Flame-Retardancy Finishing of Cotton Fabric by Surface-Initiated Photochemically Induced Atom Transfer Radical Polymerization

Gamal Zain  
Polymer Institute of the Slovak Academy of Sciences, Dubravska cesta 9, 845 41 Bratislava

Igor Jordanov  
Department of Textile Engineering, Faculty of Technology and Metallurgy, Ss. Cyril and Methodius University, Ruger Boskovic 16, 1000, Skopje

Sandra Bischof  
Department of Textile Chemistry and Ecology, Faculty of Textile Technology, University of Zagreb, Prilaza baruna Filipovica 28a, Zagreb

Eva Magovac  
Department of Textile Chemistry and Ecology, Faculty of Textile Technology, University of Zagreb, Prilaza baruna Filipovica 28a, Zagreb

Alena Opálková Šišková  
Polymer Institute of the Slovak Academy of Sciences, Dubravska cesta 9, 845 41 Bratislava

Anna Vykydalová  
Polymer Institute of the Slovak Academy of Sciences, Dubravska cesta 9, 845 41 Bratislava

Angela Kleinová  
Polymer Institute of the Slovak Academy of Sciences, Dubravska cesta 9, 845 41 Bratislava

Matej Mičušik  
Polymer Institute of the Slovak Academy of Sciences, Dubravska cesta 9, 845 41 Bratislava

Katarína Mosnáčková  
Polymer Institute of the Slovak Academy of Sciences, Dubravska cesta 9, 845 41 Bratislava

Jana Doháňošová  
Central Laboratories, Faculty of Chemical and Food Technology STU, Radlinského 9, 812 37 Bratislava

Jaroslav Mosnáček (✉ jaroslav.mosnacek@savba.sk)  
Polymer Institute of the Slovak Academy of Sciences, Dubravska cesta 9, 845 41 Bratislava

Research Article

Keywords: Fire resistant, Dimethyl(methacryloyloxy)methyl phosphonate, PhotoATRP, Grafting from, Phosphorus-nitrogen synergism

Posted Date: August 25th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1978432/v1

License: © This work is licensed under a Creative Commons Attribution 4.0 International License.  Read Full License
Abstract

Phosphorus-containing polymers are very promising because of the versatility of their applications. Polyphosphates and polyphosphonates are well-known for their excellent fire-retardant properties. In this work, a cotton fabric was grafted by oxygen-tolerant photochemically induced atom transfer radical polymerization (photoATRP) of dimethyl(methacryloyoxymethyl) phosphonate (MAPC1) in order to prepare flame resistant fabric. The photoATRP of MAPC1 was first optimized in solution and subsequently used for surface-initiated polymerization from of cotton fabric pre-functionalized by ATRP initiator in order to achieve PMAPC1 brushes onto the surface. The modified cotton fabrics were characterized by attenuated total reflection-Fourier transforms infrared spectroscopy and X-ray photoelectron spectroscopy to prove successful grafting. Minimal effect of grafting on mechanical properties of the cotton fabric was confirmed by tensile tests. The thermal properties and flammability of the modified fabric were tested by thermogravimetric analysis, horizontal and vertical flame tests. Limiting oxygen index and microscale cone calorimeter were performed as well. The results show that modified fabric has a high flame resistance making it a good candidate for flame-retardant application. Washing tests confirmed that the grafted layer on the fabric has good durability from the point of view of retention of high flame resistance.

1. Introduction

Cotton, as a natural textile fiber, has numerous advantages, such as biodegradability, breathability, softness, and comfort (Xie et al. 2013). It is widely used in garments, bedding, curtains, and carpets, etc. However, it easily combusts as it is documented based on Limiting Oxygen Index (LOI) value (Balakrishnan and Mayilsamy 2013), which was found to be as low as 19. Once cotton fabric ignites, the flames rapidly propagate, potentially leading to fatal burns within 15 s (Wang et al. 2018). Therefore, it is of great importance to impart flame resistance property to cotton fabric. The burning behavior of the flame-resistant cotton should be altered from ash burning to steady charring. Flame-retardant (FR) compounds can slow down the combustion of treated cotton and thus improve the safety.

Compounds containing phosphorus, nitrogen, silicon, and/or boron atoms are more commonly used as FRs because they are more environmentally friendly compared to the traditional halogen-based ones (Abou-okeil et al. 2013; Mohamed et al. 2014; Petkovska et al. 2022). Grafting of the FR molecules onto the fabrics by covalent bonds is perhaps the most efficient method to obtain a flame-retardant fabric with good durability. Rosace et al synthesized a novel intumescent FR, in which vinyl phosphonic acid and methacrylamide were used as reactive monomers to be grafted onto cotton fabric surface using potassium persulfate as an initiator. Data showed that the finished cotton fabrics exhibited durability and flame retardancy (Rosace et al. 2017).

In general, most of the flame-retardant modifications were conducted by free radical co/polymerization (David et al. 2012) or by the introduction of a phosphonated moiety during a post-polymerization reaction (Rixens et al. 2006). Free radical polymerization has different upsides such as its applicability to wide range of vinyl monomers, its tolerance to moisture and its straightforward setup at mild reaction conditions. However, in FRP, the prevalence of irreversible termination and transfer processes, and the absence of mediating species render the control over the polymerization, means that polymer growth affords a statistical distribution of chain lengths, over which we have only limited control. This will lead to polymer chains with high heterogeneity in chain lengths which directly impacts the final properties (Truong et al. 2021). Furthermore, the formation of unbound homopolymer is unavoidable during free radical graft polymerization where the polymerization occurs on both free initiator and substrate (Kedzior et al. 2016).

Reversible deactivation radical polymerization (RDRP) has recently been revealed as a powerful method of polymerization because it can provide control over the polymer chain growth resulting in well-defined polymer
structure and characteristic (Tsujii et al. 2006; Zoppe et al. 2017). Atom transfer radical polymerization (ATRP) is one of the RDRP techniques and it has been extremely investigated since its discovery in 1995 (Wang and Matyjaszewski 1995). ATRP offers control over the architecture, molar mass, and molar masses distribution (dispersity) in comparison with FRP (Matyjaszewski 2012, 2018).

Surface-initiated ATRP (SI-ATRP) provides a good way for surface modification of different substrates helping to impart different properties on them. A polymer brush can be created on a surface by grafting from strategy that depends on the deposition of the ATRP initiator on the substrate surface. Then, the modified surface is used as a macroinitiator. This built-in macroinitiator minimizes the homopolymer content as the polymerization occurs mainly on the substrate. SI-ATRP has previously been utilized for modification of silicon, gold and silica surfaces, and porous substrates (Carlmark 2002; Grundke 2008).

In general, the first reported normal ATRP is sensitive to oxygen and requires a large amount of transition-metal complex catalyst, which is costly and harmful to physiological systems. Therefore, many attempts were reported to overcome such issues (Krys and Matyjaszewski 2017). Contrary that, recently developed a photochemically induced atom transfer radical polymerization (photoATRP) presents several advantages concerning normal ATRP processes (Mosnáček and Ilčíková 2012; Borská et al. 2017a; Zain et al. 2019). These include the possibility of temporal control over polymer chain growth, good tolerance toward oxygen, and using ppm amounts of catalyst necessary to attain controlled polymerization. Surface-initiated photoATRP (SI-photoATRP) was already used for surface modification of filter paper where methyl acrylate and diethylene glycol acrylate were grafted from the paper surface (Larsson et al. 2015). Very recently, SI-photoATRP was reported by our group for preparation of antibacterial cotton fabric while it was demonstrated to be an easy-to-use way for surface modification (Zain et al. 2021).

Polyphosphates and polyphosphonates are known as excellent fire-retardant additives. However, phosphonate compounds are more attractive as the phosphate derivatives are known to be much more sensitive towards hydrolysis (El Asri et al. 2008). Dimethyl(methacryloyloxy)methyl phosphonate (commercially known also as MAPC1) is one of few phosphorus-containing vinyl monomers that can be radically polymerized. The first investigation of normal ATRP of MAPC1 has been reported by David et.al using toluene and 2-bromoisobutyrate as a solvent and initiator, respectively. Although different catalytic systems were studied, the polymerization of MAPC1 was not well controlled. A homopolymer with a lower molar mass than the theoretically predicted one and high dispersity was obtained. In addition, the polymerization proceeded with very low monomer conversion, which was attributed to the ability of phosphorus to interfere with the original ligand affecting the polymerization (David et al. 2009). Later, normal ATRP and initiators for continuous activator regeneration (ICAR) ATRP were reported by Matyjaszewski et.al. Ethyl α-bromophenyl acetate was used as an initiator and CuBr/CuBr$_2$ with bpy or TPMA ligand as catalyst systems. It was found that both normal and ICAR ATRP were successful, providing homopolymers with high molar mass and relatively low dispersity (Mukumoto et al. 2014). Reversible addition-fragmentation chain transfer (RAFT) polymerization of MAPC1 was reported as well by Benjamin et.al. PolyMAPC1 with controlled molar mass and low dispersity was obtained using DMF as solvent at 70°C (Cannicciioni et al. 2013). Recently, Solimando et al. have reported nitroxide-mediated polymerization of MAPC1 with 10 mol% of styrene as a comonomer. SG1-terminated alkoxyamine (BlocBuldier) was used as an initiator and it provided good control of the polymerization as was demonstrated by kinetics monitoring (Solimando et al. 2020).

Despite the above-mentioned advantages of photoATRP technique, its applicability for phosphorus-containing monomers and surface modification has not been investigated so far. In this work, the flame-retardant cotton fabric was successfully prepared by SI-photoATRP of MAPC1 monomer from the cotton fabric surface using a simple procedure without necessity to use time consuming processes for air removal. PhotoATRP of MAPC1 was first
optimized in solution and then it was applied for MAPC1 grafting from the cotton fabric surface. To our knowledge, this work is the first report on photoATRP of phosphorus-based monomers and we believe it will help to expand the applicability of the simple photoATRP technique.

2. Experimental Part

2.1. Materials and Methods

Dimethyl(methacryloyloxymethyl) phosphonate monomer (MAPC1), 98%, was provided by SPECIFIC POLYMERS Inc., France. It was purified before use by passing through a basic alumina column to remove the inhibitor. Tris(2-pyridylmethyl)amine (TPMA) was synthesized according to procedures reported by G. Britovsek (Britovsek et al. 2005). Copper (II) bromide (CuBr$_2$), ethyl α-bromoisobutyrate (EBIB), 98%, 1-oleyl-rac-glycerol (non-ionic detergent) and 3-aminopropytriethoxysilane (APTES) were purchased from Sigma-Aldrich, Sterinheim, Germany. α-Bromoisobutyryl bromide (BIBB, 97%), triethylamine (Et$_3$N), 99%, dimethyl aminopyridine, (DMAP), and all solvents were purchased from Sigma Aldrich, USA, and were used as received without further purification, except tetrahydrofuran (THF, 99.8%), used for synthesis, which was dried by distillation with Na-benzophenone. Fabric (100% cotton) was purchased from a commercial shop (Anjel) in Bratislava. The cotton fabric was washed by ultrasonic for 4 minutes with acetone, distilled water, and ethanol sequentially to remove the impurities. Then, it was dried at 70°C in a vacuum oven before use. Chitosan (CH) was purchased from Carbosynth Limited (Compton, Berkshire, UK), with Mw of 190.000-310.000 g/mol. Melamine was purchased from Sigma Aldrich USA.

2.2. Photopolymerization of MAPC1

The following procedure for photoATRP was used: purified monomer was placed into an open vessel, meanwhile, the catalytic system was prepared by dissolving CuBr$_2$ in a selected solvent together with TPMA ligand. After the complex was formed, it was added to the monomer, followed by addition of an initiator to the mixture. Then, the mixture was divided into the 2 mL GPC vials so that they were fully filled by the mixture. Afterward, the vials were closed with a standard cap and irradiated using UV-nail-gel curing lamp (Type:SMA 33A48, Germany) with continuous stirring. The samples were placed at a distance of 6.5 cm from the light source. Light intensity, at the position of the samples, was measured by a Novameter (Ophir photonics). The intensity value used in this study was 12 mW cm$^{-2}$. The samples were cooled down during irradiation by a fan (ROWENTA, Mod.SO6510, China) and the temperature at the position of the samples did not exceed 28°C. At different time points, the polymerization was stopped by exposing the vial to air.

2.3. Surface Modifications of Cotton Fabrics

2.3.1. Reaction of Cotton Fabric with APTES

A sample of dried cotton fabric (1.5 gm), was added to a two-neck round flask containing 100 mL of toluene. Then 2 mL of APTES was added dropwise at 110°C. The reaction was kept for 7 hours under stirring, then the sample was washed with ethanol and dried in a vacuum oven to constant weight.

2.3.2. Preparation of Cotton Fabric Initiator

Cotton fabric initiator (fabric-Br) was prepared as described previously (Tang et al. 2009) with little modification concerning the concentration of BIBB. Briefly, DMAP (0.5 g), TEA (7.8 mL, 0.056 mol), and anhydrous THF (100 mL) were added into a 250-mL two-necked flask under oscillation. Then, 1.5 g of cotton fabric modified previously with APTES was immersed in the freshly prepared solution mentioned above. After cooling down the flask to 0–5°C, BiBB (6.9 mL, 0.056 mol) was added dropwise in an inert atmosphere. The reaction was carried out at 0–5°C for 1 h under
stirring conditions, followed by heating to 27–30°C and continuous stirring for 24 h. The obtained samples were rinsed successively with THF, and EtOH under ultrasonic conditions, then dried in a vacuum drier oven at 70°C till constant weight was reached.

2.3.3. Grafting of MAPC1 from the Fabric-Br Surface by SI-PhotoATRP

A polymerization mixture containing solvent, catalyst, monomer, and free initiator was prepared as mentioned above in a glass vial. Then, the fabric-Br sample was immersed into the vial. The total polymerization mixture was always adjusted with the vial volume so that it was completely filled by the mixture. Afterwards, the vial was closed with a standard cap and irradiated under the same conditions as described previously in photopolymerization of MAPC1 step.

Grafting of bigger size fabric samples was conducted in a transparent zip lock LDPE bags. The polymerization mixture was absorbed by the fabric inside the bag. Then, the bag was placed inside the light source for 12 hours and after that, it was turned over and irradiated for additional 12 hours.

After the graft polymerization, the fabric sample was removed and extracted with ethanol to remove unreacted monomers and reagents. Further washing was conducted by the Soxhelt system using EtOH over 6 h to remove the homopolymer. Then, the sample was dried in a vacuum drier oven at 70°C. The grafting percentage (GP) of each sample was calculated as following:

\[
\text{Grafting Percentage} = \frac{W_2 - W_1}{W_1} \times 100
\]

where W1 and W2 represent the mass of the fabric sample before and after grafting, respectively. The grafted samples are denoted fabric-\(g\)-PMAPC1 and labeled as CgX, where x indicates the grafting percentage.

2.3.4. Treating Fabric-\(g\)-PMAPC1 with Melamine

1 g of melamine was dissolved in 100 mL distilled H\(_2\)O and the pH was adjusted for 3 to make it completely soluble. Then the fabric sample was immersed for 10 minutes at room temperature and subsequently dried in oven at 110°C to constant weight. The melamine uptake was calculated according to the weight difference.

2.3.5. Treating Fabric-\(g\)-PMAPC1 with Hydrolyzed Chitosan

Hydrolyzed chitosan solution was prepared according to the previously reported protocol of chitosan depolymerization. (Mao et al. 2004) 5 g of chitosan was added to 100 mL of distilled water. The solubility was achieved by adding a 1N solution of HCL. Then the cotton fabric sample was immersed in the chitosan solution for 10 minutes and subsequently dried in oven at 110°C to constant weight. The weight gain was calculated according to the weight difference.

3. Characterization

3.1. Gel Permeation Chromatography (GPC)

The molar masses and dispersity of the polymers were analyzed using gel permeation chromatography (GPC). First, the samples were passed through neutral alumina to remove copper catalyst. The set-up consisted of a Waters 515 pump, two PPS SDV 5-µm columns (d = 8 mm, l = 300 mm; 500 Å + 105 Å), and a Waters 410 differential refractive
index detector with TFE as an eluent at a flow rate of 1.0 mL/min. Poly(methyl methacrylate) calibration was used for the determination of molar masses and dispersity of PMAPC1.

3.2. 1H Nuclear Magnetic Resonance (1H-NMR)

Monomer conversion was determined by 1H NMR on a 300 MHz Inova Varian NMR spectrometer equipped with a 5-mm ATB 1H/19F/X PFG Broadband Probe using standard pulse sequence and deuterated chloroform as a solvent.

3.3. Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR).

The FTIR spectra were recorded using a FT-IR Nicolet 8700™ spectrometer (Thermo Scientific, Madison, WI, USA) equipped with an ATR accessory with Ge crystal. The IR spectra were measured in the mid-infrared range from 4000 to 650 cm\(^{-1}\); the resolution was set to 4 cm\(^{-1}\).

3.4. Scanning Electron Microscopy (SEM)

The morphology of the fabric was observed by scanning electron microscopy (SEM) JSM Jeol 6610 at accelerated voltage 15 kV. Qualitatively determining chemical compositions was performed using energy dispersive X-ray detector (EDS) OI X-max 50 mm\(^2\). The samples were sputtered with a thin layer of gold just before analysis to supply the necessary conductivity of the textile samples. Software AzTec was used for collecting figures and processing the results.

3.5. X-Ray Photoelectron Spectroscopy (XPS)

XPS signals were recorded using a Thermo Scientific K-Alpha XPS system (Thermo Fisher Scientific, UK) equipped with a micro-focused, monochromatic Al Kα X-ray source (1486.68 eV). An X-ray beam of 400 µm size was used at 6 mA x 12 kV. The spectra were acquired in the constant analyzer energy mode with a pass energy of 200 eV for the survey. Narrow regions were collected with a pass energy of 50 eV. Charge compensation was achieved with the system flood gun. The Thermo Scientific Avantage software, version 5.9921 (Thermo Fisher Scientific), was used for digital acquisition and data processing. Spectral calibration was determined by using the automated calibration routine and the internal Au, Ag, and Cu standards supplied with the K-Alpha system. The surface compositions (in atomic %) were determined by considering the integrated peak areas of detected atoms and the respective sensitivity factors. The fractional concentration of a particular element A was computed using:

\[
%A = \frac{I_A / s_A}{\sum (I_n / s_n)} \times 100\%
\]

where \(I_n\) and \(s_n\) are the integrated peak areas and the Scofield sensitivity factors corrected for the analyzer transmission, respectively.

3.6. Thermal Gravimetric Analysis (TGA)

Thermogravimetric analysis was conducted using the TGA instrument Mettler Toledo TGA/SDTA 851e (Mettler-Toledo, Greifensee, Switzerland) under a flow of air and nitrogen (80 mL min\(^{-1}\)) atmosphere. The measurements were performed at a temperature range from 25 to 800°C and heating rate of 10°C min\(^{-1}\). The weight of sample was \(~3.5\) mg.
3.7. Flammability Analysis

3.7.1. Horizontal Flame Test (HFT)

Horizontal flame test (HFT) was performed on 100 x 70 mm samples clamped of two matching rectangular frames and ignited in horizontal configuration for 12s by a propane gas burner. The after-flame time and flame-speed rate were determined. The residual weight and the char length were recorded as well.

3.7.2. Vertical Flame Test (VFT)

Vertical flame testing (VFT) was performed on 100 x 70 mm samples, according to ASTM D 6413-08 standard. Samples are clamped of two matching rectangular frames and held vertically, and then there were ignited by applying a propane flame for 12s at the bottom of the fabric. The time required for the lower of the flame front to travel across the specified length is measured. The residual weight after burning and the char length were also recorded.

3.7.3. Limiting Oxygen Index (LOI)

LOI was measured in a Dynisco LOI chamber (Heilbronn, Germany), according to ISO 4589:1996, using fabric strips (14 cm x 5.2 cm). The presented results are average values of three measurements.

3.7.4. Micro Cone Calorimeter (MCC)

The combustion behavior was tested with micro cone calorimeter (MCC) according to ASTM D 7309, using MCC-2 instrument (Govmark, Farmingdale, NY). A 5 mg sample (three samples per each recipe) was evaluated from 25 to 650°C at a heating rate of 1°C/s in a nitrogen gas stream of 80 mL/min.

3.8. Mechanical Properties

Tensile strength and elongation tests of cotton fabrics were used for mechanical properties evaluation. The tests were carried out according to the specification of ASTM D5035 maximum force and elongation-strip method (Nada et al. 2016; Mohamed et al. 2017) using Lloyd LR10K (Materials Testing Machine, UK). Each sample was cut into stripes with 70 mm x 20 mm, and the initial grip separation was 30 mm. Then, they were pulled out at the rate of 50 mm/min until it tears out. Storage modulus and glass transition temperature ($T_g$) of the modified fabrics were measured by dynamic mechanical analysis using Dynamic Mechanical Analyser DMA Q800 (TA Instruments, New Castle, DE, USA) in the temperature range from −50°C to 200°C with a heating rate of 3°C/min. The measurements were performed in tensile mode at a constant frequency of 1 Hz with a strain amplitude of 20 µm. The storage modulus ($E'$), loss modulus ($E''$), and loss factor (tan δ) were determined for at least three strips with specimen dimensions approximately of 20×5×0.3 mm$^3$.

3.9. Washing Procedure

The treated fabric was washed to demonstrate the chemical stability of the grafting modification. The test was performed at liquor ratio of 50:1 mL/g for 30 minutes at 40 °C, using a non-ionic detergent (1 g/L) in SDL Atlas Linitest Plus laboratory machine. The washing was performed according to the standard PN-EN ISO 105-C06:2010 Textiles—Tests for color fastness to domestic and commercial laundering. After washing, the sample was washed with distilled water and air-dried. The durability was evaluated by measuring HFT for the washed sample.

4. Results And Discussion

4.1. Photopolymerization of MAPC1
Among phosphorus-containing monomers, phosphonates derivatives are preferable to phosphate ones due to the hydrolysis problems of the later. (Matsumura et al. 2008) Four different types of phosphonate-containing monomers can be listed from the literature; allylic, vinylic, styrenic, and (meth)acrylate. Because of their high reactivity in radical (co)polymerization, the phosphonate methacrylate derivatives are the most extensively studied monomers compared to the others. Previous reports demonstrated that normal ATRP of MAPC1 is challenging due to the ability of the phosphorus to complex the copper ions, removing copper ions from the original ligand, and then stopping the MAPC1 polymerization. (David et al. 2009) Indeed, ATRP of functional monomers, in general, is challenging with a low ppm amount of catalyst as they can interfere with the ligand resulting in an inactive complex formation. To our knowledge, this work is the first report for the application of photoATRP technique for phosphorus-containing monomers in general. Catalyst concentration in photoATRP of nonfunctional monomers such as methyl methacrylate or Tulipalin A is in the range of 50–200 ppm (Borská et al. 2017b; Zain et al. 2019) Due to above mentioned reasons, the photoATRP of MAPC1 was carried out with slightly higher catalyst loading (400 ppm) relating to monomer concentration. CuBr$_2$ combined with four equivalents of TPMA ligand were used as a catalyst system. Ethyl α-bromoisobutyrate (EBIB) was used as the initiator since its structure can also be covalently attached to the cotton surface. A UV-light source of 12 mWcm$^{-2}$ intensity was used for irradiation. The setup is shown in Figure S1. The polymerization behavior was studied in anisole, DMF and acetonitrile at different time intervals as shown in Fig. 1.

As can be observed from Fig. 1A, the polymerization follows the first-order kinetics for all solvents. However, the rate of polymerization is significantly faster when polymerization was carried in DMF coming to a conversion of 76% after 13 hours where 50% and 10% were obtained after the same time in case of using acetonitrile and anisole respectively. A slight deviation from linearity was observed at a high conversion of 81% in the case of DMF which could be ascribed to the higher viscosity of the system. In ATRP, the stability of the ionic intermediates of the catalyst is influenced by solvent polarity (Ribelli et al. 2019). More polar solvents increase the stability of the ions. More generally, the polarity of the solvent can influence the radical polymerization reactions, as shown for instance in the case of methyl methacrylate (Fernández-Garcia et al. 1998). Although the experimental molar masses, in all cases, are slightly higher than the theoretical ones as can be seen in Fig. 1B, the dispersity values are as low as 1.35 in DMF and anisole but as high as 2 in acetonitrile. The higher experimental molar mass could be attributed to the difference in hydrodynamic volume between the PMMA standards and the measured polymers. Another reason can be not sufficiently fast initiation with EBiB. It is well known that sufficiently fast initiation for methacrylates can be achieved using 2-bromopropionitrile, however such structure cannot be attached on the surfaces for SI-ATRP. In general, it could be concluded that photoATRP in DMF seems to be the best controlled, therefore this system was subsequently used also for surface-initiated polymerization.

4.2. Surface-Initiated PhotoATRP of MAPC1 onto Cotton Fabric

Grafting of MAPC1 from cotton fabric surface by photoATRP technique was performed through some subsequent steps as shown in Scheme 1. First, aminopropyltriethoxy silane (APTES) was reacted with the fabric hydroxyl groups at elevated temperature (110°C) for seven hours using toluene as a solvent. The addition of the APTES layer provides amino groups onto the fabric, which react more efficiently with ATRP initiator (BIBB) than hydroxyl groups do. In addition, the APTES compound has nitrogen and silicon elements, which can also act as flame-retardants. The presence of amino groups on the APTES modified fabric (Fabric-Si) was confirmed by dipping the modified fabric in fluorescamine solution. The color became yellow, as shown in Fig. 2A vs 2B, indicating fast reaction of amino groups with the dye.
The second step was the preparation of a cotton fabric macroinitiator (Fabric-Br), which was then grafted with MAPC1 monomer. The grafting was conducted in DMF using an amount of 400 ppm of CuBr$_2$ related to monomer and four equivalents of TPMA ligand related to CuBr$_2$. The grafting was performed inside a 2 mL glass vial in the case of a small size of fabrics ($2 \times 0.5$ cm$^2$) using 15 weight equivalents of monomer to the fabric. A grafting percentage of 22% was obtained after 24 hours (Table 1, Entry 1). However, such small size fabrics are not suitable for flame tests requiring sample of at least 12 cm in length. Therefore, grafting was conducted for the larger size of fabric ($15 \times 7$ cm$^2$). It was found that the best way for using such large size fabrics, with low monomer loading, is to make the fabric to absorb the polymerization mixture. The grafting was conducted inside a zip lock LDPE bag, which can be well closed after simple manual removal of the most of the air (Fig. 2C). The grafting with this system was studied at different monomer concentrations as shown in Table 1. It was found that increasing monomer concentration from 0.6 to 1.2 mol/L has resulted in an increase of the grafting percentage (GP) from 15 to 53% (Table 1, Entries 2–4). In addition, the GP was even higher, reaching value of 65.4% (Table 1, Entry 5), when the fabric was placed vertically inside the lamp (Fig. 2D) instead of parallel position (Fig. 2E). Increasing the GP with higher monomer concentration and different positions could be attributed to the more availability of monomer molecules that could be grafted and to the more homogenous distribution of light over the sample in a vertical position, respectively. The polymerization providing GP of 65.4% was repeated once more, while GP of 63.8% was achieved, thus confirming good reproducibility (Table 1, Entry 6). In addition to monomer concentration, the effect of the light intensity on grafting percentage was also studied. It was observed that using a low light intensity source (9 mW/cm$^{-2}$) resulted in decreasing in the grafting percentage from ~65% to ~41% (Table 1, Entry 7). The higher light intensity increases the reduction of the catalyst and thus increases the growing radical concentration which in turn increases polymerization rate. In the Table 1 the prepared samples are labeled as CgX, where X is the grafting percentage rounded to whole number. Hereafter these labels are used to denote the grafted fabrics.

### Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>M : Fabric (g/g)</th>
<th>M + S : Fabric (mL/g)</th>
<th>[M] mol/L</th>
<th>Light Intensity (mW/cm$^2$)</th>
<th>Grafting percentage (%)</th>
<th>Label of Grafted Fabric</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>20</td>
<td>3.6</td>
<td>12</td>
<td>22.0</td>
<td>Cg22</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>2.5</td>
<td>1.1</td>
<td>12</td>
<td>15.3</td>
<td>Cg15</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>2.5</td>
<td>1.7</td>
<td>12</td>
<td>33.2</td>
<td>Cg33</td>
</tr>
<tr>
<td>4</td>
<td>1.2</td>
<td>2.5</td>
<td>2.2</td>
<td>12</td>
<td>53.0</td>
<td>Cg53</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>2.5</td>
<td>1.7</td>
<td>12</td>
<td>65.4</td>
<td>Cg65</td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td>2.5</td>
<td>1.7</td>
<td>12</td>
<td>63.8</td>
<td>Cg64</td>
</tr>
<tr>
<td>7</td>
<td>1.0</td>
<td>2.5</td>
<td>1.7</td>
<td>9</td>
<td>40.8</td>
<td>Cg41</td>
</tr>
</tbody>
</table>

*a Experimental conditions: MAPC1/CuBr$_2$/TPMA = 200/0.08/0.32; $T = 28^\circ$C, time = 24 h, light intensity of 12 or 9 mW cm$^{-2}$ ($\lambda = 365$ nm) in DMF.

### 4.3. Characterization of the modified fabrics

The chemical composition and the surface morphology of the modified fabrics were characterized by FTIR, XPS, EDS, and SEM analyses as discussed in the next sections. The FTIR spectra of neat and modified fabrics are shown in
Fig. 3. The broad band at 3350 cm$^{-1}$ in neat fabric spectra (a) is attributed to the hydroxyl groups and the absorption band at 2900 cm$^{-1}$ is characteristic for C-H linkages of cellulose backbone of the fabric. The weak bands at 1059 cm$^{-1}$ and 1025 cm$^{-1}$ are attributed to skeletal vibrations involving C-O stretching. In spectra of fabric-Si (b), a new peak appeared at 1580 cm$^{-1}$, which is attributed to the amine N–H deformation vibration. A peak at 1740 cm$^{-1}$ appeared in fabric-Br spectra (c), can be assigned to carbonyl group, indicating that BiBB had been successfully immobilized onto the surface of the cotton fabric. In the grafted fabrics spectra (d and e), the peak from the ester groups of the PMAPC1 is in the same position. In addition, the absorption peak at 1255 cm$^{-1}$ in the grafted fabric spectra can be assigned to -P = O. It could be observed from the Fig. 3 that the peak intensity of both carbonyl and -P = O groups clearly increased with increasing the GP from 15% (d) to 65% (e). Additional peaks at 1050, and 958 cm$^{-1}$ which could be assigned to the vibrations of -P = O, P-CO, and P-O-CH$_3$ in the grafted fabric were blurred in the cellulose fingerprint (Intharapat et al. 2010; Vahabi et al. 2012).

The XPS wide-scan spectra of native cotton fabric (a), fabric-Si (b), fabric-Br (c), and grafted cotton with two different weight gains 15% (d) and 65% (e) are shown in Fig. 4(a-c). The results from individual peaks deconvolutions and atomic ratios (bold line) are summarized in Table 2. From that results, it is clear that the pristine cotton fabric is composed of the elements C and O. In fabric-Si, two new peaks appeared at ca 399 eV and at ca 102 eV corresponding to N and Si, respectively. These two signals confirm the modification of the fabric with the APTES layer. In fabric-Br, a peak of Br$^-$ at ca 68 eV and covalently bonded Br (C-Br) appeared at ca 70 eV confirming amidation of the amine groups on the cotton fabric with BiBB. Phosphorus peak at 134 eV could be found in samples Cg15 (d) and Cg65 (e) confirming the successful grafting of MAPC1 monomer. The intensity of phosphors peak increased with increased GP. The overlapping curves of the C1s peak of the grafted fabric Cg65 were fitted to further subpeaks, which indicates the bonding states of carbon as shown in Figure S2. The appearance of the peaks of ester groups at 289 eV (O=C = O) further confirms that PMAPC1 was grafted from the cotton surface. The C1s deconvolutions shows that there is a peak at 284.9 eV which could be attributed to C-H of the cellulose backbone and additional C-C coming from some impurities.
Table 2

Surface chemical composition of neat and modified fabrics by XPS in atomic %.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Chemical Composition (at%) / Peak Positions (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1s</td>
</tr>
<tr>
<td></td>
<td>Peak Positions (eV)</td>
</tr>
<tr>
<td></td>
<td>C-H&amp;CC/O/O-C-O&amp;O=C O&amp;O=O</td>
</tr>
<tr>
<td></td>
<td>(284.9/286.3/287.2/289.0)</td>
</tr>
<tr>
<td>Neat fabric</td>
<td>65.4</td>
</tr>
<tr>
<td></td>
<td>28.1/22.4/7.9/7.0</td>
</tr>
<tr>
<td>Fabric-Si</td>
<td>57.5</td>
</tr>
<tr>
<td></td>
<td>44.8/6.1/2.5/3.8</td>
</tr>
<tr>
<td>Fabric-Br</td>
<td>56.2</td>
</tr>
<tr>
<td></td>
<td>38.0/8.1/5.0/5.1</td>
</tr>
<tr>
<td>Cg15</td>
<td>57.7</td>
</tr>
<tr>
<td></td>
<td>36.7/8.8/6.9/5.3</td>
</tr>
<tr>
<td>Cg65</td>
<td>58.3</td>
</tr>
<tr>
<td></td>
<td>34.1/11.4/5.9/6.9</td>
</tr>
</tbody>
</table>

4.4. SEM

SEM photographs of neat and modified cotton fabrics are shown in Fig. 5(a-d) where measurements at different resolutions are recorded. For the neat fabric, the surface was seen to be smooth (Fig. 5a). A slight change in surface morphology could be observed after treatment of the fabric with APTES as well as after the amidation by BIBB (Fig. 5b and 5c, respectively). Then, the surface changed more significantly after grafting with PMACP1 (Fig. 5d,e). The change was dependent on the grafting percentage where it increased with increasing the grafting from 15% till 65%. These changes in surfaces morphology of the cotton fabrics further confirms their modification.

SEM pictures were also used for EDS analysis to determine the elemental change on the cotton surface, calculated according to the peak area ratios, and the results (see Figure S3 and Table S1) were in good agreement with XPS results.

4.5. Mechanical Properties

The dynamic mechanical analysis represents a sensitive characterization method able to provide additional information related to phase or molecular structure within multiple polymer. DMTA measurements were used for analysis of the surface modified cotton fabrics in order to investigate the influence of the varying content of uniformly attached PMAPC chains on the values of storage modulus ($E'$) as well as dumping factor ($\tan \delta$). Figure 6a shows an evolution of the dynamic-mechanical traces as temperature dependencies of $E'$ before and after grafting of PMAPC1 polymer in the range of GP from 15 to 65%. Increasing amount of grafted polymer onto the cotton fabric led to
increase in $E'$ due to pronounced stiffness of the samples as it is clearly visible mainly in the case of Cg65, i.e. the cotton fabric grafted with the longest polymer chains. For comparison, the $E'$ determined for pure PMAPC1 film, prepared by solution casting, below its $T_g$ was $\sim 275$ N, that is a value close to that one obtained for Cg65, confirming effect of covalently attached polymer on enhancement of $E'$ modulus values of the cotton.

Figure 6b shows the comparison of the temperature dependence of $T_g$ pure cotton fabric before and after surface modification with different amount of grafted PMAPC1. Grafting of polymer significantly affected $T_g$ of pure fabric, which showed broad weak peak with the maxima at around 48°C. After grafting, $T_g$ at values at temperatures of around 100°C were observed. It should be mentioned that the $T_g$ of neat PMAPC1, measured in the form of film, was determined to be 28°C. It was shown by Tate et al. (Tate et al. 2001) that glass transition of polystyrene derivatives were affected by confinement and there has been a significant difference between $T_g$ of free polymer in bulk and polymer brushes covalently attached on the substrate. This is in good agreement with significant shifting of the PMAPC1 $T_g$ toward higher temperatures observed here. In addition, an increase in the height of maximum loss factor peak with increased GP was observed due to increased thickness of the polymer layer grafted onto the cotton fabric resulting in enhanced PMAPC1 chain mobility.

The existence of additional $T_g$ peak located at lower temperatures detected for cotton samples with higher GP, Cg53 and Cg65 could correspond to $\beta$-relaxations and could be attributed to more flexible polymer chains population. Based on the mechanism of ATRP, higher GP is connected with grafting of longer polymer chains. Grafting of high molar mass polymers could be accompanied with higher extend of termination reactions, which could lead in decreased grafting density at upper part of the grafted layer and thus increased flexibility of the polymer chains. This can promote the relaxation at significantly lower temperatures.

DMTA measurements also proved successful modification of the cotton fabric by PMAPC1, while two populations with various flexibility were suggested for samples with higher GP. The effect of grafting on mechanical properties of the fabrics was further tested by measuring the breaking strength, tensile strength and elongation at break. Here the mechanical properties of neat cotton fabric were compared to two samples grafted with two various amounts of PMAPC1, namely Cg41 and Cg65. As can be seen from Table 3, the values from the tensile tests for all the samples were varied within the experimental error suggesting minimal effect of the grafting on the mechanical properties of the cotton fabrics.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Breaking Strength (N)</th>
<th>Tensile Strength (N mm$^{-2}$)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat fabric</td>
<td>238 ± 2.12</td>
<td>31.5 ± 12.0</td>
<td>12.3 ± 8.13</td>
</tr>
<tr>
<td>Cg41</td>
<td>201 ± 83.8</td>
<td>34.0 ± 9.9</td>
<td>25.8 ± 8.2</td>
</tr>
<tr>
<td>Cg65</td>
<td>207 ± 80.0</td>
<td>35.7 ± 7.2</td>
<td>17.0 ± 4.74</td>
</tr>
</tbody>
</table>

### 4.6. Flammability Properties

The flammability of different modified fabrics was tested by both horizontal and vertical flame tests according to standard protocols. The data obtained from horizontal flame test (HFT) and the vertical flame test (VFT) are summarized in Table 4 and Table 5, respectively. Similarly, the photographs of the samples after burning are shown in Figs. 7 and 8 for HFT and VFT, respectively. It could be observed from the HFT results that the flammability of the pure cotton is very high leading to complete damage as shown in Fig. 7 and Table 4. The flammability resistance
significantly increased after grafting of the cotton fabric. The residual weight after HTF of Cg15 increased to 50% comparing to neat fabric. In addition, the flame retardancy was further improved with increasing the GP from 15–41% where the residual weight after HTF became 95%. The residual weight was in the range of 96–99% when grafting was increased from 41–53% or 65%. The same conclusion of improving the antiflammability with increasing grafting percentage can be found when comparing the char length, flame spread rate and the time of continuous burning after ignition the fabric (time-after flame) parameters (Table 4). To improve the flame resistance of fabrics with lower GP, an additional treatment with a nitrogen containing source was investigated as well. Therefore, the samples with grafting of 15% and 33% were dipped in 1 wt% melamine aqueous solution. The weight gain of melamine for both samples were almost 1 wt%. It was found that their flame retardancy improved significantly after melamine addition, which could be attributed to a previously described synergism effect between nitrogen and phosphorus (Alongi et al. 2013). Chitosan as a natural source of nitrogen was also used after its degradation by hydrochloric acid for treatment of the sample Cg41, while it was again proved that the addition of nitrogen containing compound improved the flame resistance of the grafted cotton fabric.

Table 4
Horizontal flame test of grafted cotton fabric.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Residual weight (%)</th>
<th>Char Length (cm)</th>
<th>Flame Spread Rate (mm/sec)</th>
<th>After-Flame Time (Sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Fabric</td>
<td>0</td>
<td>Whole</td>
<td>2.1</td>
<td>36</td>
</tr>
<tr>
<td>Fabric-Br</td>
<td>14.3</td>
<td>Whole</td>
<td>2.4</td>
<td>62</td>
</tr>
<tr>
<td>Gg15</td>
<td>48.2</td>
<td>Whole</td>
<td>2.2</td>
<td>24</td>
</tr>
<tr>
<td>Gg15 + Melamine</td>
<td>87.5</td>
<td>3.6</td>
<td>1.2</td>
<td>18</td>
</tr>
<tr>
<td>Gg33</td>
<td>57.4</td>
<td>Whole</td>
<td>2.0</td>
<td>33</td>
</tr>
<tr>
<td>Gg33 + Melamine</td>
<td>91.5</td>
<td>2.4</td>
<td>0.9</td>
<td>14</td>
</tr>
<tr>
<td>Gg41</td>
<td>96.9</td>
<td>1</td>
<td>0.8</td>
<td>No ignition</td>
</tr>
<tr>
<td>Gg53</td>
<td>98.9</td>
<td>1</td>
<td>0.8</td>
<td>No ignition</td>
</tr>
<tr>
<td>Gg65</td>
<td>96.5</td>
<td>1</td>
<td>0.8</td>
<td>No ignition</td>
</tr>
<tr>
<td>Gg41 + Chitosan</td>
<td>99.1</td>
<td>0.9</td>
<td>0.7</td>
<td>No ignition</td>
</tr>
</tbody>
</table>

Vertical flame test is known to be more aggressive than the horizontal one, therefore only 60% of residual weight was obtained in case of sample Cg53 comparing to 99% when tested by HFT (Fig. 8, Table 5). High residual weight (90%) was obtained for sample Cg65 confirming the dependence of flammability on GP. Addition of nitrogen source to the grafted samples Cg53 and Cg41 was also investigated to further improve the vertical test results. It was found that using 1 wt% of melamine with Cg53 increased the flame resistance by 20% reaching the residual weight after VFT of 80%. In addition, the sample Cg41 treated with hydrolyzed chitosan provided dramatical improvement of flame retardancy with 95% of residual weight after VFT. This improvement could be attributed to ability of the amino group of chitosan to act as a blowing agent. (Jordanov et al. 2019) SEM analysis from the char residues for Cg41 and Cg41 + chitosan are shown in Figure S4. It can be seen that the fabric maintains their structure after flame tests and also the blowing effect of chitosan can be observed.
Table 5
Vertical flame test of grafted cotton fabric.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Residual weight (%)</th>
<th>Char Length (cm)</th>
<th>Flame Spread Rate (mm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gg53</td>
<td>60</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Gg53 + Melamine</td>
<td>80</td>
<td>7.0</td>
<td>3.1</td>
</tr>
<tr>
<td>Gg64</td>
<td>86</td>
<td>6.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Gg65</td>
<td>90</td>
<td>5.0</td>
<td>4.1</td>
</tr>
<tr>
<td>Gg41 + Chitosan</td>
<td>93</td>
<td>6.5</td>
<td>No ignition</td>
</tr>
</tbody>
</table>

From the HFT and VFT results, it can be concluded that the modified cotton fabrics gave excellent flame retardancy, which depends on the GP of MAPC1. As only 41% of grafting was sufficient to achieve good flame retardancy when tested by HFT, it was further investigated also by critical (or limiting) oxygen index (LOI) and microscale cone calorimeter (MCC). LOI values denote the minimum amount of oxygen needed to sustain a candle-like flame when a sample is burned in a mixture of oxygen and nitrogen gases. Textiles are considered to be flammable when LOI values are below 21 vol% oxygen in nitrogen and are considered to be flame-retardant when LOI values fall in the range of 26–28% (Chang et al. 2017). Normal air contains about 21 vol% of oxygen and so fibers with LOI < 21 burn readily in air. While LOI value for neat cotton fabric was found to be 19%, the value for the grafted fabric (Cg41) was found to be 30% confirming its good antiammability properties. Figure 9 shows MCC results of heat release rates (HRR) as a function of temperature for pure cotton fabric and the grafted one (Cg41). Peak release rates (pHRR) of untreated cotton is 196 W/g, while total heat release (THR) is 10 kJ/g at ~378°C. pHRR values for cellulose materials vary depending on their chemical composition (content of lignin, hemicellulose, impurities, etc.) (Sonnier et al. 2015; Magovac et al. 2020). For the grafted cotton, pHRR decreased down to about half value, i.e 94 W/g, compared to the untreated cotton. Similarly, THR was only 2.9 kJ/g at ~278°C. These results correlate with the LOI and HFT results and confirms that a cotton fabric grafted by 41% of PMAPC1 can be successfully used as a material with flame-retardant properties.

4.7. TGA

Figure 10 and Fig. 11 show thermal degradation curves for neat cotton fabric and two grafted samples, Cg15 and Cg65, obtained under air and nitrogen atmospheres, respectively. The weight loss and derivative weight loss plots are shown for each condition. The data are summarized in Table 6, where decomposition temperature peaks ($T_{10\%}$, $T_{max1}$ and $T_{max2}$) are shown. $T_{10\%}$ is the temperature, at which 10% of the initial weight is lost, while $T_{max}$ is the temperature, at which maximum weight loss occurs. It can be seen from Fig. 10 that in air atmosphere the weight loss curves of the fabrics comprise of three stages. The first weight loss, 2%, starts between 50 and 100°C, due to evaporation of moisture. This moisture content is identical for neat and treated samples, which confirms the insignificant impact of water content on GP calculations. At temperatures above 200°C, two stages of thermal degradation could be visible in the presence of air. With regard to the neat fabric, the TGA curve shows the significant mass loss starting at 300°C and lasted till 320°C, which can be attributed to dehydration and depolymerization of the cellulose generating non-flammable gases, primary char residue and levoglucosan (Magovac et al. 2020). The mass loss at this stage was almost 60%. The second degradation stage started at 320°C and lasted till 500°C. In this temperature range the levoglucosan decomposes and produces flammable gases and secondary char. The same trend could be observed for the fabric macroinitiator (fabric-Br) with slightly higher char content. For the grafted fabric, the degradation seems to
be depending on the concentration of the PMAPC1 on the fabrics. While for the Cg15 the first stage of the degradation is similar to macroinitiator, in case of cotton Cg65 with high polymer content it started already at about 250°C. At the same time, the weight loss decreased to 50 and 40% for Cg15 and Cg65, respectively. The low weight loss of the modified samples comparing to the neat one could be attributed to the release of phosphoric acid that is able to acid-catalyse the dehydration, phosphorylating primary hydroxyl groups of cellulose at C(6) position. This inhibits also the C(6)-C(1) intramolecular rearrangement that generates levoglucosan and thus promoting the char formation (Alongi et al. 2013). The formed char protects the material from further degradation. Thus, the curves for the second degradation stage differ dramatically, especially in the case of Cg65 compared to that of neat cotton. This stage started at 320 and lasted till 750°C, while its maximum was at 700°C. The residual weight at $T_{\text{max2}}$ was still significantly higher compared to the neat fabric as can be seen from Table 6. These results confirm that the modification of the cotton slow down its decomposition by generating the char, which could act as a physical barrier that block heat and oxygen.

In nitrogen atmosphere, the TGA curves are different (Fig. 11). After moisture evaporation, there is only one stage of degradation, since the oxidation of the char formed after the first step of degradation is absent. The maxima of the degradation shifted only slightly to higher temperature for all samples compared to degradation in the presence of air. However, due to absence of the oxidation effect on char the residual weight dramatically increased with amount of grafted polymer confirming high thermal resistance of the char formed from phosphorus containing polymer layer.

### 4.8. Washing Test

The flammability of the sample Cg41, after washing according to standard test ISO 105-C10:2006, for 30 minutes, was also tested by HFT. The results and photographs of the sample before and after washing are shown in Table 7 and Fig. 12, respectively. It could be observed that that the residual weight after washing decreased only negligibly indicating a retention of high flame resistance also after washing procedure and thus confirming the high stability of the grafted polymer layer.

<table>
<thead>
<tr>
<th>Recipe</th>
<th>$T_{10%}$ [°C]</th>
<th>$T_{\text{max1}}$ [°C]</th>
<th>$T_{\text{max2}}$ [°C]</th>
<th>Residue at $T_{\text{max2}}$ [$%$]</th>
<th>Residue at 600°C [$%$]</th>
<th>Residue at 800°C [$%$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat fabric (air)</td>
<td>311</td>
<td>346</td>
<td>468</td>
<td>11.1</td>
<td>4.4</td>
<td>4.8</td>
</tr>
<tr>
<td>Fabric-Br (air)</td>
<td>306</td>
<td>325</td>
<td>501</td>
<td>14.5</td>
<td>8.1</td>
<td>8.5</td>
</tr>
<tr>
<td>Cg15 (air)</td>
<td>304</td>
<td>321</td>
<td>496</td>
<td>22.5</td>
<td>8.5</td>
<td>8.2</td>
</tr>
<tr>
<td>Cg65 (air)</td>
<td>256</td>
<td>258</td>
<td>700</td>
<td>23.5</td>
<td>43.0</td>
<td>10.5</td>
</tr>
<tr>
<td>Neat fabric ($N_2$)</td>
<td>326</td>
<td>362</td>
<td>-</td>
<td>-</td>
<td>22.8</td>
<td>21.8</td>
</tr>
<tr>
<td>Fabric-Br ($N_2$)</td>
<td>315</td>
<td>338</td>
<td>-</td>
<td>-</td>
<td>24.6</td>
<td>23.1</td>
</tr>
<tr>
<td>Cg15 ($N_2$)</td>
<td>308</td>
<td>327</td>
<td>-</td>
<td>-</td>
<td>33.3</td>
<td>30.6</td>
</tr>
<tr>
<td>Cg65 ($N_2$)</td>
<td>257</td>
<td>262</td>
<td>-</td>
<td>-</td>
<td>49.0</td>
<td>46.0</td>
</tr>
</tbody>
</table>
Table 7
Horizontal flame test of Cg41 after before and after washing.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Residual weight (%)</th>
<th>Char Length (cm)</th>
<th>Flame Spread Rate (mm/sec)</th>
<th>After-Flame Time (Sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before washing</td>
<td>96.9</td>
<td>1</td>
<td>No ignition</td>
<td>0</td>
</tr>
<tr>
<td>After washing</td>
<td>95</td>
<td>2.1</td>
<td>1.2</td>
<td>4.7</td>
</tr>
</tbody>
</table>

**Conclusion**

Oxygen-tolerant photomediated atom transfer radical polymerization of dimethyl(methacryloyloxyethyl) phosphonate (MAPC1) was investigated first in solution using a light source of 12 mW cm$^{-2}$. The polymerization was screened in different solvents, such as DMF, anisole and acetonitrile. A system based on EBIB initiator and CuBr$_2$/TPMA (molar ratio of 1:4) in DMF was found to provide fast polymerization with good control of molecular characteristics of the polymer. The optimized conditions were used for grafting of MAPC1 onto cotton fabric surface via SI-photoATRP. The simple setup consisting of placing the fabric into a plastic bag with subsequent absorption of certain amount of polymerization mixture by the fabric was used for the photografting. It was found that the grafting percentage increased by increasing the monomer concentration while fabrics with GP of PMAPC1 in the range of 15% – 65% were obtained. Characterization by different spectral analysis confirmed that the cotton fabric was modified and its surface morphology was roughly changed. The modification was found to preserve the mechanical properties of the fabric. The TGA, LOI, MCC and flame tests confirmed that the fabrics grafted with PMAPC1 provided high flame resistance, while only a 41% of grafting was sufficient to achieve no ignition of the cotton fabric in horizontal tests and in combination with physically absorbed chitosan, as a source of nitrogen, also in vertical tests. The modified fabric has also shown very good durability of its flame-retardant properties after washing procedure.

**Declarations**

**Acknowledgements**

The authors would like to thank the Slovak Academy of Science for DoctoGrant No. APP0073, Slovak Research and Development Agency for the financial support provided through grant APVV-19-0338 and the Slovak Grant Agency VEGA 2/0129/19. This work was performed during the implementation of the project Building-up Centre for advanced materials application of the Slovak Academy of Sciences, ITMS project code 313021T081 supported by the Integrated Infrastructure Operational Program funded by the ERDF. Authors also thank Cost Action No.17107 (Context) for funding Gamal to have a short-term scientific visit to Prof. Igor Jordanov group at Ss. Cyril and Methodius University, Skopje. The authors are also grateful to the National Research Centre, Giza, Egypt, for providing of tensile strength measurements.

**Funding:** This work was supported by the Slovak Academy of Science (DoctoGrant No. APP0073), Slovak Research and Development Agency (Grant No. APVV-19-0338), the Slovak Grant Agency VEGA (Grant No. 2/0129/19), Integrated Infrastructure Operational Program funded by the ERDF (project Building-up Centre for advanced materials application of the Slovak Academy of Sciences, ITMS project code 313021T081) and Cost Action No.17107.

**Competing Interests:** The authors have no relevant financial or non-financial interests to disclose.
Authors’ contributions: All authors had a significant participation in this work. The study conception and design were performed by Gamal Zain: conceptualization, design, methodology, synthesis, investigation, data collection, writing and editing; Igor Jordanov: investigation, methodology, writing, reviewing and editing; Sandra Bischof and Eva Magovac: formal analysis and methodology. Alena Opálková Šišková, Anna Vykydalová, Angela Kleinová and Matej Mičušík: formal analysis, methodology and editing; Katarína Mosnáčková formal analysis, methodology and writing; Jana Doháňošová: formal analysis and methodology; Jaroslav Mosnáček: supervising, conceptualization, design, methodology, writing and editing.

Consent for publication: All authors read and approved the final manuscript.

Compliance with Ethical Standards: Not applicable

Availability of data and materials: The data that support the findings of this study are available from the corresponding author, JM, upon reasonable request.

References


https://doi.org/10.1021/ja00125a035

Scheme

Scheme 1 is available in supplementary section.

Figures

Figure 1

(A) Kinetic plots and (B) evolution of the molar mass and dispersity with the conversion of MAPC1 during oxygen-tolerant photoATRP in 66 vol% of solvent. Experimental conditions: MAPC1/EBIB/CuBr₂/TPMA=200/1/0.08/0.32; [MAPC1]= 1.87 M, T=28 °C, light intensity of 12mWcm⁻² (λ= 365 nm).
Figure 2

Fabric-Si (A) and neat fabric (B), both after dipping in fluorescamine solution; plastic bag containing fabric-Br with absorbed polymerization mixture (C); SI-PhotoATRP of MAPC1 in parallel and vertical positions (D, E).

![Figure 2](image)

Figure 3

ATR-FTIR spectra of neat fabric (a), fabric-Si (b), fabric-Br (c), fabric of 15% grafting (Cg15) (d) and fabric of 65% grafting (Cg65) (e).

![Figure 3](image)

Figure 4

XPS wide spectrum of neat fabric (a), fabric-Si (b), fabric-Br (c), fabric of 15% grafting (Cg15) (d) and fabric of 65% grafting (Cg65) (e).

![Figure 4](image)
Figure 5

SEM photographs of neat cotton fabric (a), fabric modified with APTES (b), fabric-macroinitiator (c), fabric with 15% grafting (Cg15) (d) and fabric with 65% grafting (Cg65) (e) at 200× (left), 900× (middle) and 2700× (right) magnifications.

Figure 6

(a) Storage modulus and (b) tan δ of neat cotton fabric, fabric modified with APTES (Fabric-APTES), cotton fabric grafted with 15% (Cg15), 40% (Cg40), 53 % (Cg53) and 65% of PMAPC1 (Cg65).
Figure 7

Horizontal flame test of grafted cotton fabrics.

Figure 8

Vertical flame test of grafted cotton fabric.

Figure 9

Heat release rate of modified sample with 41% grafting (Cg41) measured by MCC.

Figure 10

Thermal properties by TGA in oxygen atmosphere of neat cotton fabric, fabric macroinitiator (fabric-Br), fabric with 15% grafting (Cg15) and fabric with 65% grafting (Cg65).

Figure 11

Thermal properties by TGA in nitrogen atmosphere of neat cotton fabric, fabric macroinitiator (fabric-Br), fabric with 15% grafting (Cg15) and fabric with 65% grafting (Cg65).

Figure 12

Horizontal flame test of modified fabric (Cg41) before and after washing.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.
- floatimage1.jpeg
- FlameretardantCottonFabricSupportingInformation.docx
- Scheme01.png