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ORIGINAL PAPER

Functionalization of cellulose with epoxy groups via γ-initiated RAFT-mediated grafting of glycidyl methacrylate

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Abstract Glycidyl methacrylate (GMA), was grafted from cellulose by the combination of radiation-induced initiation and the reversible addition-fragmentation chain transfer (RAFT) polymerization technique, leading to epoxy functionalized surfaces that enable further modifications. Cumyl dithiobenzoate and 2-cyanoprop-2-yl dithiobenzoate were employed as the RAFT agents. The effects of absorbed dose, monomer and RAFT agent concentrations and solvent choice on grafting yield were investigated. Characterization of the synthesized copolymers by ATR-FTIR spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, thermal analysis and contact angle measurements revealed the grafting of poly(glycidyl methacrylate) (PGMA) from cellulose. Size-exclusion chromatography analysis indicated the difficulty of controlling the polymerization of GMA due to branching and/or crosslinking reactions that might occur in PGMA structure under γ-radiation.

Keywords Cellulose · Glycidyl methacrylate (GMA) · RAFT mediated grafting · γ-Irradiation

Introduction

Graft copolymerization enables the formation of functional hybrid materials by attaching polymer chains with advantageous tailored properties to the surface of a base polymer with desirable bulk character. During the past several decades the interest in synthesis and practical applications of such systems has grown steadily. Radiation induced grafting method is one of the most promising grafting techniques as it is simple, economically favorable, easily controllable and assures the grafting of variety monomers that are difficult to polymerize by conventional methods without residues of initiators and catalyst (Bhattacharya and Misra 2004; Kato et al. 2003; Nasef and Güven 2012). Development of controlled free-radical polymerization (CRP) methods has opened up new opportunities for preparing graft copolymers with well-defined characteristics and properties (Malmström and Carlmark 2012). Among the CRP methods, reversible addition fragmentation

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chain transfer (RAFT) polymerization is the most successfully applied method to grow well-controlled brushes from polymer surfaces to alter the surface properties of base materials in conjunction with radiation-induced grafting method (Barsbay and Güven 2009, 2013; Han and Pan 2006; Hua et al. 2005).

Researchers are striving continuously to improve and optimize the properties of cellulose-based natural fibers (Carlmark 2013; Malmström and Carlmark 2012). This is simply due to a wide range of potential applications as well as the important inherent characteristics of cellulose such as availability as a renewable natural source, ease of surface modification, low cost, good mechanical properties, recyclability and biodegradability (Malmström and Carlmark 2012; Lindqvist et al. 2008; Thakur et al. 2013). In this study, RAFT-mediated and radiation-induced free-radical graft polymerization of poly(glycidyl methacrylate) (PGMA) onto cellulose fibers has been achieved. PGMA contains both acrylic and epoxy groups, providing the design and performance versatility required for the most demanding structural modifications that can result in differentiated properties and higher performance. The controlled polymerization of PGMA by the RAFT technique has been already reported for homopolymers (Zhu et al. 2004) and for copolymers (Gudipati et al. 2008). To the best of our knowledge this is the first report dealing with the γ-initiated RAFT polymerization of PGMA and investigating the grafting of this monomer from cellulose surface using the RAFT technique. The synthesized copolymers have the potential to be used for further modifications via the well known nucleophilic ring-opening reaction of the epoxy groups of PGMA grafts. Using this methodology it may be possible to obtain a library of different cellulosic materials especially useful in separation and purification applications and also to have access to materials not otherwise obtainable.

Experimental

Materials

Glycidyl methacrylate (GMA) (Aldrich, 97 %) was passed through a basic alumina column to remove the inhibitor. Cumyl dithiobenzoate, CDB, and solvents with high purity grade were purchased from Sigma-Aldrich. 2-cyanoprop-2-yl dithiobenzoate (CPDB) was synthesized according to the method described by Dureault et al. (2003). 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 (Barsbay et al. 2007).

Irradiation

Gammacell 220 ^{60}Co source with a dose rate of 0.26 kGy h^{-1} as determined by Fricke dosimetry was used for the irradiation of the samples at room temperature. Various absorbed doses, e.g. 2.1, 4.4, 6.4, 8.3, 10.4, 12.7 and 14.6 kGy, were applied throughout the study.

Grafting

In a typical RAFT-mediated grafting, a piece of cellulose paper with approximately 1.5 cm × 1.0 cm dimensions and a weight of ~0.015 g was immersed into each grafting solution prepared by dissolving necessary amounts of the monomer (GMA) and the RAFT agent (CDB or CPDB) in a solvent, e.g. DMF. The polymerization solution in purgeable glass was then connected to N_2 bubbling at room temperature for 10 min. The samples were placed in the sample chamber of ^{60}Co γ-irradiator at ambient temperature at a dose rate of 0.26 kGy h^{-1}. Samples were taken from the chamber at different time intervals. A scheme showing the general synthesis pathway from cellulose fiber to cellulose-*g*-PGMA copolymer can be seen in the Supplementary Information, Online Resource 1.

The grafted samples, i.e. cellulose-*g*-PGMA copolymers, were repeatedly washed with DMF and THF to remove surface contaminations. The solvent was changed at intervals until no homo-PGMA could be identified in the rinsing solution via size-exclusion chromatography (SEC) analysis after complete evaporation of the solvent. Finally, the cellulose-*g*-PGMA samples were dried to constant weight under vacuum at 45 °C. The degree of grafting (*DG*, wt%) was calculated gravimetrically using the following equation:

$$DG, \% = \frac{w_2 - w_1}{w_1} \times 100 \quad (1)$$

where w_1 (g) is the weight of the cellulose film before grafting and w_2 (g) is the dry weight of the PGMA grafted copolymer. Gravimetrical measurements were carried out using a Sartorius GENIUS ME model balance with sensitivity of ±0.01 mg. In most cases, RAFT agent concentration is adjusted so that free PGMA with expected molecular weight of 85.000 g mol^{-1} will be formed at complete conversion of the monomer. This has been determined to be [GMA]/[RAFT agent] = 600:1 according to following equation:

$$M_{n,Th.} = M_{RAFTagent} + \frac{[GMA]}{[RAFT\ agent]} \times M_{GMA} \times overall\ conversion \quad (2)$$

where $M_{n,Th.}$ is the theoretical number-average molecular weight of polymer; [GMA] is the initial molarity of the monomer, i.e., GMA; M_{GMA} is the molecular weight of GMA; [RAFT agent] is the initial molarity of the RAFT agent, i.e. CDB or CPDB; $M_{RAFTagent}$ is the molecular weight of the RAFT agent, i.e. CDB or CPDB. Along with the [GMA]/[RAFT agent] ratio of 600, other values of 300, 450, 900 and 1,200 were also studied to investigate the effect of target molecular weight on grafting. The monomer conversion was determined gravimetrically by precipitating PGMA in diethyl ether. Note that the grafted poly(glycidyl methacrylate) (PGMA) also contributed to the overall conversion value. In order to investigate the advantages of RAFT mediated grafting, conventional grafting studies were also carried out where cellulose substrates were grafted with PGMA identically with the exception that no RAFT agent, i.e. CDB or CPDB, was added to the medium.

Size-exclusion chromatography (SEC)

The molecular weight analysis of free (non-grafted) PGMA formed during grafting was performed in THF as the eluent at room temperature (flow rate: 1 mL min^{-1}) using a Waters Gel Permeation Chromatograph equipped with a Waters 515 model HPLC pump. The system was equipped with Styragel HR4 and HR3 columns and Waters 2414 model refractive index detector. A universal calibration was prepared with 8 polystyrene (PS) standards in molecular weight range of 1990 to 2.10^6 g mol^{-1}. The Mark–Houwink constants used in constructing the universal calibration were as follows: $K = 11.0 \times 10^{-3}$ mL g^{-1}, $a = 0.725$ for PS (Brandrup and Immergut 1989) and $K = 27.8 \times 10^{-3}$ mL g^{-1}; $a = 0.537$ for PGMA (Hutchinson et al. 1998).

ATR-FTIR spectroscopy

FTIR spectra of the samples were obtained with a Nicolet Magna-IR 750 spectrometer equipped with a DGTS detector. Spectra were recorded by cumulating 64 scans at 4 cm^{-1} resolution in Attenuated Total Reflexion mode (ATR) using a diamond-crystal with single reflection.

X-ray photoelectron spectroscopy (XPS)

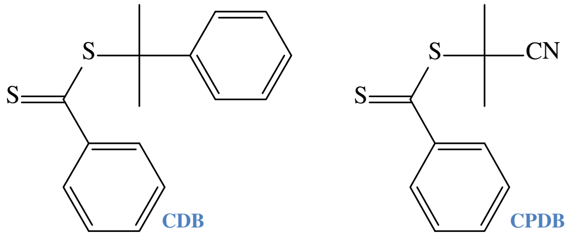
X-ray photoelectron spectra were recorded on a Thermo spectrometer with a mono-chromatized Al Kα X-ray source (1,486.6 eV photons). The details of the technique were given elsewhere (Barsbay et al. 2013). Surface elemental compositions were determined from peak-area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to ±5 %. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries.

Elemental analysis

The elemental composition of the samples was analysed using AI/AS 3000 series autosampler and Flash 2000 (Thermo Scientific) automatic elemental analyser equipped to analyse carbon, hydrogen, sulfur and nitrogen atoms. Samples were analysed in tin capsules using 5-bis-5-*tert*-butyl-2-benzoxazolylthiophene (BBOT) as the calibration standard and vanadium pentoxide (V_2O_5) as the catalyst.

Scanning electron microscopy (SEM)

The surface morphologies of the cellulose samples before and after grafting were investigated by SEM using a FEI Quanta 200FEG Scanning Electron Microscope. Samples were sputter-coated with gold prior to scanning. Electron micrographs of each sample were recorded at different magnifications.



Scheme 1 Structures of RAFT agents employed in the present study

Contact angle

Wettability of pristine cellulose and cellulose-*g*-PGMA copolymers was characterized by using Krüss DSA 100 model contact angle (CA) goniometer. A drop of water (10 µL) was placed on the dry copolymer surface, and the contact angle was determined at ambient temperature.

Results and discussion

RAFT mediated grafting and parameters influencing the grafting yield

Simultaneous irradiation technique employed during the grafting studies enables radical formation on the cellulose surface and monomer in the solution. The radicalic sites on cellulose substrate become the points of initiation and growth for the graft chains. In the mean time, radiation-induced homopolymerization of the monomer occurs in solution. Both kind of propagating chains, i.e. grafted and free in solution, then add to the thiocarbonyl group of the RAFT agent, creating the RAFT radical intermediates (Barner et al. 2002, 2003; Barsbay et al. 2007). In this way pre-equilibrium of the RAFT mechanism is established. In order to investigate the RAFT mediated polymerization and grafting of GMA two RAFT agents were employed in the present study, namely CPDB and CDB, Scheme 1. CPDB has been proven to be a good chain transfer agent for controlling the polymerization of GMA (Gudipati et al. 2008). It has also been used for the γ-initiated RAFT polymerization of other methacrylates (Barner et al. 2003). The second RAFT agent used, i.e. CDB, has been reported to be a suitable agent for the RAFT-mediated free radical polymerization of GMA (Zhao et al. 2012) and γ-initiated controlled polymerization of methyl methacrylate (Barner et al. 2003).

The molecular weight distributions of non-grafted PGMA formed in solution at different absorbed doses during graft polymerizations mediated by CDB and CPDB are depicted in Figs. 1 and 2, respectively. Comparison of the results in these figures reveals a significantly better controlled fashion for the polymerization mediated by CPDB. The leaving group is a 2-cyanoprop-2-yl radical for this RAFT agent. It is implied from the results that this leaving radical is more appropriate to initiate the growing chains at the early stage of the polymerization and to establish the addition–fragmentation equilibrium for PGMA compared to that generated by CDB. This fact, combined with the retardation/radical storage effect reported for CDB at ambient temperature (Barner-Kowollik et al. 2002; Barner et al. 2003), enables a more incremental chain growing in case of CPDB. Polymerization of GMA in the presence of both RAFT agents yielded molecular weights that increase with increasing conversion. However, the dispersity ($Đ_M$) values indicate relatively broad molecular weight distributions above 1.5 even in case of CPDB. It should be mentioned here that the multimodal SEC chromatograms with very high $Đ_M$ values up to ~15 observed during conventional polymerization were replaced with monomodal distributions with $Đ_M$ values in the range of ~1.5–2.0 in case of RAFT mediation with CPDB. This observation gives a clear indication that the main RAFT mechanism is established during grafting, but the full success over the molecular weight and $Đ_M$ control is limited probably due to the effect of radiation on PGMA. Similar results have been observed in previous studies when RAFT mechanism was carried out in the presence of crosslinking reactions (Roa-Luna et al. 2010; Kodama et al. 2014). The polymer produced under γ-radiation is exposed to radiolysis and the radicals formed on adjacent polymer chains can react together to give a covalent bond, thereby yielding a branched and/or crosslinked polymer. We have observed formation of an insoluble polymer network at absorbed doses higher than ~8 kGy when no RAFT agent was added to polymerization medium; e.g. conventional grafting carried out in polymerization solution containing 40 % GMA in DMF (v/v) and cellulose substrate yielded an insoluble gel at 8.3 kGy absorbed dose at a dose rate of 0.26 kGy h^{-1} and at ambient temperature under N_2 atmosphere. This

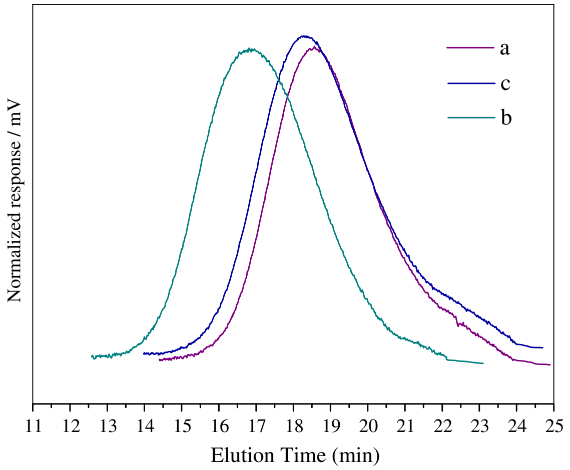


Fig. 1 SEC trace evolution of poly(glycidyl methacrylate) (PGMA) polymers formed in solution during grafting from cellulose surface at ambient temperature via RAFT polymerization mediated by CDB and initiated by γ-radiation. (*a*) $M_n = 10{,}200$, $Đ_M = 2.97$, 4.4 kGy; (*b*) $M_n = 12{,}700$, $Đ_M = 3.26$, 6.4 kGy; (*c*) $M_n = 35{,}300$, $Đ_M = 3.52$, 8.3 kGy. RAFT agent: CDB, 20 % GMA in DMF, [GMA]/[CDB] = 600

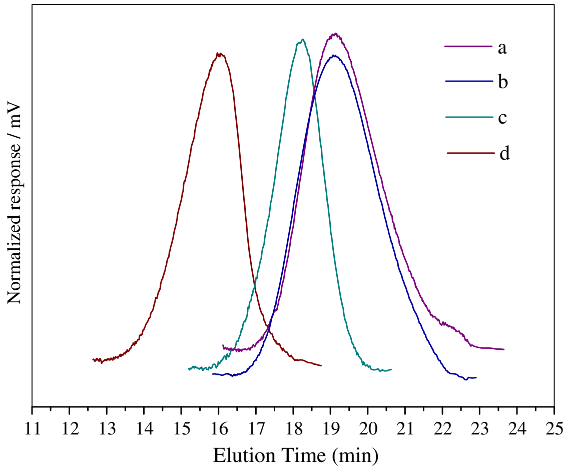


Fig. 2 SEC trace evolution of poly(glycidyl methacrylate) (PGMA) polymers formed in solution during grafting from cellulose surface at ambient temperature via RAFT polymerization mediated by CPDB and initiated by γ-radiation. (*a*) $M_n = 5{,}300$, $Đ_M = 2.1$ kGy; (*b*) $M_n = 5{,}500$, $Đ_M = 1.77$, 4.4 kGy; (*c*) $M_n = 13{,}100$, $Đ_M = 1.56$, 6.4 kGy; (*d*) $M_n = 43{,}200$, $Đ_M = 1.69$, 8.3 kGy. RAFT agent: CPDB, 20 % GMA in DMF, [GMA]/[CPDB] = 600

indicates the crosslinking tendency of GMA under γ-irradiation. Crosslinking reactions have been observed for the RAFT-mediated samples as well at higher monomer concentrations and absorbed doses compared to those applied during the conventional grafting (refer to Table S1 in the Supplementary Information, Online Resource 1). The previously published data on the radiation effects on epoxy group containing polymers are contradictory; crosslinking and branching were both reported (Laricheva 2008). The probable branching and/or crosslinking reactions that might occur in PGMA structure under γ-radiation may cause difficulties in controlling the RAFT mechanism.

The synthesis of functional polymers with desired architecture by controlled radical polymerization (CRP) of monomers in the presence of cross-linkers is a hot topic (Gao and Matyjaszewski 2009). It has been reported that the gels produced via CRP methods present remarkable differences from those prepared via conventional process, including retarded gelation kinetics, steady increase of gel fraction after gelation and higher swelling ratios of gels (Ide and Fukuda 1997, 1999; Gao and Matyjaszewski 2009). In order to study gelation kinetics and/or to synthesize branched polymers and gels with better controlled structures, ATRP (Yu et al. 2001; Isaure et al. 2004; Gao et al. 2007; Bannister et al. 2006), NMP (Ide and Fukuda 1997, 1999) and RAFT (Roa-Luna et al. 2010; Liu et al. 2005; Taton et al. 2006; Vo et al. 2007) polymerization techniques have been employed in the presence of cross-linkers. RAFT mediated grafting and polymerization at ambient temperature by means of γ-radiation have been successfully performed for a variety of monomers (Barsbay and Güven 2009). However, the synthesis of well-defined branched and/or crosslinked polymers by the combination of γ-initiation and RAFT-mediation is still unexplored. Employing these two techniques together may lead to well-defined gels with superior properties. The investigation of branching/crosslinking reactions taking place during the γ-initiated RAFT polymerization is the subject of our on-going studies. Hereafter, it will be sufficient to mention the parameters affecting the grafting yield and discuss on the characteristics of the resulting copolymers.

The major factors influencing the grafting yield include the type of solvent, concentrations of monomer and RAFT agent, and absorbed radiation dose. Cellulose is a nonbranched condensation polymer exhibiting a high degree of crystallinity in its native state and there are strong intermolecular hydrogen bonds between adjacent cellulose chains via the hydroxyl groups. Therefore, the cellulose fibers are

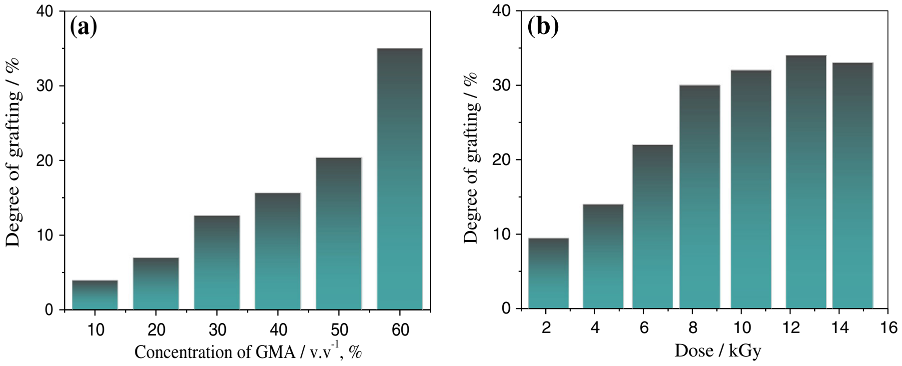


Fig. 3 Effects of monomer feed concentration (**a**), and absorbed dose (**b**) on degree of grafting. Conditions for (**a**): [GMA]/[CDB] = 600, solvent = DMF, absorbed dose = 4.4 kGy. Conditions for (**b**): [GMA]/[CDB] = 600, solvent = DMF, monomer concentration = 30 % (v/v)

not easily accessible for reactions (Krassig 1993; Klemm et al. 2005). In some particular polar solvents hydrogen bonds among the cellulose units are cleaved and the more ordered regions are opened up (Dilli and Garnett 1967). Consequently, reagents can easily penetrate into the cellulose substrate leading to higher degree of grafting (DG). In order to find a suitable solvent to increase the DG value, we performed a preliminary screening of several solvents, namely toluene, THF, DMF and DMSO, in a standard grafting condition: polymerization solutions containing 30 % GMA (v/v) and cellulose substrate were irradiated to 6.4 kGy absorbed dose at a dose rate of 0.26 kGy h^{-1} for ~24 h and at ambient temperature under N_2 atmosphere (data not shown). [GMA]/[CDB] ratio of 600:1 was chosen. Polymerization performed in DMF resulted in higher DG compared to remaining solvents. DMF is reported as a good swelling agent for cellulose (Freire et al. 2006) and it is also a good solvent for GMA, PGMA and the RAFT agents. Therefore, DMF was employed as the solvent in the further parts of this study.

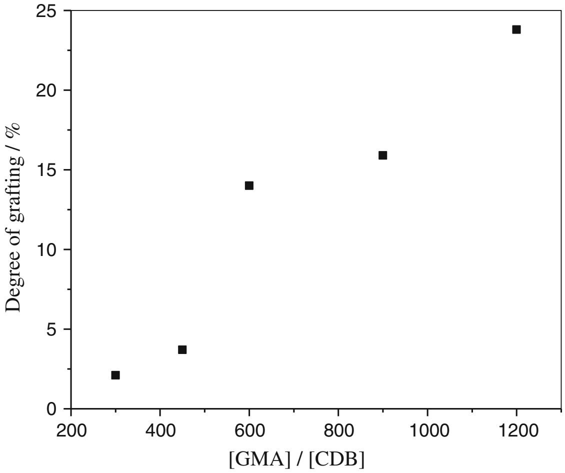


Fig. 4 Effect of [GMA]/[CDB] ratio on degree of grafting. Dose rate: 0.26 kGy h^{-1}; [GMA] = 30 %, v/v; solvent: DMF; ambient temperature and total absorbed dose is 4.4 kGy

The dependency of degree of grafting (DG) on monomer concentration is illustrated in Fig. 3a. As a general rule, the grafting reaction rate increases with the increase of monomer concentration. This is simply due to the increased availability of the monomer in close proximity to the substrate grafted. It has been often reported that the DG levels off after certain value of monomer concentration (Bhattacharya and Misra 2004). As seen in Fig. 3a, we did not experience a lowered dependence of DG on GMA concentration. This may be attributed to relatively short reaction time and low monomer conversion obtained at the end of irradiation period. In order to avoid the formation of an insoluble polymer due to probable crosslinking reactions, grafting was stopped before reaching high monomer conversion. Therefore, a gradual increase in DG was observed by increasing GMA concentration.

As seen in Fig. 3b, the degree of grafting depends on the absorbed dose as well. This figure shows that DG increases rapidly with increasing absorbed dose at an initial stage, then the curve levels off and the grafting yield does not increase significantly. This is simply because higher overall dose produces more free radicals on the substrate, which initiate more

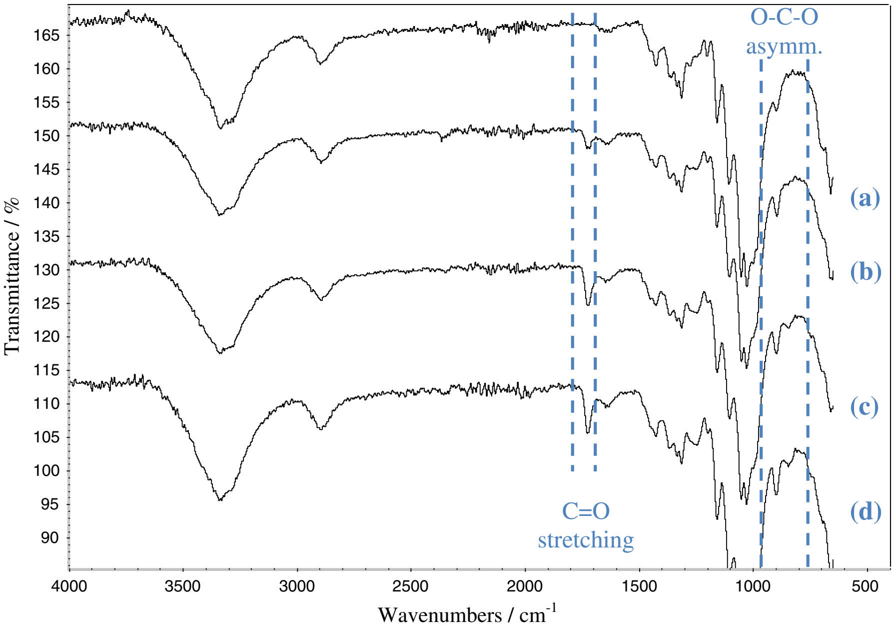


Fig. 5 FTIR spectra of (*a*) pristine cellulose and cellulose-*g*-PGMA copolymers with degree of grafting of (*b*) 10 %, (*c*) 20 %, (*d*) 27 %

grafting chains. On the other hand, as the polymerization proceeds, concentration of monomer available for grafting decreases. When the two effects counteracted, the degree of grafting levels off, reaching to its stable value (Jun et al. 2001; Barsbay and Güven 2013). We have investigated the effect of [GMA]/[RAFT agent] ratio on degree of grafting as well. As seen in Fig. 4, at constant GMA concentration (30 %, v/v), the DG value is increased by increasing the [GMA]/[CDB] ratio. This may be attributed to higher monomer conversion and molecular weight values obtained at the same grafting time when the RAFT agent concentration is lower (Kodama et al. 2014).

Characterization of cellulose-*g*-PGMA copolymers

The structures of pristine and PGMA grafted cellulose samples were studied by FTIR spectroscopy. Figure 5 compares typical ATR-FTIR spectra of cellulose and its copolymers with various DG. As seen in this figure, the measured depth in FTIR is saturated mostly by the high intensity absorption bands of cellulose. Still, an obvious new absorption peak at ~1,700 cm^{-1} is observed in the spectra of copolymers in contrast with the raw cellulose, which was assigned to the stretching vibration of –C=O in the PGMA grafts. In addition, the epoxy groups are indicated in the IR spectra of copolymers by the C–O–C asymmetric stretching observed at 750–950 cm^{-1} (Gudipati et al. 2008).

XPS analysis of the copolymers was carried out for better understanding of the chemical changes occurred upon grafting on the top ~5 nm surface layers. XPS survey wide scans of pristine cellulose and cellulose-*g*-PGMA copolymers with 16 and 35 % DG are presented in Fig. 6. The spectra of pristine cellulose and its copolymers consist of two main peaks at ~286 and 533 eV attributed to C1s and O1s, respectively (Barsbay et al. 2009). Compared to survey scan of pristine cellulose, a significant increase in C atom amount is recognized after grafting; the C atom amount increases from 57.5 to 63.1 % and 73.3 % while O atom amount decreases from 42.5 to 36.9 % and 25.7 % for copolymers with degree of grafting of 13 and 35 %, respectively. Furthermore, S2p peak centred at 169.4 eV is observed on the survey scan of the copolymer with 35 % DG as seen in Fig. 6c, which indicates the presence of the RAFT end group of PGMA.

XPS analysis was also employed to specify different forms of carbon atom by studying the changes of binding energy (BE) of electrons for this atom before and after grafting. Cellulose is a polymer exhibiting a high degree of crystallinity, therefore, grafting occurs mainly on the fiber surfaces (Barsbay et al. 2009, 2007). Therefore, the composition at the topmost

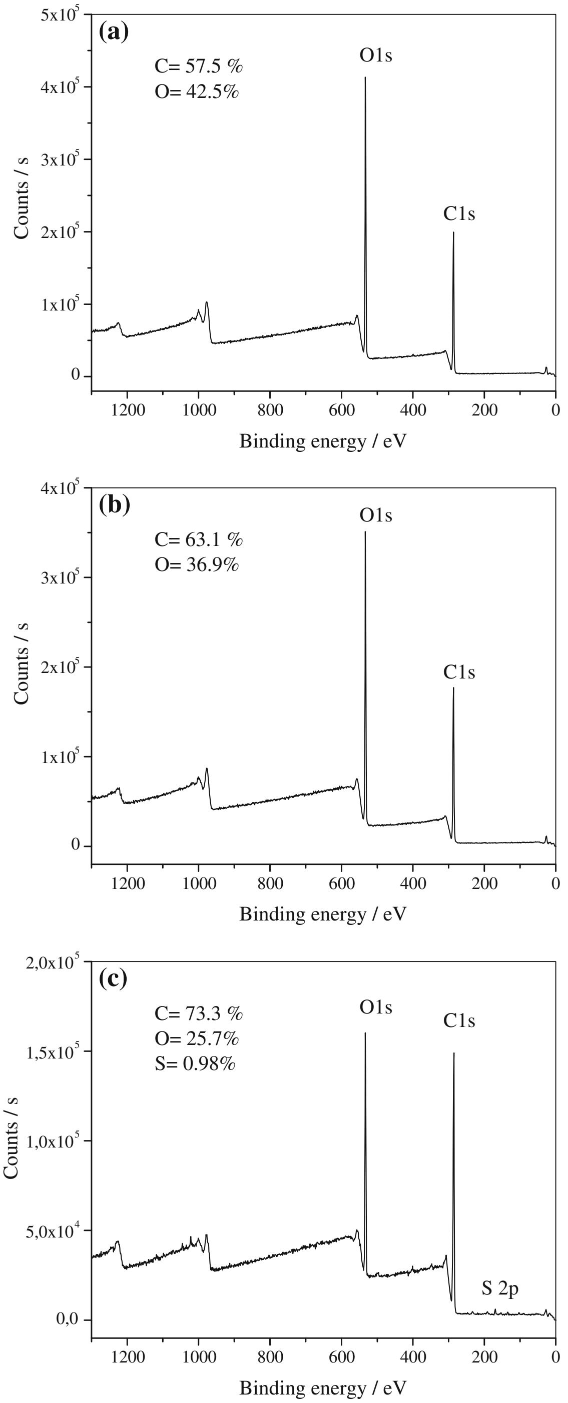


Fig. 6 XPS survey wide scan of (**a**) non-grafted cellulose and cellulose-*g*-PGMA copolymers with degree of grafting of (**b**) 13 % and (**c**) 35 %

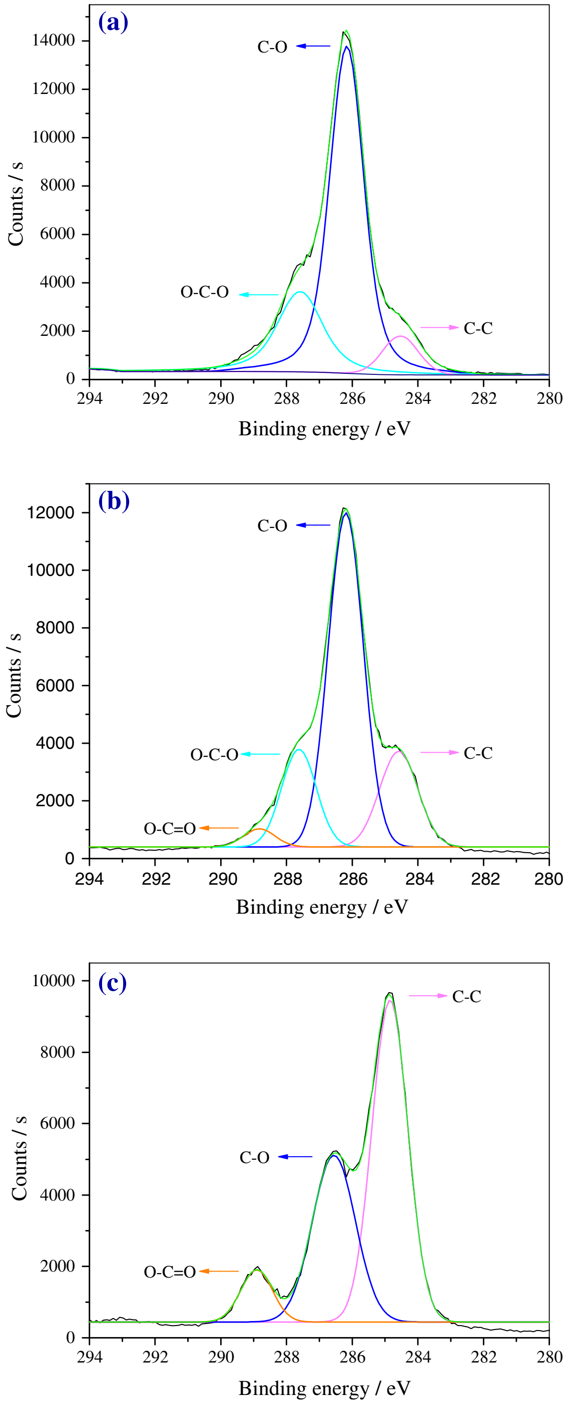


Fig. 7 C1 s XPS spectra of (**a**) pristine cellulose and cellulose-*g*-PGMA copolymers with degree of grafting of (**b**) 13 % and (c) 35 %

surface layers detected in XPS is expected to change significantly after grafting. C1s spectrum of pristine cellulose in Fig. 7a consists of a main peak with a BE of 286.5 eV, which is attributed to C–O bonds. Another component located at 287.6 eV is attributed to carbon atoms bonded to two oxygen atoms (Beecher and Frihart 2005; Morandia and Thielemans 2012; Labet and Thielemans 2011). The small component at the lowest binding energy of ~284.5 eV is attributed to electrons emitted from hydrocarbon-like carbon atoms. Cellulose does not possess this kind of carbons, but it easily attracts hydrocarbon contaminations as it is a high-surface energy material (Beecher and Frihart 2005). Therefore, C–C contribution to the cellulose chemical structure is common, even in purified (soxhlet-extracted) cellulose (Morandia and Thielemans 2012; Labet and Thielemans 2011). Upon grafting of PGMA, the relative amount of C–O groups at 286.5 eV decreases and the main peak appears at 284.9 eV, attributed to C–C species (Fig. 7c). Moreover, a new peak corresponding to O–C=O groups appears at ~289.2 eV, and the relative amount of this component increases with the progression of grafting. The complete alteration of surface composition detected by XPS clearly reveals that the surface grafting occurred on cellulose substrate.

In order to investigate to the fullest extent of the composition of copolymer, elemental analysis has been performed, Table 1. In contrast to XPS, sulfur atoms existing at chain-ends as RAFT agent moieties cannot be detected in elemental analysis due to their relatively lower amounts in the overall composition. The subtraction of percentages of carbon and hydrogen atoms from 100 % indicates the approximate amount of oxygen atoms. As seen in Table 1, grafting of PGMA to cellulose results in a clear increase in C atom amount and a decrease in O amount, which is in agreement with XPS results. If the weight percentages obtained in elemental analysis are converted into atomic percentages like in XPS, the C/O ratios determined by two methods, i.e. XPS and elemental analysis, give remarkable information concerning the compositional differences on the surface and in the bulk. The atomic C/O ratios calculated by XPS are 1.71 and 2.85 for the copolymers with 13 and 35 % DG, respectively. On the other hand, the atomic C/O ratios calculated by elemental analysis yield remarkably lower values of ~1.21 and 1.28 for the copolymers with similar DG of 16 and 31 %, respectively. This clearly indicates that the amount of C atom on the surface is significantly higher compared to bulk, and hence grafting of PGMA occurs mainly on the surface of cellulose, not inside its matrix.

Table 1 Elemental analysis results of pristine cellulose and copolymers with various graft ratios

Sample	C %	H %	O %[a]
Pristine cellulose	42.1	6.0	51.9
Cellulose-*g*-PGMA, DG: 16 %	44.6	6.1	49.3
Cellulose-*g*-PGMA, DG: 31 %	45.9	6.1	48.0

Sulfur atoms existing as chain end moieties of the grafted chains could not been detected due to the detection limits of the instrument

[a] Approximate amount of oxygen atoms by subtracting the percentages of carbon and hydrogen atoms from 100 %

SEM images given in Fig. 8 show that significant morphological changes occurred on the surface of cellulose due to grafting. When the degree of grafting is 10 %, the fibers of cellulose are entirely apparent as seen in Fig. 8b, even though a layer of PGMA has already started to cover them. With increasing degree of grafting, the coverage of fiber surfaces progresses as demonstrated in Fig. 8c. Further grafting makes cellulose fibers completely indistinguishable; the whole surface is already covered by a PGMA layer at a DG of 35 % as seen in Fig. 8d, which is in good agreement with XPS results.

We have previously verified that the surface hydrophobicity may completely be altered even at very low degrees of grafting (Barsbay and Güven 2013). In order to further study the surface properties, contact angle (CA) measurements were carried out. The pristine filter paper uptakes water very quickly, rendering the measurement of CA impossible. However, the cellulose-*g*-PGMA copolymers with degree of grafting (DG) of 10, 20, and 35 % became more hydrophobic with CAs of 28°, 72.7°, and 73.7°, respectively, as seen in Fig. 9. It was observed that the water droplet was partly absorbed in case of low DG; the water droplet almost disappeared at the end of second minute for the sample with 10 % DG. The CA decreased to 73.5° for the copolymer with 35 % DG after 2 min. Afterwards, no more water absorption could be detected for this sample, suggesting sufficient surface coverage as revealed by the SEM images.

TGA was performed to study the decomposition pattern and thermal stability of the pristine and grafted

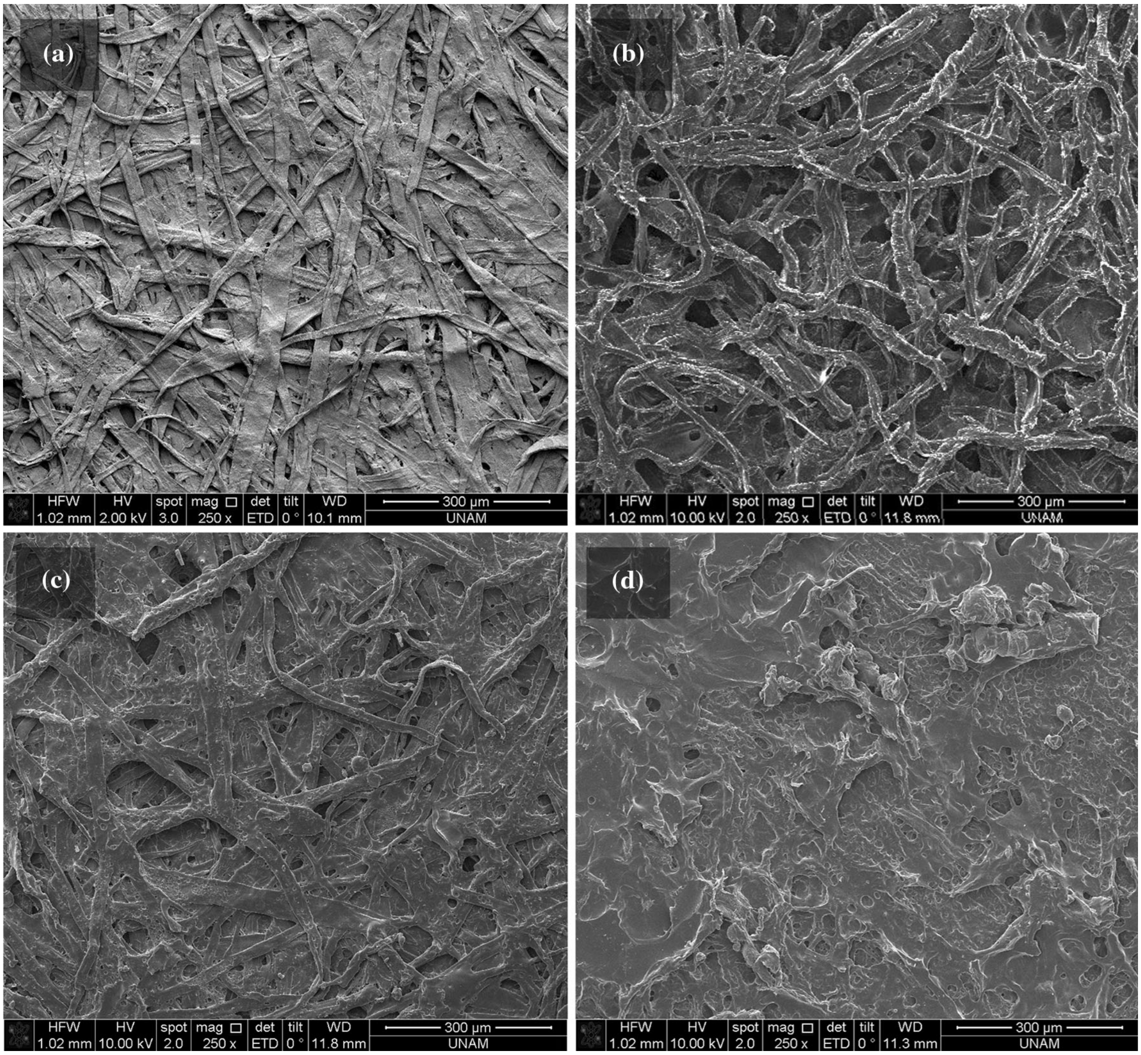


Fig. 8 SEM images of (**a**) pristine cellulose and cellulose-*g*-PGMA copolymers with degree of grafting of (**b**) 10 %, (**c**) 20 % and (**d**) 35 %

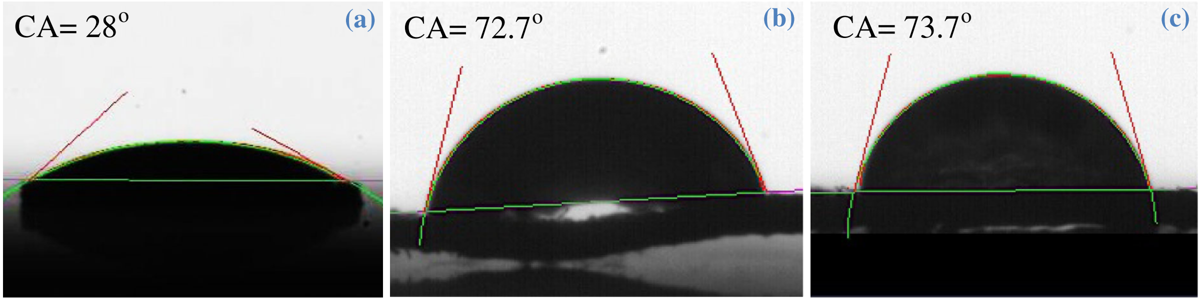


Fig. 9 Contact angle (CA) values at the end of 5th second for cellulose-*g*-PGMA copolymers with degree of grafting of (**a**) 10 %, (**b**) 20 % and (**c**) 35 %

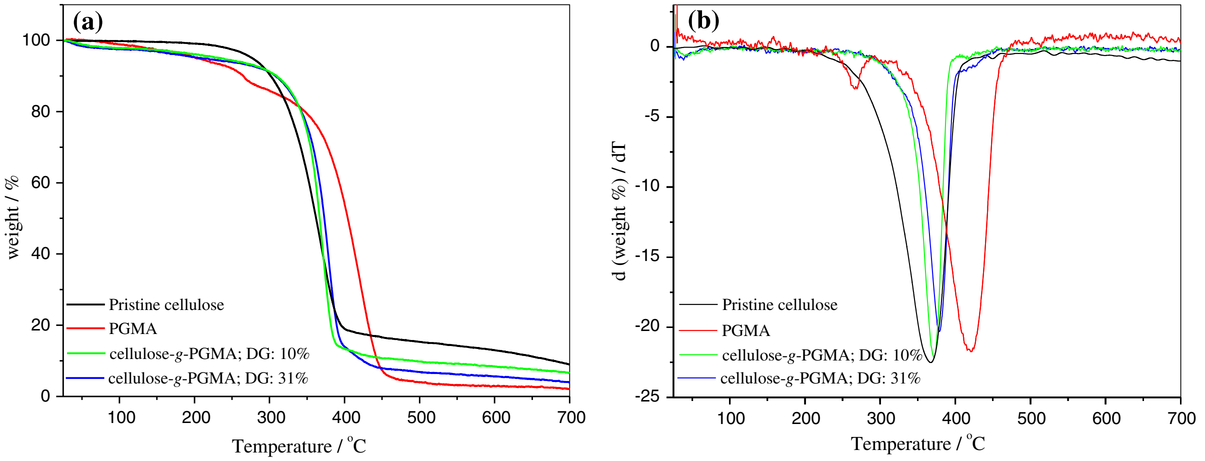


Fig. 10 **a** Thermogravimetry (TG), and **b** derivative thermogravimetry (DTG) curves of cellulose, PGMA, and cellulose-*g*-PGMA copolymers

polymers. Thermogravimetry (TG) and derivative thermogravimetry (DTG) thermograms of cellulose, PGMA and cellulosic copolymers with different graft ratios are shown in Fig. 10, the data are summarized in Table 2. TG and DTG curves show that the degradation profile of pristine cellulose contains one step. The weight loss of cellulose occurs after around 250 °C at a relatively slow rate, then the rate of weight loss reaches its maximum value at 368 °C. In PGMA, on the other hand, a two-step decomposition process is observed. The first minor degradation step is attributed to the depolymerization starting at the chain ends, which is followed by random chain scissions at higher temperature range with a maximum weight loss rate at 420 °C (Ahmad and Zulfiqar 2002). The first degradation step of PGMA is not observed in the thermograms of copolymers. This implies that the depolymerization of PGMA chains mainly disappears after grafting. As evident from the derivative thermograms and from Table 2, both the initial decomposition (T_{di}) and the maximum decomposition (T_{dm}) temperatures of cellulose-*g*-PGMA copolymers are higher than those of pristine cellulose, indicating the increased thermal stability of cellulose after grafting. A second degradation peak is observed at about 418 °C in the DTG curve of the copolymer with DG of 31 %. However, the area of this peak cannot account for all the PGMA existing in copolymer composition, indicating that the major amount of PGMA species are decomposed together with cellulose substrate. In addition, the amount of residual weight (%) decreases with increasing DG. This is quite reasonable considering the residual weights accompanied by pristine cellulose and PGMA.

Table 2 Thermostability of cellulose, PGMA and cellulose-g-PGMA copolymers

Sample	T_{di}^{a}/°C	T_{dm}^{b}/°C	Residual mass[c]/ wt%
Pristine cellulose	246	368	9.14
Cellulose-*g*-PGMA, DG: 10 %	298	371	6.73
Cellulose-*g*-PGMA, DG: 31 %	298	378	3.97
PGMA	320[d]	420[d]	2.12

[a] The initial thermal decomposition temperature, T_{di}, is the temperature at which the decomposition rate points out a significant weight loss ($\mathrm{d(wt\%)/d}T > 1\ \%\ {}^{\circ}\mathrm{C}^{-1}$)

[b] The maximum decomposition temperature, T_{dm}, is the temperature at which the highest decomposition rate is observed for the corresponding pattern

[c] residual weight (%) at 700 °C

[d] These values belong to second degradation step of PGMA

Conclusion

In summary, grafting of PGMA on cellulose by radiation-induced RAFT polymerization was successfully achieved. To the best of our knowledge this is the first report dealing with the γ-initiated RAFT polymerization of GMA and investigating the grafting of this monomer from cellulose surface using the RAFT technique. Due to the versatility of the grafted polymer, i.e. PGMA, the synthesized cellulosic copolymers possess the attitude to formulate tailor-made and natural-based end products capable to meet a wide variety of demanding specifications. In addition, it has been implied that the facile combination of γ-radiation and RAFT polymerization may lead to crosslinked polymers at ambient temperature without addition of a crosslinker.

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