Polymer 50 (2009) 973–982

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

RAFT-mediated polymerization and grafting of sodium 4-styrenesulfonate from cellulose initiated via γ-radiation

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ARTICLE INFO

Article history:
Received 9 August 2008
Received in revised form
10 November 2008
Accepted 13 December 2008
Available online 24 December 2008

Keywords:
Cellulose
Grafting
Gamma-irradiation

ABSTRACT

Ambient temperature (20 °C) reversible addition fragmentation chain transfer (RAFT) polymerization of sodium 4-styrenesulfonate (SS) conducted directly in aqueous media under γ-irradiation at different dose rates (0.09, 0.03 and 0.02 kGy h^{-1}) proceeds in a controlled fashion (typically, $M_w/M_n < 1.25$) to near quantitative conversions via 4-cyanopentanoic acid dithiobenzoate (CPADB) mediation. By applying CPADB modified cellulose as a macro chain transfer agent, a graft copolymer with SS was prepared in aqueous media under γ-irradiation. RAFT mediated graft polymerizations provided copolymers with higher graft frequencies compared to those obtained by conventional methods. Thermally initiated grafting of SS from a CPADB-functionalized cellulose surface at 70 °C was also studied which resulted in a reduced graft frequency in comparison to γ-initiated ones.

1. Introduction

Most conventional polymers do not combine the desired bulk and surface properties necessary for specific purposes such as biomedical applications [1]. This has sparked considerable effort in research aiming to develop surface modification techniques in order to achieve new materials from known and commercially available polymers having desirable bulk properties like thermal stability, elasticity, and permeability, in conjunction with advantageous newly tailored surface properties such as biocompatibility, biomimicry, and adhesion. Surfaces can be modified using a range of techniques like the adsorption of Langmuir–Blodgett layers [2], the layer-by-layer deposition technique [3,4] or the grafting from substrates method [5–7]. Especially the grafting from technique results in polymer brushes with a high stability against erosion [8,9]. Reversible addition fragmentation chain transfer (RAFT) polymerization [10–14] is one of the most prominent controlled/living free-radical polymerization methods used for the synthesis of well-defined, low polydisperse polymers. RAFT has been successfully applied to grow well-controlled brushes from polymer surfaces to alter the surface properties of several materials [12,15–23]. It also has been reported that immobilization of RAFT agents on the surfaces enables an easy control on the thickness and density of the polymer grafts [5].

The synthesis of cellulose-based materials with tuneable surface properties is of great interest due to a wide range of potential applications as well as the important inherent characteristics of cellulose (i.e. availability as a renewable natural source, ease of surface modification, low cost, good mechanical properties, recyclability and biodegradability) [24–26]. Therefore, researchers are striving continuously to optimize the hydrophobicity, wettability and adhesion properties of cellulose-based natural fibres through immobilization of suitable chemical functional species including grafting of polymers to achieve improved performance.

Previously, we have reported that RAFT polymerization can be performed at ambient temperature using γ-irradiation as source of initiation [27–32]. We also demonstrated that γ-initiated RAFT polymerization is an efficient tool to graft polymers from polymeric surfaces [33–35]. In addition, we proved that the molecular weights

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doi:10.1016/j.polymer.2008.12.027

of free and grafted polymers are almost identical in a RAFT mediated graft polymerization [36]. The present study reports the RAFT homo and graft (from RAFT agent functionalized cellulose) polymerizations of sodium 4-styrenesulfonate (SS) in aqueous medium by employing γ-irradiation or – alternatively – a thermal azo-initiator as the sources of initiation. To the best of our knowledge this is the first report detailing the γ-initiated RAFT polymerization of SS and the investigation of the grafting of this monomer from cellulose using the RAFT technique. It is also the first study using a RAFT agent modified substrate in γ-initiated graft polymerizations instead of a pristine surface. An added advantage of these polymerizations is that they occur in an environmentally friendly solvent like water and – for the γ-initiated ones – at ambient temperatures.

2. Experimental part

2.1. Materials

All chemicals and solvents where purchased from Sigma–Aldrich, Acros, and Fluka at the highest available purity and were used as-received unless otherwise noted. The chain transfer agents (CTAs) used in this study; 4-cyanopentanoic acid dithiobenzoate (CPADB) and 3-benzylsulfanylthiocarbonylsulfanyl propionic acid (BPATT) were prepared according to the procedures described elsewhere [37,38]. Whatman No. 1 filter paper was used as cellulose substrate due to its high cellulose content (98% α-cellulose), lesser amount of impurities, and ease of chemical modification [39].

2.2. Size exclusion chromatography (SEC) analysis

The molecular weight distributions were analyzed by SEC in water (0.1 mol L^{-1} NaN_3, 0.01 mol L^{-1} NaH_2PO_4, pH = 6.3) at 35 °C (flow rate: 1 mL min^{-1}) using a Gynkotek model 300 pump, an ERC column oven, and a Bischoff 8110 refractive index detector. The system was equipped with a Polymer Laboratories (PL) PLaquagel-OH 8 μm bead-size guard column (50 × 7.5 mm^2) followed by two 300 × 7.5 mm^2 columns; a PLaquagel-OH mix 8 μm and a PLaquagel-OH 30.8 μm. Primary calibration was performed with low polydispersity poly(sodium 4-styrenesulfonate) (PSS) standards.

2.3. X-ray photoelectron spectroscopy (XPS) measurements

XPS measurements were carried out on a VG ESCALAB220i-XL surface analysis instrument with a mono-chromatized Al Kα X-ray source (1486.6 eV photons) at a constant dwelling time of 100 ms for several scans and a pass energy of 20 eV for region scan spectra and 100 eV for survey scan spectra. The anode current was 20 mA. The pressure in the analysis chamber was maintained at 2×10^{-9} Torr or lower during each measurement. The cellulose samples were mounted on the standard sample studs by means of double-sided adhesive tapes. The core-level signals were obtained at the photoelectron takeoff angle (α, with respect to the sample surface) of 90°. All binding energies (BEs) were referenced to the C1s hydrocarbon peak at 285 eV. In peak synthesis, the line width (full width at half-maximum) for the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak-area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to ±5%. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries.

2.4. Raman spectroscopy (FT-Raman)

Raman spectra of the samples were recorded in the frequency range of 50–3600 cm^{-1} using a Bruker IFS 66 spectrometer with a FRA 106/S module. The laser source was a Nd:YAG laser.

2.5. Thermogravimetric analysis (TGA)

Thermal decomposition properties of polymers were recorded using a Perkin–Elmer thermogravimetric analyzer (Pyris 1 TGA). Analyses were conducted over the temperature range from 0 to 750 °C with a programmed temperature increment of 10 °C min^{-1} under N_2 atmosphere.

2.6. Pretreatment of cellulose

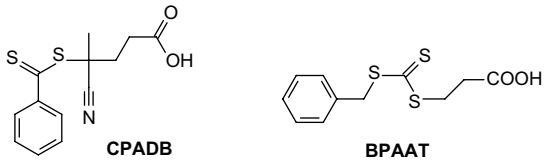
Whatman No. 1 filter paper was cut into approximately 1 cm × 0.4 cm dimensions with an average weight of about 0.01 g. Pieces of cellulose were first washed with ethanol, subsequently immersed into an aqueous solution (150 mL) of 10 wt.% NaOH to break down the extensive hydrogen bonding between the OH groups of cellulose and to open up the ordered regions, so that the reagents could easily penetrate inside the cellulose substrate. The samples were placed on a shaker and shaken for 24 h at an ambient temperature. The swollen cellulose samples were repeatedly washed with absolute ethanol until a neutral solution was achieved. The use of ethanol for washings prevents the formation of extensive interchain hydrogen bonds [40] and results in a higher reactivity of cellulose towards esterification reaction used for the immobilization of CPADB. Ethanol in the cellulose samples was then displaced by dichloromethane (DCM; 10 × 50 mL). The cellulose samples were directly used for the next step (esterification) without any drying.

2.7. Immobilization of 4-cyanopentanoic acid dithiobenzoate (CPADB) to the cellulose

Approximately 0.05 g pretreated cellulose (number of moles of active hydroxyl groups = 0.96 mmol) was immersed into a reaction vessel containing 4-cyanopentanoic acid dithiobenzoate (0.51 g, 1.82 mmol) dissolved in 10 mL of DCM. *N*,*N*′-Dicyclohexylcarbodiimide (DCC; 0,4 g, 2 mmol) was dissolved in 5 mL DCM and added to the cellulose containing reaction vessel at room temperature. 4-(Dimethylamino)pyridine (DMAP; 0.22 g, 1.80 mmol) was dissolved in DCM (10 mL) and slowly added to the reaction mixture. The reaction mixture was left on a shaking device for 48 h at room temperature. Following the completion of the reaction, the samples were thoroughly washed with DCM, THF, THF:water (1:1), water, and methanol. Finally, the pinkish product was placed in a vacuum oven at 60 °C to dry overnight. The modified cellulosic product is termed CPADB-immobilized cellulose in the rest of this paper. After the immobilization of CPADB to the cellulose, the mass increase due to esterification was 14%.

2.8. Polymerization

In a typical homopolymerization, the reaction solution is prepared by dissolving sodium 4-styrenesulfonate (SS) with chain transfer agents (CTAs); CPADB or BPATT (Scheme 1) in a mixture of pure water and ethanol (water/EtOH = 93:7 v/v). A small amount of EtOH was required to allow complete dissolution of the RAFT agents. The monomer concentration was 1 mol L^{-1} and in most cases the monomer/CTA ratio in solution was such that a theoretical molecular weight of 80,000 g mol^{-1} at 100% conversion was expected, i.e. [SS]/[CPADB] = 387 (see Table 2 for other monomer/



Scheme 1. Structures of RAFT agents employed in the present study.

CTA ratios used in this work). After complete dissolution of the reactants, the stock solution was divided into 10 mL aliquots and transferred to glass sample vials. The vials were capped with rubber septa and deoxygenated by purging with nitrogen gas for 20 min each. In graft polymerizations, CPADB-immobilized cellulose (≈0.01 g) was also added to vials containing the polymerization mixture before degassing. In the case of initiation by γ-irradiation, samples were placed in a shielded irradiation room with a ^{60}Co source at an ambient temperature and different dose rates (0.09, 0.03 and 0.02 kGy h^{-1}). Samples were taken from the chamber at different time intervals and PSS was purified by precipitation into a methanol/acetone solution followed by filtration before SEC analysis. Thermally initiated polymerizations were achieved using 4,4′-azobis(4-cyanopentanoic acid) as the thermal initiator for the generation of radicals instead of γ-radiation. The molar ratio of CPADB to initiator was 5:1. Following the degassing process, polymerization solutions were heated in an oil-bath at 70 °C. Polymerizations were terminated by rapid cooling of the samples in an ice bath. Following the precipitation of the polymer into methanol/acetone mixture and isolation by filtration, PSS was analyzed by SEC. Synthesized cellulose-*g*-PSS copolymers were repeatedly washed with water to remove surface contamination: Each cellulosic copolymer was subsequently placed in a bottle, and 75 mL of pure water was added. The bottles were placed on a shaker and shaken for several days. The solvent was changed every day and this process was repeated until no homo-PSS could be identified in the rinsing solution via SEC analysis. After removal of surface contaminations, cellulose-*g*-PSS samples were dried to a constant weight under vacuum at 45 °C. The graft ratio (*G*, wt.%) was calculated using the following equation:

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

where W_1 (g) is the weight of the CPADB-immobilized cellulose and W_2 (g) is the dry weight of the cellulose-*g*-PSS sample. Conversion (%) was taken as the fraction of the monomer that polymerized and was determined via ^{1}H NMR spectroscopy (in D_2O) using the relative integration of peaks associated with the monomer in relation to those associated with the polymer. The monomer peak chosen as reference was the vinylic peak at $\delta = 5.89$–5.83 ppm (dd, 1H), which was compared to the backbone protons of polymer at 0.8–2.0 ppm (m, 3H).

The graft frequency (G.F.), i.e. number of grafted PSS chains per cellulose chain, was calculated using the following equation:

$$\text{G.F.} = \frac{(W_2 - W_1) \times \text{MW}_{\text{cellulose}}}{M_{\text{n,SEC}} \times W_i} \quad (2)$$

where W_i is the initial weight of pristine cellulose before any modification and grafting, $M_{\text{n,SEC}}$ is the number-average molecular weight of the free (non-grafted) PSS formed in solution and $\text{MW}_{\text{cellulose}}$ is the molecular weight of Whatman No.1 cellulose paper. We have recently verified that the molecular weights of free and grafted polymers are almost identical in a RAFT mediated graft polymerization and the molecular weight distributions of grafted polymers are very narrow [36]. Therefore, calculation of graft frequency for the grafted polymer chains using the molecular weight of free (non-grafted) polymers should be reliable. $\text{MW}_{\text{cellulose}}$ was calculated using the published value of degree of polymerization (DP) for Whatman No.1 filter paper (i.e. DP = 1521; $\text{MW}_{\text{cellulose}} = 477{,}600$ g mol^{-1}) [41]. The theoretical number-average molecular weight, M_n^{th}, was calculated according to the following equation:

$$M_n^{th} = M_{CTA} + \frac{n_m^0 \cdot M_M}{n_{CTA}^0} \cdot \text{conversion} \quad (3)$$

where M_n^{th} is the theoretical number-average molecular weight of the polymer, n_m^0, number of moles of the monomer initially present in the system, M_M, molecular weight of the monomer, n_{CTA}^0, number of moles of CTA initially present in the system and M_{CTA}, molecular weight of the CTA. It should be noted here that the number of moles of CTA on the surface of substrate was also taken into consideration in case of graft polymerizations (e.g. the overall [SS]/[CPADB] ratio decreased to 324 in graft polymerizations while this value was 387 in solution due to the immobilized CPADB to the cellulose surface), see Supporting information for the details of this calculation.

2.9. Cleaving of PSS chains from cellulose backbone

Two transesterification procedures (i.e. acid and base catalyzed) were examined to cleave the PSS chains from the cellulose backbone. In a typical base catalyzed hydrolysis experiment, 0.04 g cellulose-*g*-PSS sample were immersed into a round bottom flask containing 15 mL of KOH (1.5 M solution in ethanol). 3 mL of water was also added to the mixture to help the solubilization of the PSS grafts. The reaction mixture was refluxed for 72 h. After the completion of the reaction, 10 mL of water was added to the flask and the solid cellulose substrate was removed from the mixture, subsequently the solvents were evaporated. The solid was washed with methanol to remove the excess of KOH, the remaining product (cleaved PSS grafts) was separated by filtration. In the acid base hydrolysis, 0.04 g cellulose-*g*-PSS sample was immersed into a round-bottomed flask containing 15 mL of 1.5 M HCl aqueous solution. The flask was stirred at 90 °C for 72 h. The reaction mixture was filtered to separate the solid cellulose particles, and the HCl aqueous solution was removed by evaporation.

3. Results and discussion

3.1. Radiation-induced RAFT polymerization of sodium 4-styrenesulfonate mediated via CPADB

The effects of the irradiation dose and the dose rate on the γ-initiated RAFT polymerization of SS were investigated. Table 1 summarizes the homopolymerization of SS (CPADB-immobilized cellulose was not added to the medium) in water–EtOH (93:7 v/v) mixture at room temperature and [SS]/[CPADB] = 387.

The controlled fashion of the polymerization at all dose rates is demonstrated in Table 1 and corresponding figures (Supporting information; Fig. S1), where the linear evolution of the number-average molecular weight, M_n, with conversion (which is expected for a controlled/living polymerization), is depicted. Furthermore, the PDI remains in the range of 1.13–1.26, well below the theoretical lower limit of 1.5 for conventional free-radical polymerization, throughout the duration of the polymerization at all dose rates studied. The agreement with the theoretical number-average molecular weight, $M_{n,theor}$, is also good. It should be mentioned here that the experimental molecular weights are generally higher than the corresponding theoretical values, especially at the beginning of polymerizations. The reason for this may be that the

Table 1
Reversible addition fragmentation chain transfer homopolymerization of sodium 4-styrenesulfonate in water–EtOH (93:7 v/v) mixture by γ-initiation at different dose rates and room temperature with CPADB as RAFT agent, [SS] = 1 mol L^{-1}, [SS]/[CPADB] = 387:1.

Entry	Dose rate (kGy h^{-1})	Time (h)	Convn[a] (%)	$M_{n,SEC}$[b] (g mol^{-1})	$M_{n,theor}$[c] (g mol^{-1})	PDI[b]
1	0.02	19	25	38,800	20,230	1.17
2	0.02	46	69	63,600	55,340	1.21
3	0.02	59	87	72,600	69,700	1.24
4	0.02	87	95	80,900	76,090	1.25
5	0.02	105	98	84,500	78,480	1.26
Control[d]	0.02	3	10	419,300	–	2.15
Control[d]	0.02	45	98	207,100	–	2.46
6	0.03	7	4	12,400	3470	1.13
7	0.03	19	52.6	56,300	42,250	1.21
8	0.03	46	91.5	76,300	73,300	1.20
9	0.03	59	96	79,500	76,890	1.25
Control[d]	0.03	3	14	453,000	–	1.58
Control[d]	0.03	45	>99	428,300	–	1.69
10	0.09	7	11	21,500	9060	1.15
11	0.09	19	82	70,600	65,710	1.24
12	0.09	46	98	73,400	78,480	1.14
13	0.09	59	99	74,200	78,560	1.18
Control[d]	0.09	3	21	489,500	–	1.82
Control[d]	0.09	19	>99	357,900	–	1.78

[a] Monomer conversion was determined via ^{1}H NMR spectroscopy.
[b] Number-average molecular weight, M_n, and polydispersity indices, PDI, determined via size-exclusion chromatography, SEC, using water as eluent with poly (sodium 4-styrenesulfonate) (PSS) standards.
[c] Theoretical number-average molecular weight, $M_{n,theor}$, was calculated from the monomer conversion using Eq. (3).
[d] Conventional homopolymerization results of SS (1 mol L^{-1}) initiated via γ-irradiation in water–EtOH (93:7 v/v) at room temperature.

establishment of the RAFT equilibrium is slow, while the calculation of theoretical molecular weight is based on a fast establishment of the main RAFT mechanism [42]. In addition to the RAFT-mediated polymerization, conventional polymerizations were also achieved at all dose rates studied (denoted as control in Table 1) and results clearly show the uncontrolled fashion of the polymerization in the absence of CPADB.

Fig. 1 depicts the first-order time–conversion plots at the studied dose rates – ranging from 0.02 to 0.09 kGy h^{-1} – which indicates an inhibition period at the beginning. Such inhibition periods are sometimes observed during a RAFT polymerization process, and may be caused by slow fragmentation of intermediate radicals as evidenced by experimental data [43] and *ab initio*

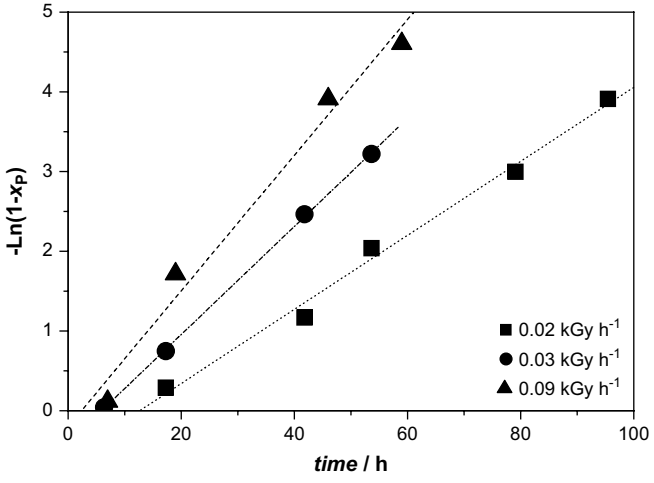


Fig. 1. Pseudo-first-order conversion vs. time plots at different dose rates for γ-initiated RAFT polymerization of SS (1 mol L^{-1}) in water–EtOH (93:7 v/v) at [SS]/[CPADB] = 387:1 and room temperature, X_p is the monomer conversion.

Table 2
Influence of the monomer/CPADB ratio on the RAFT homopolymerization of SS in water–EtOH (93:7 v/v) mixture, initiated by γ-irradiation (0.02 kGy h^{-1}) at room temperature with CPADB as RAFT agent, [SS] = 1 mol L^{-1}.

[SS]/[CPADB]	Convn[a] (%)	$M_{n,SEC}$[b] (g mol^{-1})	$M_{n,theor}$[c] (g mol^{-1})	PDI[b]
193	86	40,300	34,500	1.14
290	81	57,700	48,700	1.17
484	90	105,200	90,100	1.25

[a] Monomer conversion was determined via ^{1}H NMR spectroscopy.
[b] Number-average molecular weight, M_n, and polydispersity indices, PDI, determined via size-exclusion chromatography, SEC, using water as an eluent with poly (sodium 4-styrenesulfonate) (PSS) standards.
[c] Theoretical number-average molecular weight, $M_{n,theor}$, was calculated from the monomer conversion using Eq. (3).

calculations [44]. McCormick and coworkers [45] and some other groups [46,47], offered an alternative explanation of inhibition, which is the slow reinitiation of the initial RAFT agent leaving group. Fig. 1 shows that increasing the dose rate leads to an increase in the polymerization rate due to the higher concentration of radicals generated. Furthermore, Fig. 1 also indicates that the inhibition period becomes shorter at higher dose rates indicating a faster establishment of the main RAFT equilibrium for CPADB. Inhibition of the polymerization becomes more evident at lower dose rates.

The influence of the monomer/CPADB ratio was also studied at 0.02 kGy h^{-1}. As can be seen from Table 2, high molecular weight and well-defined PSS with low PDI values were obtained (at a comparable conversion) by increasing the monomer/CPADB ratio. All these results indicate the controlled fashion of the PSS RAFT polymerization under γ-radiation with CPADB as RAFT agent.

3.2. Radiation-induced RAFT polymerization of sodium 4-styrenesulfonate mediated via BPATT

The choice of the chain transfer agent (CTA) for any particular monomer is extremely important in controlled polymerization. RAFT agents must include a good leaving group (R) that is able to reinitiate polymerization and a Z-group that strongly influences the stability of the intermediate RAFT macroradical species. For the RAFT mechanism to work, it is desirable to attain fast rates for both addition of a given radical species to the C=S double bond and fragmentation of the intermediate radical species (producing R) relative to the rate of propagation. Fast rates of addition can be achieved when the Z species has a stabilizing effect on the intermediate radical, such as a phenyl group. BPATT mediated RAFT homopolymerization results of SS given in Table 3 indicate that

Table 3
Reversible addition fragmentation chain transfer homopolymerization of sodium 4-styrenesulfonate (SS) in water–EtOH (93:7 v/v) mixture by γ-initiation (0.02 kGy h^{-1}) at room temperature with BPATT as RAFT agent. [SS] = 1 mol L^{-1}, [SS]/[BPATT] = 387:1.

Time (h)	Convn[a] (%)	$M_{n,SEC}$[b] (g mol^{-1})	$M_{n,theor}$[c] (g mol^{-1})	PDI[b]
7	5	39,800	4260	1.89
11	13	66,500	10,600	1.48
27	37	70,500	29,800	1.62
39	63	77,800	50,500	1.51
54	84	90,100	67,300	1.52
67	98	84,900	78,500	1.64
97	98	87,300	78,500	1.58

[a] Monomer conversion was determined via ^{1}H NMR spectroscopy.
[b] Number-average molecular weight, M_n, and polydispersity indices, PDI, determined via size-exclusion chromatography, SEC, using water as eluent with poly (sodium 4-styrenesulfonate) (PSS) standards.
[c] Theoretical number-average molecular weight, $M_{n,theor}$, was calculated from the monomer conversion using Eq. (3).

there are significant differences in the efficiency of the two CTAs to mediate the RAFT polymerization of SS in aqueous media; BPATT mediated RAFT polymerization yields homopolymers with quite broad molecular weight distributions (PDI changes in the range of 1.48–1.89) and average molecular weights significantly higher than the theoretical values especially until approximately 30% monomer conversion. Moreover, the change of M_n with conversion is not linear. On the other hand, the usage of BPATT significantly suppresses the increase of molecular weight (compare the results in Table 3 with the conventional polymerizations in Table 1). These results show that BPATT is not efficient enough to establish the RAFT mechanism for the polymerization of SS; therefore an uncontrolled polymerization takes place in the case of BPATT as RAFT agent.

The first employed RAFT agent, 4-cyanopentanoic acid dithiobenzoate (CPADB), yields a tertiary radical whereas the latter, 3-benzylsulfanylthiocarbonylsulfanyl propionic acid (BPATT), gives a primary radical species upon fragmentation. Therefore, the rate of fragmentation of the intermediate radical species (producing R•) is expected to be faster in the case of CPADB due to the inherent stability of the radicals formed. Moreover, the rate for addition for a given radical species to the C═S double bond is also expected to be higher for CPADB since the Z group of this RAFT agent has a stabilizing effect, i.e. phenyl group, on the intermediate radical. Due to the cooperative effect of the above aspects the overall polymerization tendency was obviously less controlled in the case of BPATT, as a consequence the grafting reactions were not performed using this RAFT agent in the present work.

3.3. Immobilization of 4-cyanopentanoic acid dithiobenzoate (CPADB) to cellulose surface

Immobilization of the RAFT agent onto the cellulose substrate was achieved by the esterification of 4-cyanopentanoic acid dithiobenzoate (CPADB) with the hydroxyl groups of the cellulose for 48 h at room temperature. The attachment of the RAFT agent to a solid support can be performed using either the R-group approach (the RAFT agent is attached to the support via the leaving and re-initiating R group), or the Z-group approach (the RAFT agent is attached to the support via the stabilizing Z group) [48,49]. R-designed attachments allow the termination of two macro-radicals on the surface and detachment of the RAFT agent during the polymerization which may result in the loss of immobilized functionalities [22,38]. On the other hand, the Z-group approach prevents these side reactions, but suffers from hindrance problems [5,38]. In this study, the RAFT agent (CPADB) was attached to the cellulose fibre surface via its R group in order to form a cellulose-supported macro chain-transfer agent (Scheme 2).

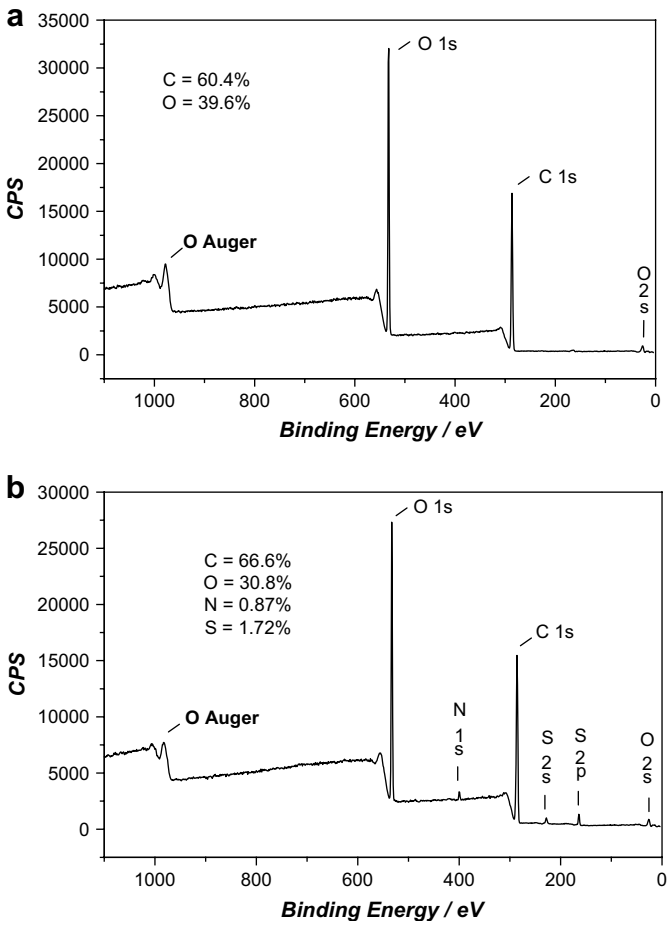
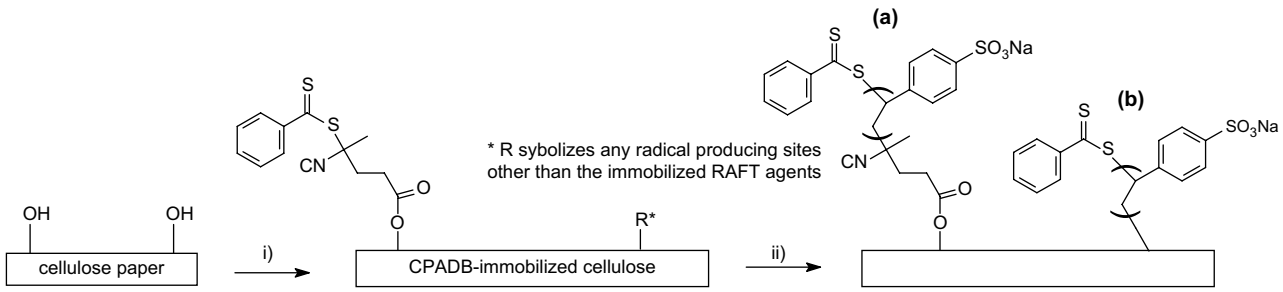


Fig. 2. XPS survey wide scan of (a) native cellulose, (b) CPADB-immobilized cellulose.

The attachment of CPADB to the surface was confirmed by XPS, Raman and TGA studies. The surface compositions of pristine and CPADB immobilized celluloses were investigated by XPS (Fig. 2a and b). The surface chemical compositions calculated using the peak areas of the XPS spectra are inserted to the survey wide scans. As can be seen from these values, the amount of carbon atoms for CPADB immobilized cellulose increases from 60.4% to 66.6% whereas the amount of oxygen atoms decreases from 39.6% to 30.8%. Furthermore, new bands at 399.8, 227.8 and 163.7 eV appeared as shown in Fig. 2b, which correspond to the N1s, S2s and S2p peaks of the immobilized CPADB on the surface, respectively. The Raman spectrum of CPADB-immobilized cellulose (Fig. 3) also



Scheme 2. Formation of poly(sodium 4-styrenesulfonate) grafts on cellulose. Conditions: (i) CPADB, DCC, DMAP and DCM; (ii) sodium 4-styrenesulfonate, CPADB and γ-irradiation or 4,4′-azobis(4-cyanopentanoic acid) at 70 °C. Chain (a) symbolises a PSS graft grown via an immobilized CPADB which can be cleaved by transesterification reactions whereas chain (b) is the representative of a chain grafted via any other radical source.

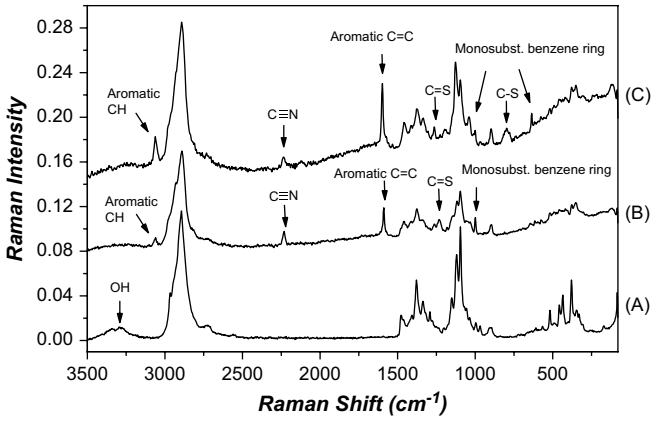


Fig. 3. Raman spectra of (A) native cellulose, (B) CPADB-immobilized cellulose and (C) cellulose-*g*-PSS copolymer with 15% graft ratio.

confirms the successful attachment of the RAFT agent to cellulose; the peak at 2232 cm^{-1} is attributed to the C≡N group of CPADB [50]. The peaks at 3060, 1591 and 997 cm^{-1} correspond to the aromatic CH, aromatic C=C and monosubstituted benzene ring, respectively [6]. The C=S band [51] observed at 1226 cm^{-1} confirms the attachment of CPADB (see Scheme 1 for the structure of CPADB). It should be mentioned that Raman measurements were repeated for different regions of the functionalized surface, and the results showed that the immobilized RAFT agent is distributed uniformly on the cellulose surface. TGA was also performed to study the decomposition pattern and thermal stability of the native and CPADB-immobilized celluloses, the results will be discussed in the further parts of this report.

3.4. Graft polymerization

Grafting from the cellulose surface was accomplished by immersing the CPADB modified cellulose into the polymerization solution containing sodium 4-styrenesulfonate (SS) and free CPADB. The added free RAFT agent is essential to suppress the formation of dead polymer in solution, hence, enhancing the livingness of the system [22]. When a solid organic support is subjected to γ-irradiation, radicals will be produced in bulk and on its surface and hence grafting will be initiated regardless if the substrate is modified with a RAFT agent or not. Consequently, in γ-initiated graft polymerizations, the growing of PSS grafts from the surface of CPADB-immobilized cellulose may be initiated both via immobilized CPADB and any other kind of species producing radicals under γ-irradiation (Scheme 2). Grafting via immobilized CPADB offers an advantage compared to grafting via other radical source since it enables the attachment of the grafts to the surface via ester linkages. These bonds can later be cleaved by some mild transesterification reactions, which allow further characterization of the grafted polymer chains. In contrast to γ-initiated graft polymerizations, a RAFT agent modified substrate (i.e. a macro chain-transfer agent) is essential to accomplish the grafting from the surface in thermally initiated graft polymerizations. For the sake of comparison of the results, both methods were applied (i.e. γ- and thermally initiated graft polymerizations). Due to the possibility to cleave the grafts by transesterification, a RAFT agent immobilized substrate was preferred over pristine (i.e. unmodified) cellulose in the present study. For both grafting methods applied, the ungrafted (free) polymers were analyzed by SEC with respect to their molecular weights and polydispersity and cellulose-*g*-PSS copolymers were subjected to transesterification reactions to cleave and then analyze the grafts (it should be mentioned again that just the grafts grown via immobilized CPADB are cleavable in the case of γ-initiated grafting).

Table 4 and Fig. 4 summarize the results of free poly(sodium 4-styrenesulfonate), PSS, formed during the γ-initiated RAFT graft polymerization of SS from CPADB-immobilized cellulose at room temperature and overall [SS]/[CPADB] = 324, that is the ratio of SS to the total amount of CPADB (i.e. CPADB in the solution and immobilized to cellulose). As can be seen from Table 4, the polydispersity indices (PDI, i.e. the ratio of weight-average molecular weight, M_w, to M_n) of the resulting polymers are narrow, i.e. PDI < 1.25, indicating a well-controlled polymerization via the RAFT process. The apparent number-average molecular weights, M_n, are comparable to the theoretical M_n values of PSS. As can be seen from Fig. 4a, there is a linear dependence of the molecular weight with conversion indicating the controlled fashion of the process. Fig. 4b depicts that the SEC traces are unimodal and narrow at all conversions and the PDI remains below 1.25 which again demonstrates the well-controlled behaviour of the polymerizations under the given reaction conditions. Here it should be mentioned that the difference between the theoretical and the experimental molecular weights are more prominent for the graft polymerizations than for homopolymerizations (compare Table 1 and Table 4). This can be assigned to the fact that not all the immobilized CPADB is actually on the surface of cellulose (refer to TGA results in Section 3.5) and therefore available to mediate the

Table 4
Reversible addition fragmentation chain transfer graft polymerization of sodium 4-styrenesulfonate by γ-initiation (0.02 kGy h^{-1}) with CPADB as the RAFT agent[a] from a cellulose surface.

Entry	Time (h)	Convn[b] (%)	Graft ratio[c] (wt.%)	G.F.[d]	$M_{n,SEC}$[e] (g mol^{-1})	PDI[e]	$M_{n,theor}$[f] (g mol^{-1})
1	19	30	5	0.68	43,200	1.14	20,300
2	46	73	NA	NA	69,800	1.23	49,050
3	59	81	10	0.76	74,600	1.24	54,400
4	87	94	12	0.80	82,900	1.18	63,100
5	105	97	15	0.96	84,200	1.15	65,100
6	125	99	14	0.90	87,300	1.23	66,420
Blank[g]	45	>99	13	0.32	189,500	2.35	–

[a] Reversible addition fragmentation chain transfer (RAFT) graft-polymerization of sodium 4-styrenesulfonate, SS, (1 mol L^{-1}) from 4-cyanopentanoic acid dithiobenzoate (CPADB) functionalized cellulose (≈0.01 g) initiated via γ-irradiation (0.02 kGy h^{-1}) in water–EtOH (93:7 v/v) mixture at [SS]/[CPADB] = 324:1 and room temperature.
[b] Monomer conversion was determined from NMR analysis.
[c] Graft ratio determined gravimetrically.
[d] Graft frequency is the number of PSS chains grafted to a single cellulose chain and calculated using Eq. (2).
[e] Number-average molecular weight, M_n, and polydispersity indices, PDI, determined via size-exclusion chromatography, SEC, using water as eluent with poly(sodium 4-styrenesulfonate) (PSS) standards for the non-grafted PSS formed during grafting.
[f] Theoretical number-average molecular weight, $M_{n,theor}$, was calculated from the monomer conversion using Eq. (3).
[g] The filter paper was not modified with CPADB but subjected to polymerization conditions and no CPADB was added to the medium.

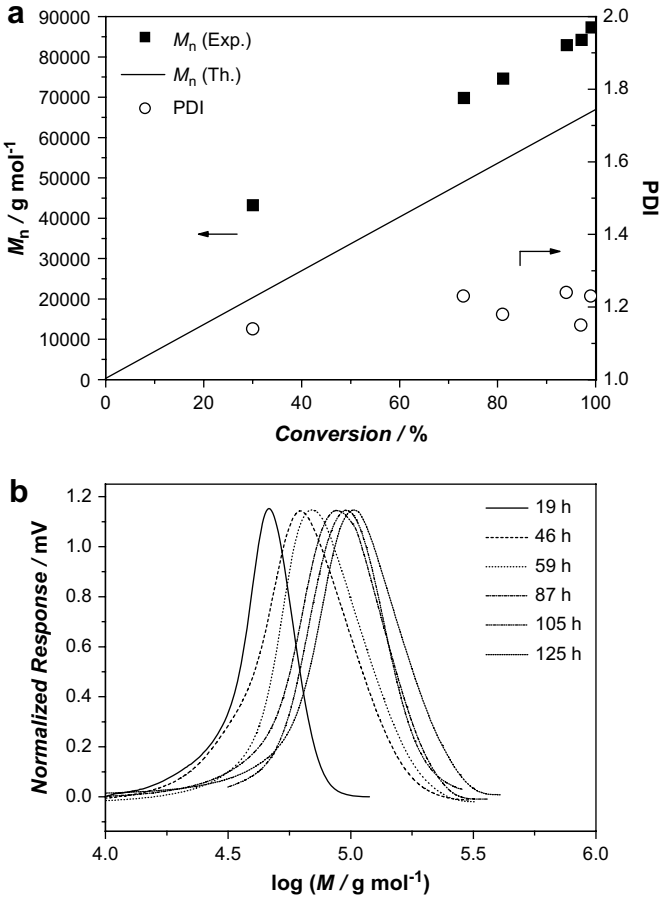


Fig. 4. (a) Evolution of number-average molecular weight, M_n, and polydispersity indices, PDI, vs. the monomer conversion, and (b) evolution of molecular weight distribution vs. time: free PSS formed during γ-initiated graft polymerization from CPADB-immobilized cellulose mediated via the RAFT agent 4-Cyanopentanoic Acid Dithiobenzoate (CPADB), [SS] = 1 mol L^{-1}, CPADB-immobilized cellulose (≈0.01 g), 0.02 kGy h^{-1}, in water–EtOH (93:7 v/v) at [SS]/[CPADB] = 324:1 and room temperature.

RAFT mechanism. In addition, transfer of the macroradical to the RAFT agent is taking place in close vicinity to the cellulose surface. With increasing chain length, immobilized RAFT agents may be less and less accessible and the growing polymer chain will develop a shielding effect [52]. The effective [SS]/[CPADB] ratio should therefore be higher than the calculated [SS]/[CPADB] (i.e. 324) value which further rebound to the difference between the theoretically calculated and experimentally observed molecular weights.

In a parallel study, a conventional grafting was also performed (denoted blank in Table 4). This sample was treated identically with the samples subjected to polymerization with the exception that no CPADB was immobilized to the cellulose surface and no free RAFT agent was added to the medium. As can be seen from Table 4, the graft ratio of the blank sample seems to be very close to those of the RAFT mediated ones – presented graft ratios may contain minor errors most likely due to the intense washing procedures, the trends however are still evident. In our recent work, we verified that it is a valid approach to analyze the free (non-grafted) polymer to gain information on the molecular weight and PDI of the grafted polymer in RAFT polymerization [36]. Therefore, taking into account the big difference in molecular weight of the non-grafted polymer presented in Table 4, it is recognized that the observed graft ratio should be mainly attributed to high M_W of the grafts for the blank sample. More meaningful comparison can be achieved from the graft frequencies (calculated using Eq. (2)), i.e. number of grafted PSS chains per cellulose chain, given in the same table. Results show that the graft frequency increases by applying a RAFT mediated grafting (e.g. the number of grafted PSS chains for the blank sample with 13% grafting is even less than entry 1 whose graft ratio is just 5%) and an uncontrolled polymerization and hence grafting occurs in the absence of the RAFT agent as indicated by the high PDI value of the blank sample. It should be mentioned that the calculation of the grafting frequency is based on all cellulose chains of the filter – not just on the cellulose chains on the surface. Therefore an 'average' grafting frequency is calculated, that means the grafting frequency of the 'surface' cellulose chains should be higher than the 'average' grafting frequency.

Application of γ-radiation generates radicals on the cellulose surface and in the monomer solution. Monomer radicals and radicals formed on the surface initiate propagating chains, which subsequently add to the thiocarbonyl group of the RAFT agent. In general, grafting from a polymer substrate is preferred over homopolymerization of the monomer if the free-radical radiation chemical yield, G_R (i.e. number of radicals formed per 100 eV) of the substrate to be grafted is larger than that of the monomer and grafting will be favoured with increasing the G_R value of the substrate (i.e. the number of radicals on the surface) [53]. Given the structure of CPADB (e.g. leaving R group), G_R value of cellulose (and therefore the number of available radicals on the surface) may be expected to increase after the immobilization of CPADB compared to unmodified cellulose. Therefore grafting of SS from CPADB-immobilized cellulose is – in general – likely to be favoured over grafting from native cellulose, which may be the reason of the lower graft frequency observed for the blank sample.

Thermally initiated grafting of SS from CPADB-immobilized cellulose surface was accomplished using 4,4′-azobis(4-cyanopentanoic acid) as thermal azo-initiator, and the radicals were generated at 70 °C in the presence of CPADB. Mitsukami et al. investigated thermally initiated RAFT polymerization of SS, and found that polymerization of this monomer in aqueous media by RAFT mediated with CPADB occurs in a controlled fashion [54]. Our results also demonstrated the controlled attitude of the polymerizations as given in Table 5; molecular weights of free (non-grafted) polymers are in agreement with theoretically calculated ones and low PDI values expected for a controlled polymerization are achieved.

It might be expected that increasing the temperature will enhance the swelling of the cellulose and the mobility of reactants which further causes an increase in diffusion, and hence in grafting. However, the graft ratios in Table 5 indicate a smaller grafting ratio

Table 5
Reversible addition fragmentation chain transfer graft polymerization of sodium 4-styrenesulfonate (SS, 1 mol L^{-1}) in water–EtOH (93:7 v/v) mixture at 70 °C with 4-cyanopentanoic acid dithiobenzoate (CPADB) as RAFT agent and 4,4′-azobis(4-cyanopentanoic acid) as thermal initiator, [SS]/[CPADB] = 324:1, from a cellulose surface.

Entry	Time (h)	Convn[a] (%)	Graft ratio[b] (wt.%)	G.F.[c]	$M_{n,SEC}$[d] (g mol^{-1})	PDI[d]	$M_{n,theor}$[e] (g mol^{-1})
1	2	23	–	–	26,700	1.27	18,600
2	6	43	2	0.25	43,100	1.21	34,600
3	12	92	5	0.40	78,900	1.23	74,500

[a] Monomer conversion was determined from NMR analysis.
[b] Graft ratio determined gravimetrically.
[c] Graft frequency is the number of PSS chains grafted to a single cellulose chain and calculated using Eq. (2).
[d] Number-average molecular weight, M_n, and polydispersity indices, PDI, determined via size-exclusion chromatography, SEC, using water as eluent with poly (sodium 4-styrenesulfonate) (PSS) standards for the non-grafted PSS formed during grafting.
[e] Theoretical number-average molecular weight, $M_{n,theor}$, was calculated from the monomer conversion using Eq. (3).

compared to γ-initiated RAFT graft copolymerizations. Under γ-irradiation, additional radicals will be formed on the cellulose surface which subsequently can act as initiation sites as well as those generated via the immobilized CPADB. During thermally initiated graft polymerizations the immobilized CPADB groups are the only initiation sites on the surface. This should be the main reason for the higher grafting observed in γ-initiated graft polymerizations compared to thermally initiated ones. Here, it should be mentioned that the graft frequencies of copolymers prepared via the thermally initiated RAFT method still seems to be higher compared to copolymers synthesized via conventional γ-initiation (compare the entry 3 in Table 5 and blank entry in Table 4). It should also be pointed out that the conditions for the thermally initiated grafting need to be optimized to achieve higher graft ratios and frequencies.

3.5. Characterization of cellulose-g-poly(sodium 4-styrenesulfonate) copolymers

Thermogravimetric analysis (TGA) was used to study the thermal degradation occurring in the course of heating under an inert atmosphere for native, CPADB-immobilized and PSS grafted celluloses and PSS synthesized via γ-induced RAFT polymerization ($M_n = 84{,}200\ g\ mol^{-1}$, PDI = 1.15). Thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of above-mentioned samples are shown in Fig. 5.

The TGA traces related to cellulose fibres follows a single weight-loss step with a maximum decomposition temperature at about 361 °C (derivative thermogravimetry curves in Fig. 5b illustrates this more clearly) which is in accordance with the previous publications [36,55]. Cellulosic materials present amorphous and crystalline domains or more exactly a more or less high degree of organization [56]. The crystallinity of cellulose results partly from hydrogen bonding between the cellulosic chains, but some hydrogen bonding also occurs in the amorphous phase [45] although its organization is low. Many publications report that the thermal stability of cellulose esters decreases compared to native cellulose due to the decrease in crystallinity associated with the esterification reactions [55,57–60]. As can be seen from Fig. 5, we also obtained a decrease in thermal stability of cellulose after the attachment of CPADB; the maximum decomposition temperature (T_{dm}) of cellulose decreased by 46 °C (from 361 °C to 315 °C) after the immobilization of CPADB. It should be pointed out that the basic treatment itself also decreases the T_{dm} of cellulose by around 20 °C due to the opening up of the ordered regions. However, this cannot account for the complete reduction of the T_{dm}; a significant decrease is associated with the immobilization of CPADB. Such a high decrease due to the esterification may seem to be unexpected at first sight, since the immobilization of CPADB is expected to take place just on the surface of the cellulose. It was reported that reagents first react with the disordered chains on the surface during the esterification of cellulose with different chemical reagents due to the highly ordered structure of the crystalline part preventing the penetration of the reagents [61]. This process opens up the hydrogen bonded cellulose chains contributing to the crystallinity [58]. This and the basic treatment applied prior to esterification may cooperatively lead to diffusion of the reagents into more crystalline areas where the structure is thermally more stable and resistant to modifications. The significant decrease in the thermal stability of CPADB-immobilized cellulose supports this claim; the esterification reactants probably diffused into the cellulose as well, and CPADB is immobilized not only on the surface but also inside the cellulose to some degree which adversely affects its crystallinity and thus the thermal stability.

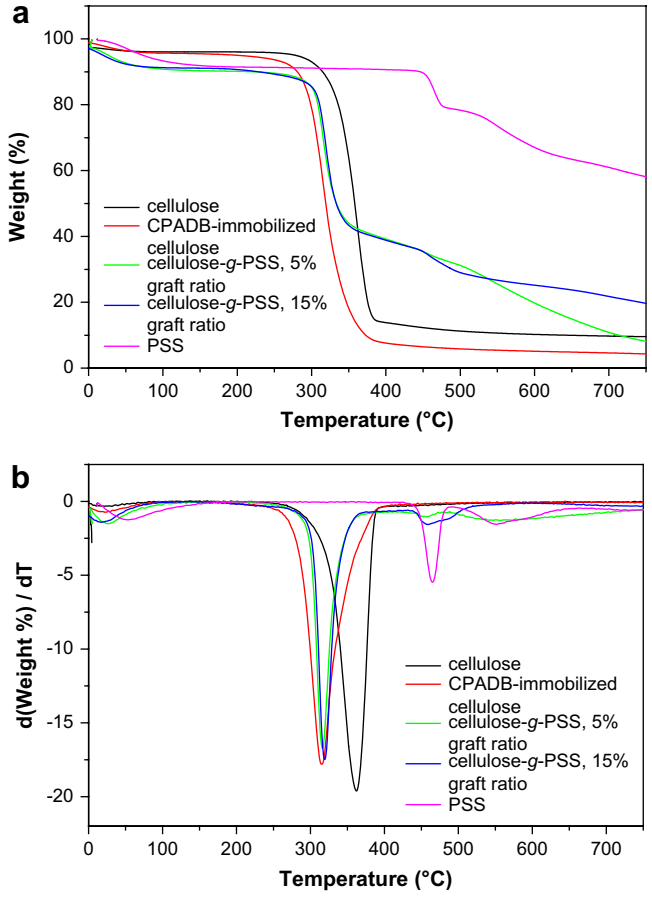


Fig. 5. (a) Thermogravimetry, and (b) derivative thermogravimetry curves of cellulose; CPADB-immobilized cellulose, cellulose-g-PSS copolymers and PSS.

From the degradation curves given in Fig. 5, it is seen that after the grafting of PSS from CPADB-immobilized cellulose, the degradation profile of the copolymers contains additional steps at above 450 °C which are also existent in the degradation curve of pure PSS. These steps are attributed to the grafted PSS on the cellulose substrate. It is also seen that the degradation step at around 315 °C which is attributed to the degradation of CPADB modified cellulose increases a bit after the grafting compared to that of CPADB-immobilized cellulose. A similar increase in thermal stability of cellulose substrates was reported previously for other cellulosic copolymers [6,36,45,50]. Furthermore, the grafted samples yielded a residual mass that increased with the PSS content: the residual mass increased from 4.2 wt.% to 8.6 wt.% and 19.6 wt.% for the cellulose-g-PSS copolymers with 5% and 15% graft ratios, respectively.

The XPS survey scan of cellulose-g-PSS copolymer with 15% graft ratio presented in Fig. 6i shows characteristic peaks belonging to PSS; at 168.1 eV (S2p3, corresponding to sulfonate), 1076.7 eV (Na 1s), and 497.8 eV (Na KLL). These peaks are entirely absent from the XPS survey scan of pristine cellulose whereas S2p3 peak at 163.8 eV assigned for sulfur atoms of the attached RAFT agents appears in the XPS survey scan of CPADB-immobilized cellulose with a lower intensity (please compare Fig. 2 and Fig. 6i for the changes in surface chemical composition). The C1s XPS spectra (Fig. 6ii–iv) clearly indicate a considerable change in four components that correspond to carbon atoms in different functional groups: the carboxylate carbon (O–C=O, around 289.3 eV, peak A), the carbonyl C (C=O, around 288 eV, peak B), the C in C–O bonds (around 286.7 eV, peak C), and the non-oxygenated C (e.g. C–C, C–H, around 285 eV, peak D). Although the C1s XPS spectrum of PSS

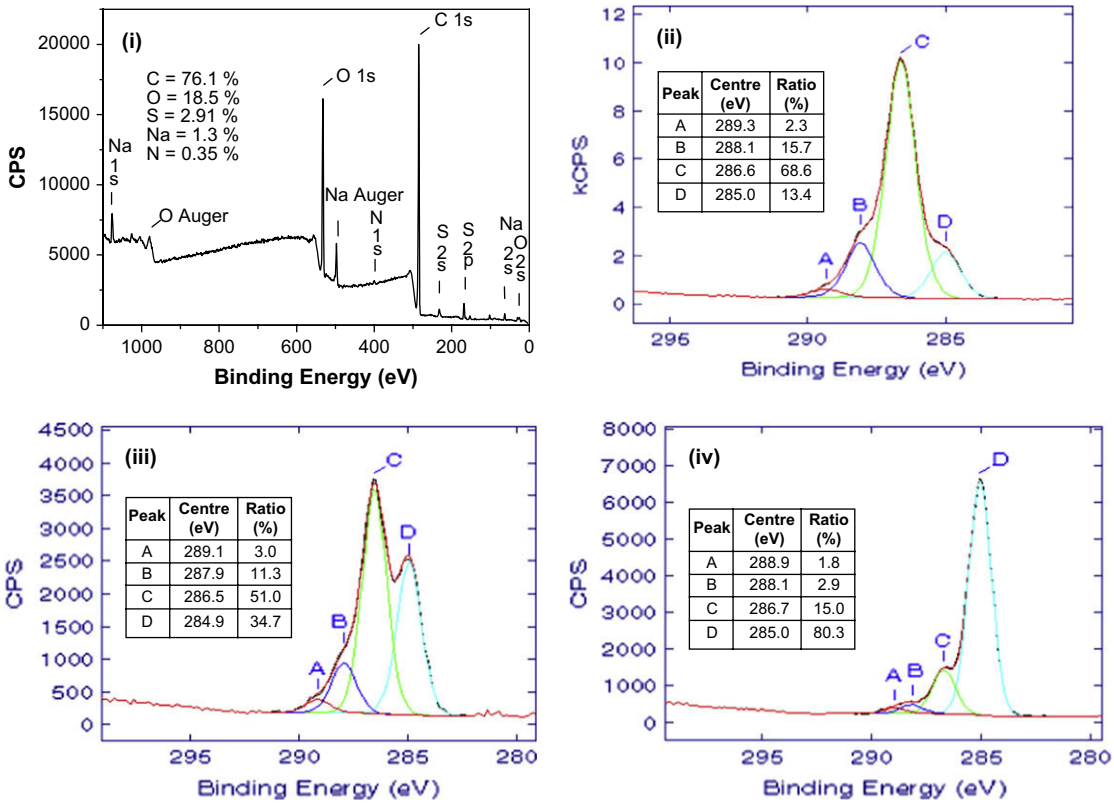


Fig. 6. The XPS survey wide scan of cellulose-*g*-PSS copolymer with 15% graft ratio (i); C 1s XPS spectrum of (ii) pristine cellulose; (iii) CPADB-immobilized cellulose; (iv) cellulose-*g*-PSS copolymer with 15% graft ratio. The percentages in the quantification tables inserted to C 1s spectra show the individual amounts of carbon atoms in different functional groups per total carbon atom amount. Peak A: the carboxylate carbon (O–C=O, around 289.3 eV); Peak B: the carbonyl C (C=O, around 288 eV); peak C: the C in C–O bonds (around 286.7 eV); peak D: non-oxygenated C (e.g. C–C, C–H, around 285 eV). Peak D is used as binding energy reference.

grafted cellulosic copolymer (Fig. 6iv) also exhibit the same oxygenated C bonds that have been assigned for cellulose substrate, the peak intensities of these components are much smaller than those in the native cellulose. In contrast, the amount of non-oxygenated C bonds is significantly higher for the PSS-grafted sample confirming successful attachment of PSS chains to the cellulose surface (please see the quantification tables inserted to the C1s spectra).

The Raman spectra of PSS grafted copolymer with 15% graft ratio is given in Fig. 3. The C≡N band appearing in the spectrum at 2232 cm^{-1} is attributed to CPADB existing either as the end groups of PSS chains or as the immobilized functionalities on cellulose [50]. As can be seen in Fig. 3, a new C–S band also appears in the spectrum at 793 cm^{-1} which can be assigned to the sulfonate groups of PSS [62,63] (please compare Fig. 3(B) and (C)).

3.6. Cleaving of PSS chains from cellulose backbone for further analysis

In γ-initiated RAFT graft polymerization, there will be a number of propagating polymeric chains in the solution, in addition to those immobilized on the substrate. The R-group approach ensures that the thiocarbonyl thio group can be transferred between these immobilized and free chains, thus the control over molecular weight for both types of chains is promoted. Tsuji et al. [22] reported that when the grafting is achieved using a RAFT agent immobilized substrate in the absence of added free RAFT agent to solution, the resulting concentration of thiocarbonyl thio capped chains in solution is too low to control the polymerization effectively, leading to a conventional free-radical polymerization occurring both at the surface of the substrate and in solution. However, they observed that addition of free chain-transfer agent to the system allows the control of both graft polymerization and solution polymerization. Roy et al. [64] confirmed these results, and they found that introduction of free chain-transfer agent has a direct effect on the molecular weight of the grafted chains, with their molecular weight getting very close to that predicted.

Fig. 2S (please see Supporting information) presents the evolution of molecular weight distribution for the free PSS formed in solution during grafting, for the immobilized PSS cleaved from the surface and for the free PSS subjected to the same acidic transesterification procedure applied for the cleaving. It is seen from the figure that graft (cleaved) polymers have larger M_w/M_n (Fig. 2Sb) as compared with that of free polymer (Fig. 2Sa) as a result of widening of the SEC chromatogram in the lower molecular weight region. At first sight, this may be interpreted as an uncontrolled growing of grafts on the surface. However, the SEC chromatogram of free PSS subjected to the same cleaving procedure (Fig. 1Sc) also presented a broader distribution in the lower molecular weight region. The shoulders appearing on the low molecular weight side are attributed to chain scission due to the hydrolysis conditions. Despite the occurrence of these shoulders, the components of SEC chromatograms computed using the PeakFit programme (Jandel Scientific Software) show that the molecular weights of freely formed PSS (Fig. 2Sa) and cleaved PSS (Fig. 2Sb) have a very similar order of magnitude (please compare Fig. 2Sa with the red coloured peak component of Fig. 2Sb). This indicates that the molecular weights of the grafted chains are close to those of freely formed ones in solution and thus to those predicted.

4. Conclusions

It has been demonstrated for the first time that RAFT polymerization of SS can be carried out directly in aqueous solution at room temperature under γ-irradiation. Controlled/living characteristics were proven for CPADB mediated RAFT polymerization at different dose rates and [Monomer]/[CTA] ratios whereas another CTA, BPATT showed lack of control under the same conditions. For CPADB mediated RAFT polymerizations – even at a monomer conversion exceeding 90% – control of the polymerization was maintained. The RAFT graft polymerization of SS from CPADB-functionalized cellulose was also studied. The graft frequency was found to be higher in the RAFT mediated graft polymerizations compared to the conventional grafting. However, the RAFT graft polymerization conditions need optimization to obtain higher graft ratios and graft frequency. Given the environmental benefits associated with aqueous polymerizations at room temperature, it is believed that the reported method including the immobilization of CTAs to the substrates to be grafted may represent an advantage in the ability to prepare well-defined graft copolymers.

Acknowledgements

M.B. is grateful to the Australian Government Department of Education, Science and Training (DEST) for an Endeavour Postgraduate Award. O. G. appreciates the supports of the Academy of Sciences of Turkey. L.B. acknowledges financial support from the University of New South Wales and the Australian Research Council (ARC). C.B.K. acknowledges past-support via an Australian Professorial Fellowship from the ARC. T.P.D acknowledges an ARC Federation Fellowship. All authors thank A/Prof. Martina H. Stenzel for useful discussions. We would also like to thank Mr. Istvan Jacenyik for his excellent management of the CAMD.

Appendix. Supporting information

Figures summarizing the γ-initiated RAFT homopolymerization results of SS and SEC chromatograms related to cleaving studies are available free of charge via the Internet. Supplementary data associated with this article can be found in the online version at doi:10.1016/j.polymer.2008.12.027.

References

[1] Kato K, Uchida E, Kang ET, Uyama Y, Ikada Y. Prog Polym Sci 2003;28:209–59.
[2] Ou SH, Ishida H, Lando JB. J Polym Sci Part B Polym Phys 1991;29:67–73.
[3] Lvov Y, Ariga K, Ichinose I, Kunitake T. J Am Chem Soc 1995;117:6117–22.
[4] Yap HP, Hao X, Tjipto E, Gudipati C, Quinn JF, Davis TP, et al. Langmuir 2008;24(16):8981–90.
[5] Stenzel MH, Zhang L, Huck WTS. Macromol Rapid Commun 2006;27:1121–6.
[6] Roy D, Guthrie JT, Perrier S. Macromolecules 2005;38:10363–72.
[7] Li Y, Schadler LS, Benicewicz BC. In: Barner-Kowollik C, editor. Handbook of RAFT polymerization. 1st ed. Weinheim: Wiley-VCH; 2008. p. 423.
[8] Edmondson S, Osborne VL, Huck WTS. Chem Soc Rev 2004;33:14–22.
[9] Boyes SG, Granville AM, Baum M, Akgun B, Mirous BK, Brittain WJ. Surf Sci 2004;570:1–12.
[10] Perrier S, Takolpuckdee P. J Polym Sci Part A Polym Chem 2005;43:5347–93.
[11] Barner-Kowollik C, Davis TP, Heuts JPA, Stenzel MH, Vana P, Whittaker M. J Polym Sci Part A Polym Chem 2003;41:365–75.
[12] Moad G, Rizzardo E, Thang SH. Aust J Chem 2005;58:379–410.
[13] Barner-Kowollik C, editor. Handbook of RAFT polymerization. Weinheim: Wiley-VCH; 2008.
[14] Lowe AB, McCormick CL. Prog Polym Sci 2007;32(3):283–351.
[15] Zhao Y, Perrier S. Macromolecules 2007;40:9116–24.
[16] Barner L, Li C, Hao X, Stenzel MH, Barner-Kowollik C, Davis TP. J Polym Sci Part A Polym Chem 2004;42:5067–76.
[17] Wang Z, He J, Tao Y, Yang L, Jiang H, Yang Y. Macromolecules 2003;36:7446–52.
[18] Baum M, Brittain WJ. Macromolecules 2002;35:610–5.
[19] Sumerlin BS, Lowe AB, Stroud PA, Zhang P, Urban MW, McCormick CL. Langmuir 2003;19:5559–62.
[20] Roy D, Guthrie JT, Perrier S. Aust J Chem 2006;59:737–41.
[21] Yoshikawa C, Goto A, Tsujii Y, Fukuda T, Yamamoto K, Kishida A. Macromolecules 2005;38:4604–10.
[22] Tsujii Y, Ejaz M, Sato K, Goto A, Fukuda T. Macromolecules 2001;34:8872–8.
[23] Raula J, Shan J, Nuopponen M, Niskanen A, Jiang H, Kauppinen EI, et al. Langmuir 2003;19:3499–504.
[24] Trejo-O'Reilly JA, Cavaille JY, Gandini A. Cell 1997;4:305–20.
[25] Kuruvilla J, Varghese S, Kalaprasad G, Thomas S, Prasannakumari L, Koshy P, et al. Eur Polym J 1996;32:1243–50.
[26] Trejo-O'Reilly JA, Cavaille JY, Paillet M, Gandini A, Herrera-Franco P, Cauich J. J Polym Compos 2000;21:65–71.
[27] Quinn JF, Rizzardo E, Davis TP. Chem Commun 2001:1044–5.
[28] Quinn JF, Barner L, Rizzardo E, Davis TP. J Polym Sci Part A Polym Chem 2002;40:19–25.
[29] Quinn JF, Barner L, Davis TP, Thang SH, Rizzardo E. Macromol Rapid Commun 2002;23:717–21.
[30] Barner L, Quinn JF, Barner-Kowollik C, Vana P, Davis TP. Eur Polym J 2003; 39:449–59.
[31] Millard PE, Barner L, Stenzel MH, Davis TP, Barner-Kowollik C, Müller AHE. Macromol Rapid Commun 2006;27:821–8.
[32] Quinn JF, Davis TP, Barner L, Barner-Kowollik C. Polymer 2007;48:6467–80.
[33] Barner L, Zwaneveld N, Perera S, Pham Y, Davis TP. J Polym Sci Part A Polym Chem 2002;40:4180–92.
[34] Barner L, Pereira S, Sandanayake S, Davis TP. J Polym Sci Part A Polym Chem 2006;44:857–64.
[35] Barner L. Aust J Chem 2003;56:1091.
[36] Barsbay M, Güven O, Stenzel MH, Barner-Kowollik C, Davis TP, Barner L. Macromolecules 2007;40:7140–7.
[37] Thang SH, Chong YK, Mayadunne RTA, Moad G, Rizzardo E. Tetrahedron Lett 1999;40:2435–8.
[38] Stenzel MH, Davis TP. J Polym Sci Part A Polym Chem 2002;40:4498–512.
[39] Carlmark A, Malmström E. J Am Chem Soc 2002;124:900–1.
[40] Zeronian SH. In: Nevell TP, Zeronian SH, editors. Cellulose chemistry and its application. New York: Ellis Horwood Limited; 1985. p. 168–70.
[41] Piantanida G, Bicchieri M, Coluzza C. Polymer 2005;46:12313–21.
[42] Moad G, Chiefari J, Chong YK, Krstina J, Mayadunne RTA, Postma A, et al. Polym Int 2000;49:993–1001.
[43] Perrier S, Barner-Kowollik C, Quinn JF, Vana P, Davis TP. Macromolecules 2002;35:8300–6.
[44] Coote MJ, Radom L. J Am Chem Soc 2003;125:1490–1.
[45] Donovan MS, Lowe AB, Sumerlin BS, McCormick CL. Macromolecules 2002;35:4123–32.
[46] McLeary JB, Calitz FM, McKenzie JM, Tonge MP, Sanderson RD, Klumperman B. Macromolecules 2004;37:2383–94.
[47] McLeary JB, Calitz FM, McKenzie JM, Tonge MP, Sanderson RD, Klumperman B. Macromolecules 2005;38:3151–61.
[48] Barner L, Barner-Kowollik C, Davis TP, Stenzel MH. Aust J Chem 2004;57: 19–24.
[49] Barner L, Davis TP, Stenzel MH, Barner-Kowollik C. Macromol Rapid Commun 2007;28:539–59.
[50] Joo S-W, Chung TD, Jang WC, Gong M-S, Geum N, Kim K. Langmuir 2002;18:8813–6.
[51] Colthup NB, Daly LH, Wiberley SE. Introduction to infrared and Raman spectroscopy. San Diego: Academic Press; 1990.
[52] Hernández-Guerrero M, Barner-Kowollik C, Davis TP, Stenzel MH. Eur Polym J 2005;41:2264–77.
[53] Chapiro A. Radiation chemistry of polymeric systems. New York: Interscience; 1962.
[54] Mitsukami Y, Donovan MS, Lowe AB, McCormick CL. Macromolecules 2001;34:2248–56.
[55] Freire CSR, Silvestre AJD, Pascoal Neto C, Belgacem MN, Gandini A. J Appl Polym Sci 2006;100:1093–102.
[56] Gauthier R, Joly C, Coupas AC, Gauthier H, Escoubes M. Polym Compos 1998;19:287–300.
[57] Kondo T, Sawatari C. Polymer 1996;37:393–9.
[58] Pandey JK, Chu WS, Kim CS, Lee CS, Ahn SH. Adv Mater Res 2008;47–50: 435–8.
[59] Jandura P, Riedl B, Kokta BV. Polym Degrad Stab 2000;70:387–94.
[60] Sealey JE, Samaranayake G, Todd JG, Glasser WG. J Polym Sci Part B Polym Phys 1999;34:1613–20.
[61] Wang N, Ding E, Cheng R. Polymer 2007;48:3486–93.
[62] Edwards HGM, Brown DR, Dale JR, Plant S. J Mol Struct 2001;595:111–25.
[63] Edwards HGM, Brown DR, Dale JA, Plant S. Vib Spectrosc 2000;24:213–24.
[64] Roy D, Guthrie JT, Perrier S. Soft Matter 2008;4:145–55.