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Modification of cellulose by RAFT mediated graft copolymerization

RAFT aracılıklı aşı kopolimerizasyonu ile selülozun modifikasyonu

Review Article

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ABSTRACT

Cellulose is the most abundant organic material on the earth: it is the main constituent of plants, also present in bacteria, fungi, algae and even in animals. Despite all its advantageous properties like high strength, durability, thermal stability, biocompatibility, biodegradability, relatively low cost and low density, cellulose lacks some of the versatile properties of synthetic polymers. Therefore, chemical modification of the cellulose structure is necessary in most cases to overcome the existing drawbacks. The synthesis of cellulosic graft copolymers through the introduction of branches (grafts) of synthetic polymers that impart specific properties onto the cellulose substrate is one of the key ways of modifying the physical and chemical properties of cellulose. The recent advances in the field of controlled radical polymerization (CRP) methods provide unique opportunities to tailor the surface properties of graft copolymers by controlling the graft length, the architecture and the composition. This study reviews our previous works investigating the modification of cellulose via graft copolymerization mediated by Reversible Addition Fragmentation chain Transfer (RAFT) polymerization, one of the most powerful CRP methods.

Key Words
RAFT mediated grafting, cellulose, γ-irradiation, styrene, 2-hydroxyethyl methacrylate, 4-styrene sulfonate, glycidyl methacrylate, acrylic acid, N-isopropylacrylamide.

ÖZET

Selüloz dünyada en sık bulunan organik maddedir: bitkilerin temel bileşenidir, bakterilerde, mantarlarda, alglerde ve hatta hayvanlarda bile bulunur. Yüksek derecede mukavemet, ısıl kararlılık, biyouyumluluk, biyobozunurluk, nispeten uygun maliyet ve düşük yoğunluk gibi avantajlı özellikleri olsa da, sentetik polimerlerin kimi kullanışlı özelliklerini taşımamaktadır. Bu nedenle, birçok durumda selülozun yapısının eksikliklerinin giderilmesi amacıyla modifiye edilmesi gerekmektedir. Selülozun kimyasal ve fiziksel özelliklerinin modifiye edilmesinde kullanılan önemli yollardan biri, istenilen özellikleri taşıyan sentetik polimer zincirlerinin (aşılarının) selüloz yapısına katılması suretiyle selülozik aşı kopolimerlerin sentezlenmesidir. Kontrollü radikal polimerizasyonu (CRP) alanındaki son gelişmeler, aşılanan zincirlerin uzunluklarının, yapısının ve bileşiminin kontrol edilmesiyle aşı kopolimerlerin yüzey özelliklerinin ayarlanması adına eşsiz imkanlar sağlamıştır. Bu çalışma, en başarılı CRP yöntemlerinden biri olan Tersinir Katılma-Ayrılma Zincir Aktarım (RAFT) polimerizasyonu aracılıklı aşı kopolimerizasyonu ile selülozun modifikasyonunu inceleyen daha önceki çalışmalarımızı derlemektedir.

Anahtar Kelimeler
RAFT aracılıklı aşılama, selüloz, γ-ışınlaması, stiren, 2-hidroksietil metakrilat, 4-stiren sülfonat, glisidil metakrilat, akrilik asit, N-izopropilakrilamit.

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INTRODUCTION

A renewed interest in cellulose research and application has been sparked in recent years, mostly by technological interests in renewable raw materials and more environmentally friendly and sustainable resources[1, 2]. In some previous works to date cellulose-based intelligent materials such as self-cleaning filter paper surfaces [3], thermo-responsive [4, 5] and pH-responsive [4] cellulosic materials and electroactive paper [2] have been fabricated. In order to carry out and control the modification of cellulose, understanding its structure is a pre-requisite. As can be seen in Figure 1, the molecular structure of cellulose is composed of linear chains with a large number of hydroxyl groups (three OH groups per the repeating unit). These hydroxyl groups are capable of forming extensive hydrogen bonds between and within the chains, yielding a straight and crystalline chain nature [6-9]. They also provide chemical activity to cellulose through the well-established methods such as esterification [1].

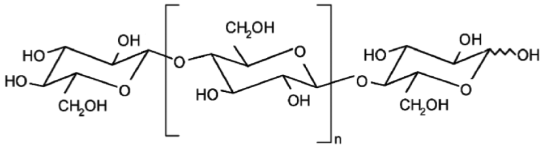

Figure 1. Molecular structure of cellulose

In 1943, Ushakov synthesized the first cellulosic graft copolymers by copolymerizing some allyl esters and vinyl esters of cellulose with the esters of maleic acid [10]. Since this pioneering work, extensive studies have been carried out on the synthesis, properties and applications of cellulosic graft copolymers [11-13]. Some of these research studies have been reviewed by Hebeish and Guthrie [14] by Samal et al. [15] and by Roy et al. [1]. Carrying out the grafting of a surface via the controlled radical polymerization (CRP) methods provides unique opportunities to tailor the surface properties of this surface by controlling the attitudes of the grafted chains [16-19]. Nitroxide mediated polymerization (NMP) was the first CRP method to be used in cellulose grafting [20]. However, the utilization of NMP in controlling the cellulose modification was limited as it is applicable to some monomers only and required the use of high temperatures. Among the CRP techniques, Atom Transfer Radical Polymerization (ATRP) is the most used with respect to the modification of the surface properties of cellulose and its derivatives [3, 21-27]. On the other hand, there is a very limited number of studies concerning the modification of cellulose surface via RAFT-mediated grafting [1]. Among the CRP methods, i.e. RAFT, NMP and ATRP, RAFT is of particular interest as a very wide range of functional monomers can be polymerized in a controlled manner under non-demanding reaction conditions (e.g., tolerance to oxygen and low temperatures) via this technique [19]. The following part of this report summarizes our previous works concerning the RAFT agent-mediated free-radical graft polymerization of various monomers onto cellulose fibres in a "grafting-from" approach under the γ-irradiation [28-30].

Modification of cellulose via RAFT-mediated grafting

Grafting of styrene from cellulose and verification of controlled attitude of the grafting process

We applied RAFT polymerization to graft polystyrene (PSt) to cellulose using γ-irradiation as the source of initiation [28]. The cellulose sample used in all works was Whatman No.1 filter paper due to its high cellulose content (98% α-cellulose), lesser amount of impurities, and ease of chemical modification. The homo and graft polymerizations proceeded in a controlled fashion as demonstrated in Table 1 by the agreement between the experimental ($M_{n,GPC}$) and theoretical ($M_{n,Th.}$) number-average molecular weights. Furthermore, the polydispersities (PD) remained in the range of 1.13–1.26, well below the theoretical lower limit of 1.5 for conventional free-radical polymerization. The synthesized graft copolymers were characterized by various methods like SEM, XPS, Raman, FT-IR, DSC, TGA and contact angle measurements [28]. Assessment of the enzymatic hydrolysis of cellulosic materials indicated that the grafted PSt

Table 1. Comparison of the Results of Homo[a] and Graft[b] Polymerizations of Styrene mediated by the RAFT agent cumyl phenyldithioacetate (CPDA).

irradiation time / h	Convn * / %	$M_{n,GPC}$ * / g mol^{-1}	$M_{n,Th.}$ * / g mol^{-1}	PD *	convn / % **	M_n ** /g mol^{-1}	$M_{n,Th.}$ ** / g mol^{-1}	PD **	graft ratio / wt.%♣
17	0.84	-	870	-	0.91	-	920	-	<0.5
24	0.92	-	930	-	1.36	760	1250	1.17	1.30
41	1.68	780	1470	1.15	3.15	2200	2530	1.15	5.00
48	1.66	750	1460	1.16	4.00	2820	3140	1.15	8.00
72	4.11	2230	3220	1.12	7.06	4740	5340	1.16	15.10
96	6.11	3050	4660	1.08	9.18	6050	6870	1.24	20.10
160	10.70	7880	7960	1.12	16.50	10760	12130	1.21	30.00
232	14.50	10500	10690	1.11	19.70	13750	14440	1.23	39.10

[a] RAFT homo-polymerization of styrene (3.45 mol L^{-1}) initiated via γ-irradiation (dose rate, 0.09 kGy h^{-1}) in dioxane-water (98:2 v/v) at [St]/[CPDA] = 690:1 and room temperature.

[b] RAFT graft copolymerization of styrene (3.45 mol L^{-1}) from cellulose (0.04 g) initiated via γ-irradiation (dose rate, 0.09 kGy h^{-1}) in dioxane-water (98:2 v/v) at [St]/[CPDA] = 690:1 and room temperature.

* Presented values correspond to the results of homo-polymerization of styrene, i.e. no cellulose substrate was added to medium.

** Presented values correspond to the results of the free homo-polystyrenes formed during the graft polymerization. The presented results were taken from ref. [28].

chains are efficiently covering the surface of the cellulose, protecting it from being attacked by the enzyme.

The molecular weights and molecular weight distributions of grafted PSt chains were obtained by cleaving the grafts from the cellulose surface by acidic treatment of cellulose-*g*-PSt copolymers, followed by SEC analysis which depicted narrow polydispersities (PD). As well as having low PD, the number-average molecular weight (M_n) values of cleaved PSt grafts were very close to those of the corresponding free (non-grafted) PSt chains in solution, and thus to the theoretical molecular weight values. This invention clearly proved for the first time the controlled growing of the grafted chains via RAFT mechanism without any prior functionalization of the surface. It was therefore showed that analyzing the free (non-grafted) polymer in solution to gain information on the molecular weight and PD of the grafted chains is a valid approach. This finding is of extremely high significance as the modification of many polymeric surfaces (e.g. by RAFT agents or ATRP initiators) and the cleaving of the grafted chains from the surfaces are often impossible or very time consuming [28]. As well as resulting in this important finding, this study also yielded smart surfaces with self-cleaning property. The self-cleaning ability controlled by the hydrophobicity and the roughness of the cellulose-*g*-PSt copolymer surfaces was tested by contaminating the surfaces with carbon black, and then by applying water droplets. As soon as the cellulosic paper was tilted, water drops promptly rolled off the surface, collecting dirt along the way and leaving a clean surface.

Grafting of sodium 4-styrene sulfonate from cellulose

We have demonstrated for the first time that RAFT polymerization of Sodium 4-Styrene Sulfonate (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 to near quantitative conversions via 4-cyanopentanoic acid dithiobenzoate (CPADB) mediation [29]. Under the same conditions RAFT polymerization of SS mediated with 3-benzylsulfanylthiocarbonylsulfanyl propionic acid (BPATT) resulted in an uncontrolled fashion. Using CPADB modified cellulose as a macro chain transfer agent, a graft copolymer with SS has been prepared in aqueous media under γ-irradiation. Attachment of RAFT agent to the surface enables grafting with a higher efficiency. The RAFT mediated graft polymerization of SS from CPADB-functionalized cellulose yielded significantly higher graft frequency compared to the conventional grafting. Thermally initiated grafting of SS has also been studied which results in a reduced graft frequency in comparison to γ-initiated ones due to increased termination/detachment of surface functionalities. Immobilization of RAFT agents to cellulose and grafting of SS from these modified surfaces has been characterized by Raman, FT-IR, XPS, TGA and DSC methods [29]. The controlled fashion indicated by the homopolymerization was demonstrated in Figure 2 by the linear evolution of the number-average molecular weight, M_n, with conversion and the unimodal and narrow GPC traces observed at all conversions.

To the best of our knowledge this was the first report dealing with the γ-initiated RAFT polymerization of SS and investigating the grafting of this monomer from cellulose surface using the RAFT technique. An added advantage of these controlled polymerizations was that they occurred in an environmentally friendly solvent like water and for the γ-initiated ones at ambient temperatures. This makes the applied polymerization procedure suitable in biomedical studies such as generating

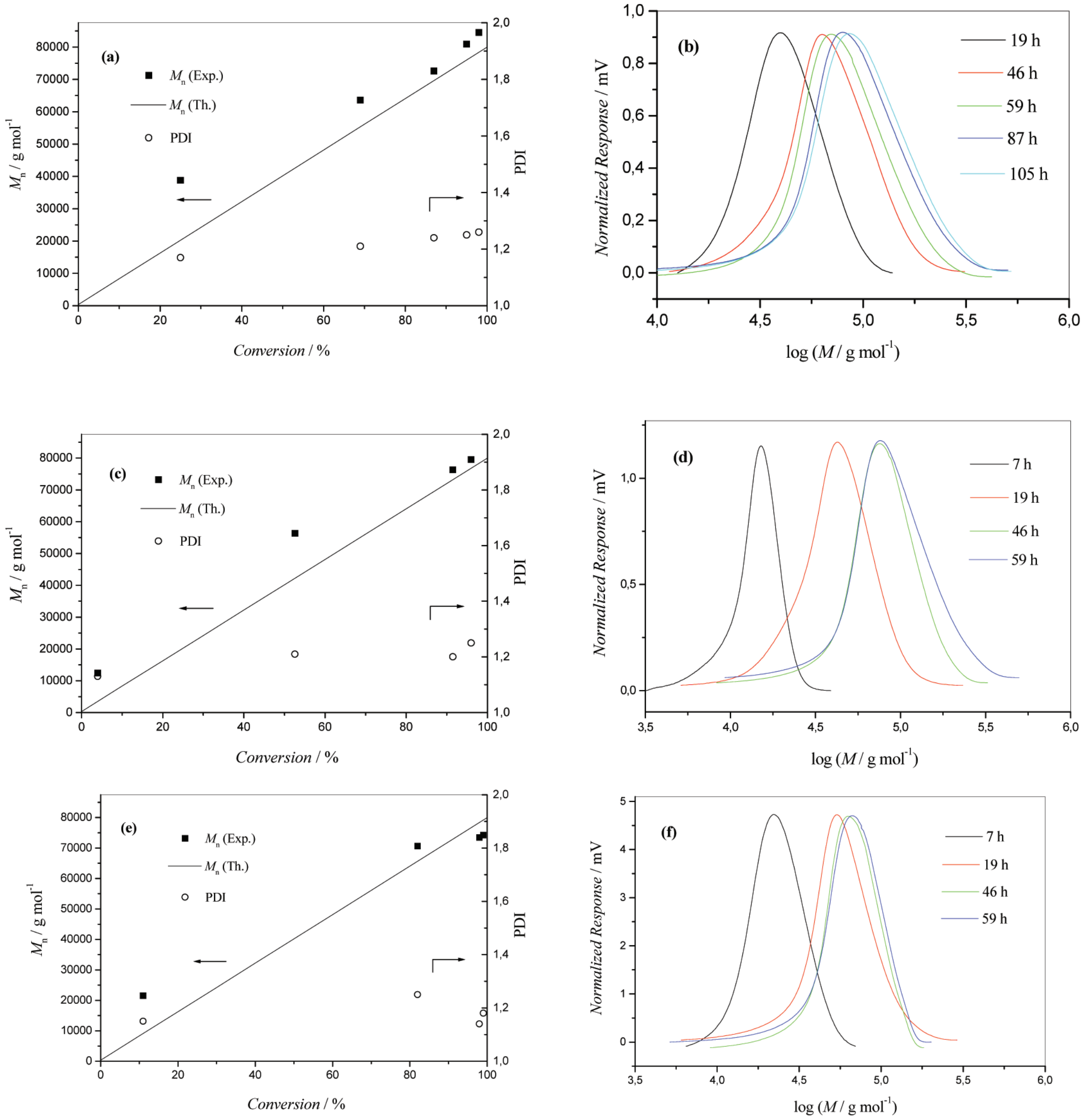

Figure 2. Evolution of number-average molecular weight, M_n, and polydispersity, PD, versus the monomer conversion graphs for PSS at (a) low dose, (c) mid. dose, (e) high dose; and evolution of molecular weight distribution versus time graphs for PSS at (b) low dose, (d) mid. dose, (f) high dose: γ-initiated homopolymerization of PSS mediated via the RAFT agent 4-cyanopentanoic acid dithiobenzoate (CPADB), [SS] = 1 mol L^{-1} in water-EtOH (93:7 v/v) at [SS]/[CPADB] = 387:1 and room temperature. The presented results were taken from the supporting information of ref. [29].

protein–polymer conjugates with defined properties requiring generally low temperatures (T < 37 °C) to avoid protein/biomolecule denaturation.

Grafting of 2-hydroxyethyl methacrylate from cellulose

Poly(2-hydroxyethyl methacrylate) (PHEMA) has been widely used in many biomedical applications. Moreover, the hydroxyl groups of PHEMA can be used for the immobilisation of different compounds. We carried out the RAFT-mediated free-radical graft polymerization of HEMA onto cellulose fibres in a "grafting-from" approach under the γ-irradiation [30]. This study was the first report dealing with the γ-initiated RAFT polymerization of HEMA and investigating the grafting of this monomer from cellulose surface using the RAFT technique. The effects of absorbed dose and monomer concentration on the graft ratios were investigated at different monomer (HEMA) to RAFT agent (cumyl dithiobenzoate, CDB) ratios. Cellulose-g-PHEMA copolymers with various graft ratios up to 92 % (w/w) were synthesized. The synthesized copolymers were characterized by various techniques results of which confirmed the existence of PHEMA in the copolymer composition. The GPC analysis results indicated that a full control over the molecular weight and PDs could not be achieved due to probable radiation effects on PHEMA structure such as branching or chain scission/crosslinking reactions. As can be seen in Figure 3, the PD values are indicating broad molecular weight distributions near 2. It should be mentioned here that the PD values were significantly lower compared to polymerization in the absence of RAFT agent. The multimodal GPC chromatograms with very high PDs up to ~19 observed for conventional polymerization were replaced with monomodal distributions for the RAFT mediated ones as seen in Figure 3. Despite the weak control over the M_n and PD, the degree of grafting of PHEMA could be controlled smoothly by changing the [HEMA]/[CDB] ratio in RAFT mediated grafting which was not possible with conventional polymerization.

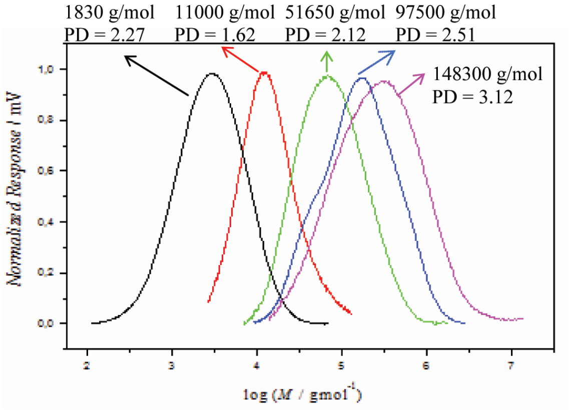

Figure 3. Evolution of molecular weight distribution vs time for free PHEMA formed during γ-initiated graft polymerization from cellulose mediated via the RAFT agent CDB at room temperature. Solvent: DMF, [HEMA]/[CDB] = 722:1.

Grafting of glycidyl methacrylate, acrylic acid and N-isopropylacrylamide from cellulose

We have grafted glycidyl methacrylate (GMA) from cellulose by the combination of radiation-induced initiation and the RAFT technique, leading to epoxy functionalized surfaces that enable further modifications. The results indicated that the graft ratio of PGMA could be controlled smoothly via this combination, which was not possible with conventional polymerization. Although the molecular weight and distribution of grafted PGMA chains could be significantly controlled in the presence of RAFT grafting as compared to uncontrollable fashion in its absence, a full control over the molecular weight and PDs could not been achieved. Cumyl dithiobenzoate (CDB) mediated RAFT polymerization of GMA revealed the difficulty of controlling the polymerization of GMA due to high crosslinking tendency of this monomer under γ-irradiation.

We utilized the powerful combination of γ-irradiation and RAFT polymerization technique in order to prepare intelligent flat cellulosic surfaces by grafting poly(acrylic acid) (PAA) and poly(N-isopropylacrylamide) (PNIPAAm) onto cellulose in a controlled manner. The graft polymerization of NIPAAm and AA from cellulose substrate under γ-irradiation at room temperature in aqueous media led to well-defined smart surfaces. PNIPAAm is one of the most studied synthetic responsive polymers and it undergoes a sharp coil-to-globule transition in water around its lower critical solution temperature (LCST) of 32 °C, changing from a hydrophilic state below this temperature to a hydrophobic state above it [5]. PAA responds to changes in pH and ionic

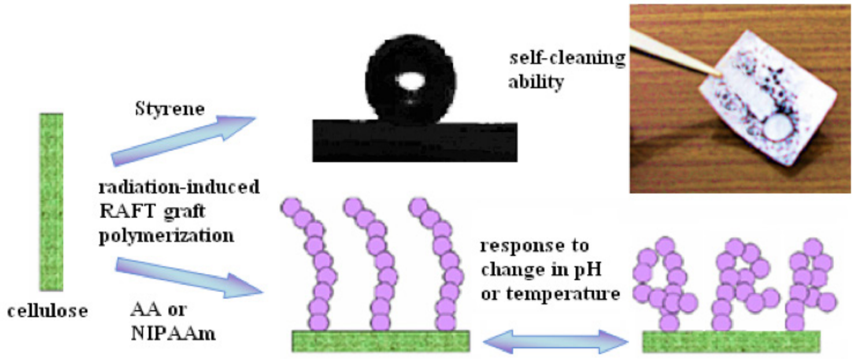

Figure 4. Schematic illustration of smart attitudes of cellulosic copolymers: Self-cleaning ability of PSt grafted cellulose and pH and temperature responsiveness of PAA and PNIPAAm grafted cellulose surfaces.

strength by changing coil dimensions and solubility. In general, PAA displays a broad pKa value of 4–5 and thus a proportion of its side chain carboxyls are ionized around pH 5–6. Below this pH value, a PAA-grafted surface is hydrophobic with collapsed polymer brushes whereas it becomes hydrophilic in neutral and alkaline aqueous media [31]. The effect of temperature on the wettability of the surfaces was characterized by static contact angle (CA) measurements. The responses of PNIPAAm-grafted cellulose to change in temperature and PAA-grafted cellulosic copolymer to change in pH was characterized by static contact angle (CA) measurements at various temperatures and pH values, respectively. The collapses of the PNIPAAm and PAA brushes by changes in temperature or pH were reflected by changes in the wettability of the surface. The intelligent attitudes that respond to change in temperature and pH for PNIPAAm and PAA grafted cellulose and self-cleaning ability of PSt grafted cellulose surfaces were schematically displayed in Figure 4.

Conclusion

We combined γ-radiation and RAFT polymerization for the preparation of graft copolymers of cellulose with styrene, 4-styrene sulfonate, 2-hydroxyethyl methacrylate, glycidyl methacrylate, acrylic acid and N-isopropylacrylamide. The use of radiation as an initiation source in RAFT polymerization opens the door to designing new tunable surfaces in a controlled manner by a one-step method that leads to stable bonding between the surface and the grafted polymer under mild conditions without prior functionalization of the surface.

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