C for 3 weeks until the cellulose was completely dissolved. The reaction mixture was filtered, and the solvent (THF) in the filtrate was evaporated off using a rotary evaporator and, finally, dried at 50 °C in a vacuum oven. The resulting viscous liquid was dissolved in dichloromethane (DCM, 5 mL) and then extracted with a small amount of distilled water (10−15 mL). After separation of the water layer, the organic phase was dried under anhydrous sodium sulfate for 16 h. After filtration of the sodium salt, poly(styrene) chains were collected by complete evaporation of the solvent (DCM). The highly viscous poly(styrene) product was then dissolved in THF, and the molecular weight (M_n) and molecular weight distribution (M_w/M_n) were analyzed by SEC.

Results and Discussion

Cellulose Pretreatment. Cellulose is a nonbranched condensation polymer consisting of D-anhydroglucose units joined together by β-1,4-linkage. Although cellulose is a linear polymer, it exhibits a high degree of crystallinity in its native state, and there is strong intermolecular hydrogen bonding between adjacent cellulose chains due to the hydroxyl groups. All of the OH groups of cellulose are therefore not accessible for reaction. Thus, the cellulose fibers required pretreatment with an aqueous solution of NaOH to break down the extensive hydrogen bonding and open up the more ordered regions, so that the reagents could easily penetrate inside the cellulose substrate. The use of absolute ethanol (instead of water) to remove the alkali from the pretreated cellulose samples prevents formation of extensive interchain hydrogen bonds and confirms the higher reactivity (and accessibility) of cellulose.[45] Moreover, after the pretreatment the use of never-dried cellulose samples in the esterification process has also a beneficial effect on the reactivity of cellulose.[45] The cellulose samples were esterified without any pretreatment; either no reaction occurred or a lower degree of substitution was obtained. Higher degrees of substitution at the esterification stage also lead to higher loadings of RAFT agent onto the cellulose substrate.

Synthesis of the Cellulose Ester and Cellulose-Based RAFT Agent. The hydroxyl groups of the cellulose were treated with 2-chloro-2-phenylacetyl chloride (CPAC) and converted to the corresponding thiocarbonyl-thio compound to be used as the RAFT agent for graft polymerization. The formation of cellulose 2-chloro-2-phenylacetyl chloride (cellulose-CPAC) and cellulose-based RAFT agent (cellulose-CTA) was confirmed by elemental analyses, ATR FT-IR spectroscopy, and FT-Raman spectroscopy. From the elemental analyses on duplicate cellulose-CPAC samples, 11.88 wt % (average) chlorine was detected, whereas the virgin filter paper showed almost nil (<0.3%) chlorine contents. This indicates that successful substitution of OH group by CPAC (about 37%) has occurred in the first step. Elemental analyses of cellulose-CTA (duplicate samples) have also demonstrated the successful loading of RAFT agent onto cellulose surface showing sulfur contents with an average of 12.15 wt %. Moreover, the chlorine content in the case of cellulose-CTA was less when compared with cellulose-CPAC. This indicates that chlorine of cellulose-CPAC has been substituted by the RAFT agent of cellulose-CTA.

Figure 1 shows the infrared spectrum of cellulose before (Figure 1a) and after (Figure 1b) the esterification process. The infrared spectrum of cellulose-CPAC shows a very strong band for the C=O group at 1747 cm^{-1}, demonstrating the successful formation of the cellulose ester. The two weak bands at 1280 and 1185 cm^{-1} are due to C−O stretch modes. The C=C stretching bands for the aromatic ring appear at 1630, 1485, and 1455 cm^{-1}. The monosubstitution pattern is recognized by the medium-strong band at 694 cm^{-1} due to out-of-plane CH bending. The C−Cl stretching vibration is observed at 728 cm^{-1}.

Further confirmation was also obtained from Raman spectroscopy (Figure 2b). The monosubstituted benzene ring is more clearly identified in the Raman spectrum by the presence of an intense band at 1004 cm^{-1} due to an in-plane ring deformation (ring breathing vibration), a medium band at 1032 cm^{-1} due to an in-plane CH bending, an intense band at 1602 cm^{-1} due to C=C stretching vibration, a weak band at 618 cm^{-1} due to

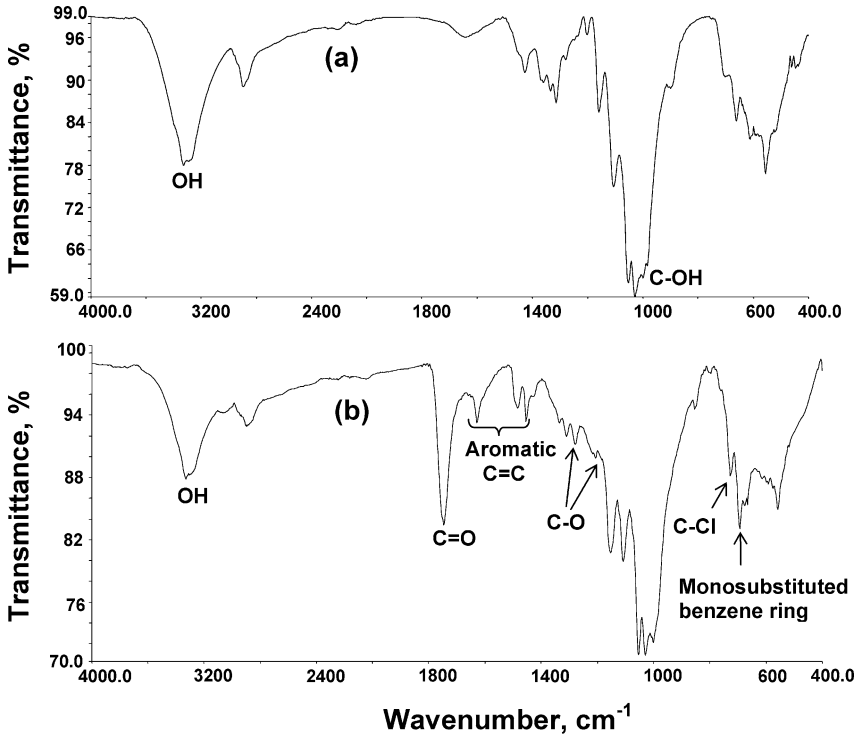


Figure 1. ATR FT-IR spectra of (a) unmodified cellulose and (b) cellulose treated with 2-chloro-2-phenylacetyl chloride (cellulose-CPAC).

in-plane ring bending mode, and a band at 3066 cm^{-1} due to the CH stretching bend. The Raman band at 850 cm^{-1} shows the C−Cl stretching vibration, and the medium intensity band at 340 cm^{-1} represents the C−C−Cl bending. Both of these bands are absent from in the Raman spectrum of the cellulose-CTA sample. Furthermore, in the case of cellulose-CTA, the Raman bands at 1234 and 651 cm^{-1} show the incorporation of C=S and C−S bonds, respectively (Figure 2a). Although they are slightly shifted to lower frequencies, an increase of intensity is observed for the peaks of monosubstituted aromatic structure at 3062, 1591, 1002, and 618 cm^{-1}, which, along with a new out-of-plane ring bending of the monosubstituted phenyl at 403 cm^{-1}, demonstrates the incorporation of an extra phenyl ring.

Graft Polymerization. A series of cellulose-*g*-poly(styrene) copolymers was prepared using RAFT polymerization. The graft ratio of poly(styrene) on the cellulose substrate was calculated by gravimetric analysis. To ensure complete removal of physically adsorbed, or loosely attached homopolymers, the samples were repeatedly washed and Soxhlet extracted with hot THF for a minimum of 36 h. The weight gain of cellulose-*g*-poly(styrene) copolymers was then compared with cellulose-CTA. Table 1 shows the increase in graft ratio with polymerization time.

Table 1 shows that the graft ratio is similar to that observed in the case of ATRP,[22] and increases regularly up to 20%. Further increase in polymerization time (samples A5, A6, and A7) or in the monomer:cellulose-CTA ratio (sample B) does not seem to affect the percentage graft ratio. A decrease in the monomer concentration, although the ratio of monomer/CTA is lower, leads to a higher (or similar) graft ratio for similar polymerization times (see samples A5 and C). This is due to the ease of diffusion of the monomer to the cellulose substrate at low monomer concentration, leading to a more efficient use of the monomer available.[46]

The spectral features of the grafted copolymers were studied by ATR FT-IR spectroscopy. Although the characteristic absorption bands of poly(styrene) appear in the same spectral regions as the bands of the cellulose-CTA samples (Figure 3c), the ATR FT-IR spectra of grafted samples (Figure 3b) show new peaks at 3057, 3024, 1600, 1492, 1452, 758, and 695 cm^{-1} which are characteristic peaks of poly(styrene) (Figure 3a). The medium to strong absorption band at 695 cm^{-1}, which represents the deformation vibration of the −CH− group of the monosubstituted benzene ring in poly(styrene), illustrates the successful grafting between cellulose and poly(styrene), as there is no intense characteristic band appearing in that spectral region for the cellulose-CTA sample. The absorption band at about 700 cm^{-1} has also been used as the main proof of grafting and quantitative determination of the poly(styrene) in cotton cellulose−poly(styrene) copolymers by Imrisova et al.[47]

Cleaving of the Poly(styrene) Chains from the Cellulose Substrate. To quantify the molecular weight and molecular weight distribution of the poly(styrene) chains that become attached to the cellulose substrate, each sample was hydrolyzed by a solution of 37% HCl. When the solution was heated to 75 °C, the unmodified cellulose sample was quickly hydrolyzed, leading to a homogeneous brown solution, while the hydrolysis of the cellulose-CTA was slower. Hydrolysis of the cellulose-*g*-poly(styrene) was not observed even after 7 days, as the hydrophobic poly(styrene) layer on the cellulose surface increased the acid resistance of the copolymer. Similar acid resistance of cotton−poly(styrene) graft copolymers has been reported by Thejappa et al.[48] To hydrolyze fully the cellulose substrate of the cellulose-*g*-poly(styrene) copolymer, a solution of 37% HCl in THF was utilized, and the reaction was stirred at 80 °C for 3 weeks. However, in most cases, the amount of cleaved poly(styrene) was too low for analysis. In the case of a ratio monomer:cellulose-CTA = 1000:1 (Sample B),

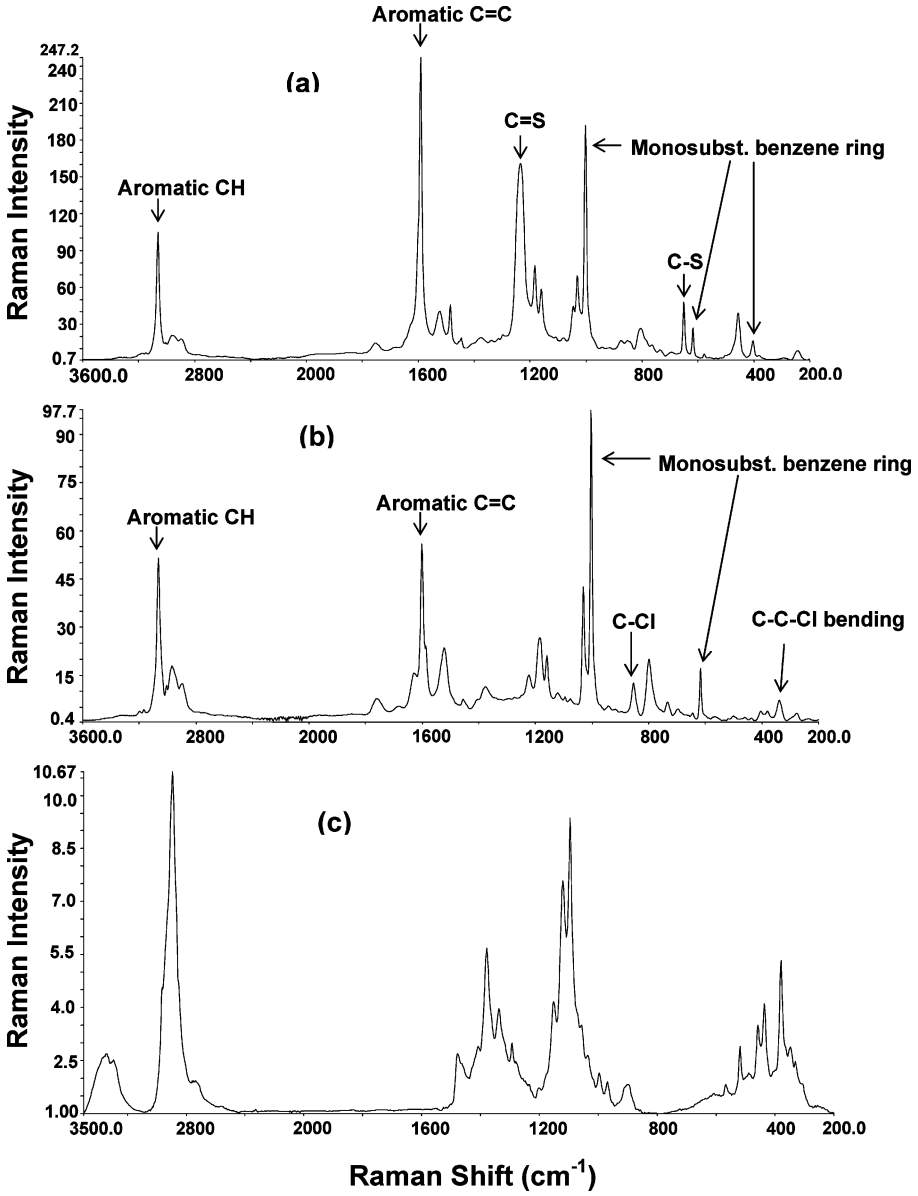


Figure 2. FT-Raman spectra of (a) cellulose treated with *S*-methoxycarbonylphenylmethyl dithiobenzoate (cellulose-CTA), (b) cellulose treated with 2-chloro-2-phenylacetyl chloride (cellulose-CPAC), and (c) unmodified cellulose.

Table 1. Graft Polymerization[a] of Styrene in the Presence of Cellulose-CTA and Gravimetric Measurements of Cellulose-*g*-Poly(styrene) Samples

sample	monomer/ cellulose-CTA/ initiator (mol)	monomer/ solvent (v/v)	time (h)	graft ratio[b] (wt %)
A1	500/1/0.1	1/1	4	11
A2	500/1/0.1	1/1	8	17
A3	500/1/0.1	1/1	16	19
A4	500/1/0.1	1/1	24	20
A5	500/1/0.1	1/1	48	21
A6	500/1/0.1	1/1	72	22
A7	500/1/0.1	1/1	96	26
B	1000/1/0.1	1/1	168	28
C	100/1/0.1	1/3	48	23

[a] Experimental conditions: solution, solvent = toluene; monomer = styrene; temperature = 60 °C (oil bath temperature); thermal initiator = 2,2′-azobis(isobutyronitrile) (AIBN); cellulose-CTA (RAFT agent) = cellulose *S*-methoxycarbonylphenylmethyl dithiobenzoate (cellulose-MCPDB). [b] Graft ratio was calculated according to eq 1.

cleaved poly(styrene) chains were successfully analyzed by SEC and values of M_n = 21 000 g/mol and PDI = 1.11 were obtained (Figure 4). Although this result demonstrates the poor efficiency of monomer grafting (assuming all polymeric chains are attached to the cellulose substrate and the process is living, M_n = 21 000 g/mol corresponds to a conversion of ~20%), they clearly show the excellent control over the molecular weight distribution of the chains that grow from the cellulose substrate.

Thermal Analyses. DSC and TGA were used to verify the success of the grafting process. Table 2 shows that a poly(styrene) (M_n = 12 800 g/mol) sample, prepared via the RAFT method, shows one thermal transition at around 93 °C corresponding to the glass transition temperature (T_g) of this polymer. The glass transition temperature of cellulose-*g*-poly(styrene) samples was also identified closer to 100 °C. Since the T_g value of poly(styrene) is dependent on its molecular weight, the cellulose-*g*-poly(styrene) samples may have a higher molecular weight than 12 800 g/mol, confirmed by SEC analysis of the cleaved poly(styrene). The similar T_g values of the cellulose graft copolymers with different graft ratios may be explained on the basis of

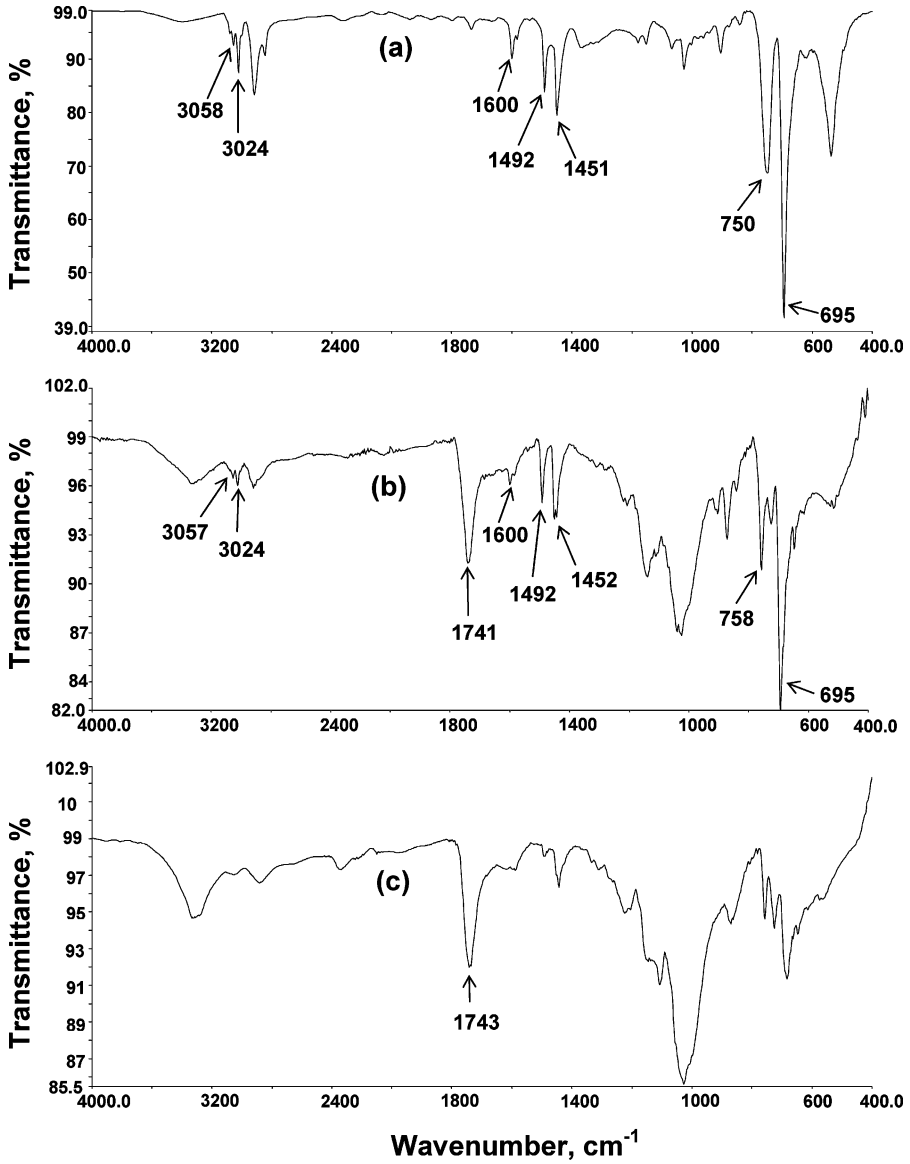


Figure 3. ATR FT-IR spectra of (a) poly(styrene); (b) cellulose-*g*-poly(styrene) (26% graft ratio), and (c) cellulose treated with *S*-methoxycarbonylphenylmethyl dithiobenzoate (cellulose-CTA).

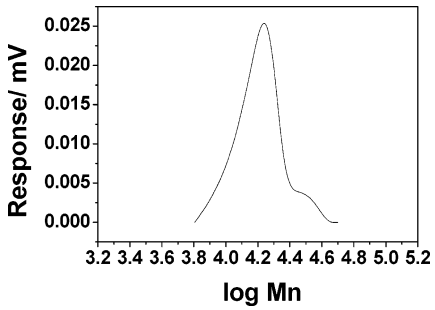


Figure 4. Size exclusion chromatogram showing molecular weight distribution of cleaved poly(styrene) from cellulose substrate; M_n = 21 000 g/mol and PDI = 1.11.

Table 2. DSC (T_g) Data for Cellulose-*g*-Poly(styrene) Samples and Linear Poly(styrene) Calculated by TA Instruments Thermal Advantage Universal Analysis Software

sample	onset temp (°C)	end temp (°C)	inflection (midpoint) temp (T_g) (°C)
A1	99	102	100
A4	98	102	100
A7	99	102	100
poly(styrene)[a]	89	96	93

[a] Poly(styrene) prepared by RAFT polymerization method; number-average molecular weight = 12 800 g/mol and polydispersity index = 1.10.

degree of polymerization (DP value). The target DP for all three samples was similar; hence, the molecular weights of attached poly(styrene) may also be similar for these samples.

Figure 5 shows the DSC curves (from room temperature to 500 °C) of cellulose-CTA and of copolymer samples of different graft ratios. An exothermic enthalpy change at 252 °C was observed in the cellulose-CTA sample (Figure 5a) and was associated with the cleavage of the *S*-methoxycarbonylphenylmethyl dithiobenzoate CTA from the cellulose surface, and the formation of thermolysis byproducts such as odorous carbon disulfide. This was confirmed by the DSC plot of the free *S*-methoxycarbonylphenylmethyl dithiobenzoate CTA (not immobilized onto the cellulose surface), which showed an exothermic peak at 238 °C. These results are in good agreement with the results recently published by Postma et al.,[50] who observed the elimina-

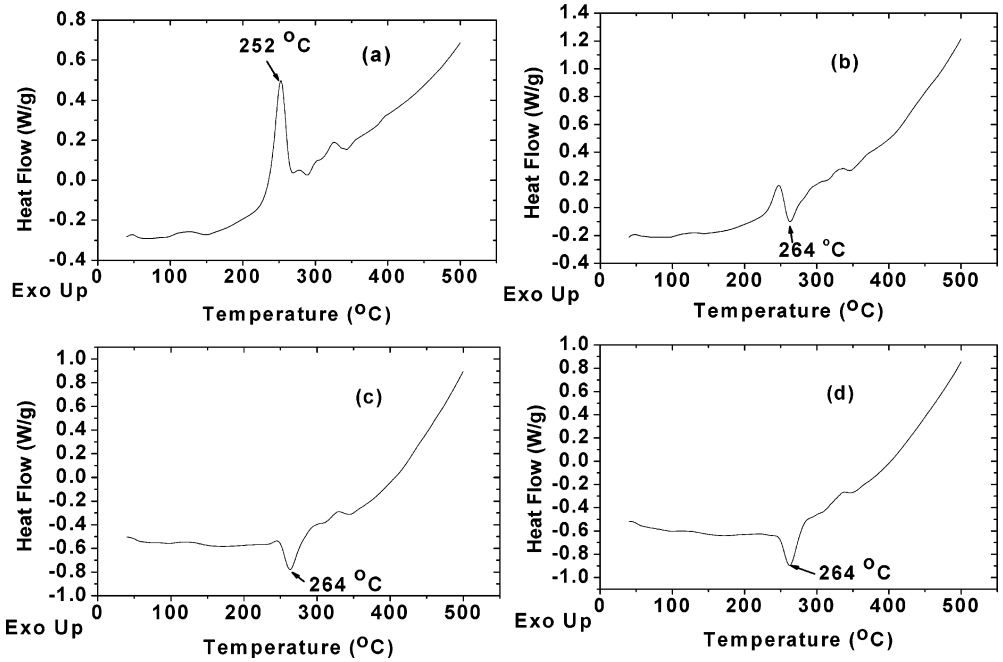


Figure 5. DSC thermograms of (a) cellulose treated with *S*-methoxycarbonylphenylmethyl dithiobenzoate (cellulose-CTA); (b) cellulose-*g*-PS, 11% graft ratio; (c) cellulose-*g*-PS, 20% graft ratio; and (d) cellulose-*g*-PS, 26% graft ratio.

tion of the thiocarbonyl-thio moiety via the thermolysis of RAFT-synthesized polymers at 210−250 °C. Furthermore, the exothermic peak at 238 °C observed for the free *S*-methoxycarbonylphenylmethyl dithiobenzoate RAFT agent is shifted to a higher temperature (252 °C, Figure 5a) in the case of cellulose-supported CTAs, due to the covalent attachment of the chain transfer agent to the cellulose. There is no exothermic enthalpy change observed at this temperature range for unmodified cellulose. Moreover, this exothermic peak gradually decreased with the increase in the samples of higher graft ratio owing to a dilution effect. The cellulose-*g*-poly(styrene) samples also show an endothermic peak around 264 °C that may be correlated to the melting transition range of poly(styrene). Pure homopoly(styrene) exhibits a melting point at 240 °C, and this temperature is shifted to a higher temperature due to grafting of poly(styrene) onto the cellulose. This peak was not observed in the DSC plot of the cellulose-CTA sample. A physical mixture of homopoly(styrene) and cellulose-CTA showed a different DSC thermogram from those obtained from the cellulose-*g*-poly(styrene) copolymers and confirmed the true covalent grafting of poly(styrene) onto the filter paper (see Supporting Information).

Thermogravimetric (TGA) analysis was used to study the decomposition pattern and the thermal stability of the grafted cellulosic copolymers. Figure 6 shows the thermograms of cellulose-CTA, poly(styrene), and cellulose copolymers with different graft ratios. Poly(styrene) decomposes in the range of 350−460 °C and yields a very small amount of residual mass (0.52 wt %), while the decomposition of cellulose ranges from 225 to 375 °C and yields a higher amount of residual mass (18.23 wt %), mainly due to the formation of levoglucosan.[49]

Grafted samples show a two-step-degradation profile, with the first degradation step due to cellulose, which triggers the degradation of poly(styrene). An increase in degradation temperature for the second step was observed on increase of the poly(styrene) content. Furthermore, the grafted samples yielded a residual mass that decreased with the poly(styrene) content. In the case of the 26% grafted sample, the residual mass was 11.75 wt %. Similar behavior of grafted cellulose has been observed in the past, and illustrated the covalent attachment of the poly(styrene) chains to cellulose.[51]

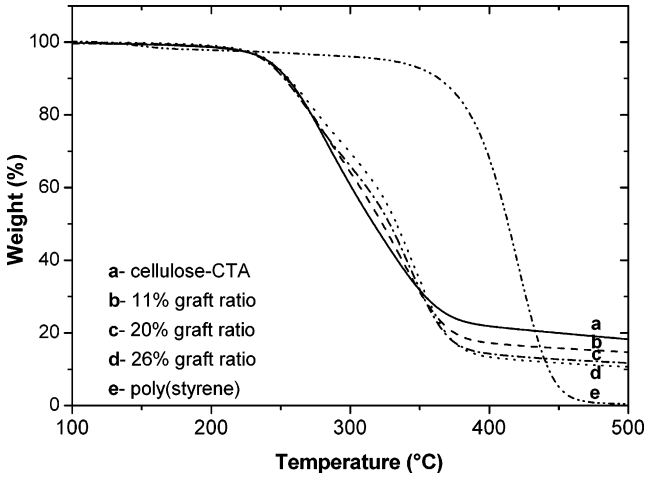


Figure 6. TGA curves of cellulose treated with *S*-methoxycarbonylphenylmethyl dithiobenzoate (cellulose-CTA), poly(styrene) (PS), and cellulose-*g*-PS at various graft ratios.

Assessment of the Hydrophobicity of Cellulose-*g*-poly(styrene) Graft Copolymers. The degree of hydrophobicity of the cellulose-*g*-poly(styrene) copolymers was estimated by static contact angle measurements. The unmodified filter paper and the cellulose-CTA substrates adsorbed water very quickly, rendering measurement of the contact angle impossible. However, the cellulose-*g*-poly(styrene) sample, with a graft ratio of 11%, adsorbed water slowly (complete adsorption taking 5 min), while the samples with graft ratios of 20% and 26% did not adsorb water at all. The results suggest that the hydrophobicity of the graft copolymers increased with increasing percentage of grafting. Static contact angle values for all the graft copolymers were found to be around 130°, thus demonstrating the

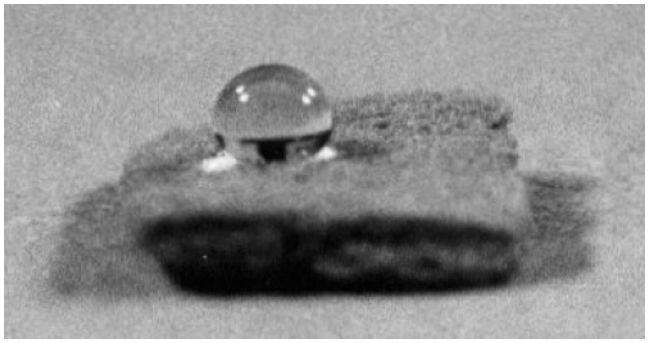


Figure 7. Water droplet on cellulose-*g*-poly(styrene) copolymer (26% graft ratio) surface.

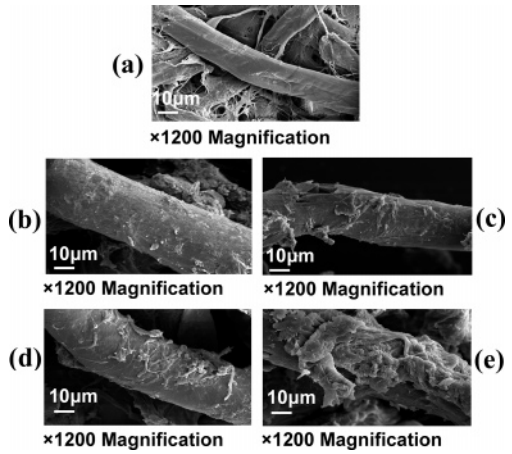


Figure 8. SEM photomicrographs of (a) unmodified cellulose fiber; (b) cellulose-CTA; (c) cellulose-*g*-poly(styrene), 11% graft ratio; (d) cellulose-*g*-poly(styrene), 20% graft ratio; and (e) cellulose-*g*-poly(styrene), 26% graft ratio.

increase in hydrophobicity of the poly(styrene)-modified cellulose surface. A similar contact angle value was observed after grafting of poly(methyl acrylate) onto a cellulose surface via ATRP.[23] Figure 7 illustrates the hydrophobic nature of the cellulose-*g*-poly(styrene) copolymer with a graft ratio of 26%.

Scanning Electron Microscopy. SEM micrographs of unmodified cellulose, cellulose-CTA, and cellulose-*g*-poly(styrene) copolymers (of different graft ratios) are shown in Figure 8 from which it is evident that the grafted cellulose has different structural features compared with the unmodified cellulose and cellulose-CTA. It should be noted that the grafting occurred mainly at the surface of the cellulose and the surface coverage of the cellulose fibers of graft copolymers increased with increasing graft ratio.

Conclusions

A novel approach to the synthesis of cellulose-*g*-poly(styrene) copolymers, via the RAFT process, has been demonstrated. An increase in reaction time leads to an increase in graft ratio, as characterized by the increase in the mass of cellulose-*g*-poly(styrene) copolymers compared to the cellulose-CTA samples, by the observation of new bands characteristics of the poly(styrene) by ATR FT-IR analyses, by the thermal behavior of the modified cellulose, and by SEM micrographs. Contact angle measurements revealed a dramatic increase in the hydrophobicity of the cellulose surface after RAFT polymerization. This reduced hydrophilicity of cellulose fiber is an essential criterion for use in hydrophobic composites. The SEC analysis of the cleaved poly(styrene) grafts from the cellulose surface also demonstrated that the molecular weight distribution of the grafted poly(styrene) chains was narrow. However, the RAFT graft polymerization conditions need optimization to obtain higher graft ratios and graft efficiency, and a more uniform distribution of poly(styrene) chains on the cellulose fibers.

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Supporting Information Available: DSC and TGA curves; tables summarizing the grafting polymerization results. This material is available free of charge via the Internet at http://pubs.acs.org.

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