Electronic Supplementary Material (ESI) for Polymer Chemistry.

Antibacterial Cotton Fabric Prepared by Surface-Initiated Photochemically Induced Atom Transfer Radical Polymerization of 2-(Dimethylamino)ethyl Methacrylate with Subsequent Quaternization

Gamal Zain [a,b], Mária Bučková [c], Katarína Mosnáčková [a], Jana Doháňošová [d], Alena Opálková Šišková [a,e], Matej Mičušík [a], Angela Kleinová [a], Peter Matúš [f] and Jaroslav Mosnáček*[a,g]

[a] *Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 84541 Bratislava, Slovakia*

[b] *Pretreatment and Finishing of Cellulose Based Textiles Dept., Textile Research Division, National Research Centre, Dokki, Giza, Egypt*

[c] *Institute of Molecular Biology, Slovak Academy of Sciences, Dúbravská cesta 21, 845 51 Bratislava*

[d] *Central Laboratories, Faculty of Chemical and Food Technology STU, Radlinského 9, 812 37 Bratislava, Slovakia*

[e] *Institute of Materials and Machines Mechanics, Slovak Academy of Sciences, Dúbravská cesta 9, 845 13 Bratislava, Slovakia*

[f] *Institute of Laboratory Research on Geomaterials, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, 842 15 Bratislava, Slovakia*

[g] *Centre for Advanced Materials Applications, Slovak Academy of Sciences, Dúbravská cesta 9, 84511 Bratislava, Slovakia*

** Corresponding author: jaroslav.mosnacek@savba.sk*

Supporting Information

Materials

DMAEMA, 98 %, was purchased from Sigma-Aldrich, Sterinheim, Germany, and 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 31. Copper(II) bromide (CuBr2), ethyl α-bromoisobutyrate (EBiB), 98 %, 2-bromopropionitrile (BPN), 97 %, benzyl bromide, 98 %, 1-oleoyl-rac-glycerol (non-ionic detergent), were purchased from Sigma-Aldrich, Sterinheim, Germany. Ethyl α-bromophenylacetate (EBPA), 97 %, α-bromoisobutyryl bromide (BiBB, 97 %), triethylamine (Et3N), 99 %, dimethyl aminopyridine (DMAP), and all solvents were purchased from Sigma Aldrich, USA, and were used as received without further purification. Fabric (100 % cotton) was purchased from a commercial shop in Bratislava, Slovakia. 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 60 oC in a vacuum oven before use. Tetrahydrofuran (THF, 99.8 %), used for synthesis, was dried by distillation from sodium/benzophenone.

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.

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

The FTIR spectra were recorded using an 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.

Scanning Electron Microscopy (SEM)

The fabric morphology 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 mm2. 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.

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 × 12 kV. The spectra were acquired in the constant analyser 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 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:

$$\%\, A = \frac{I_A/s_A}{\sum(I_n/s_n)} \times 100\% \qquad \text{(S1)}$$

where I_n and S_n are the integrated peak areas and the Scofield sensitivity factors corrected for the analyser transmission, respectively.

Durability Test

The stability of the grafted polymer onto the fabrics was investigated by evaluating the antibacterial efficiency after washing. First, the modified fabric was washed at a liquor ratio of 50:1 mL/g for 18 washing cycles at 40 °C, with a non-ionic detergent (1 g/L). Samples were washed with distilled water and EtOH and oven-dried. The concentration of bacteria in test was 5,00 x 105 inoculum (CFU/mL). S. aureus bacteria were used for that test which was obtained from the Czech Collection of Microorganisms (CCM) Masaryk University, Faculty of Science, Brno Czech Republic.

Table S1. Molecular characteristics of PDMAEMA prepared using photoATRP with various monomer/initiator molar ratios (M/I). Experimental conditions: $CuBr_2$/TPMA=1/4; [DMAEMA]= 2.3 M, T=28 ˚C, 60 vol% of anisole, light intensity of 9 mW cm^{-2} (λ= 365 nm).

Entry	M:EBiB:$CuBr_2$	Time (hours)	Conversion (%)	M_n (g/mol)	$Đ$
1	200:1:0.04	5.5	62	19,900	1.26
2	400:1:0.08	8	51	34,800	1.18
		18	93	43,900	1.29
3	2000:1:0.4	7	61	88,700	1.18
		20	82	137,000	1.41

Table S2. Elemental composition of neat and modified cotton fabrics (in weight %) from EDS.

Sample	C	O	N	Br
Neat Fabric	56.22	43.88		
Cell-Br	57.94	40.83	0.39	1.84
Cg27	65.87	27.46	5.40	1.27
Cg37Q70	62.83	7.74	2.79	26.64

Table S3. Apparent surface chemical composition as determined by XPS.

Sample	Surface Chemical Composition (at%) / Peak Positions (eV)				
	C1s	**O1s**	**N1s**	**Si2p**	**Br3d**
	sp^3/C-O/C=O/OC=O	**C=O/C-O/C-O*/O_2C=O[x]**	**-NR_2/-NH_2/-NR_3^+/ N-O**	**Si-O**	**Br^-/C-Br**
	(285.0/286.4/287.6/ 289.0)	**(530.3/532.7/ 533.6/535.0)[x]**	**(398.8/400.1/401.8/ 403.6)**	**(102.2)**	**(67.0/69.7)**
Neat Fabric	**65.4** 28.1/22.4/7.9/7.0	**33.2** 0.6/28.9/2.6/ 1.1	**0.3** -/0.3/-/-	**1.0**	**-**
Cell-Br	**63.4** 24.2/24.8/7.0/7.4	**34.3** 0.5/30.0/2.8/ 1.0	**1.0** 0.4/0.4/0.2/-	**0.5**	**0.7** 0.1/0.6
Cg51	**96.5** 50.2/17.2/-/9.4	**14.2** 0.4/5.8/7.6/ 0.4	**7.1** 5.5/1.1/0.5	**0.7**	**-**
Cg51Q78	**77.4** 42.6/24.3/5.3/5.2	**12.7** 0.6/7.1/3.8/1 .2	**5.3** 0.7/0.5/3.5/0.6	**0.6**	**3.9** 3.4/0.5

[x] these assignments and peak positions are for Neat Fabric, after modification the assignment and peak positions are slightly different

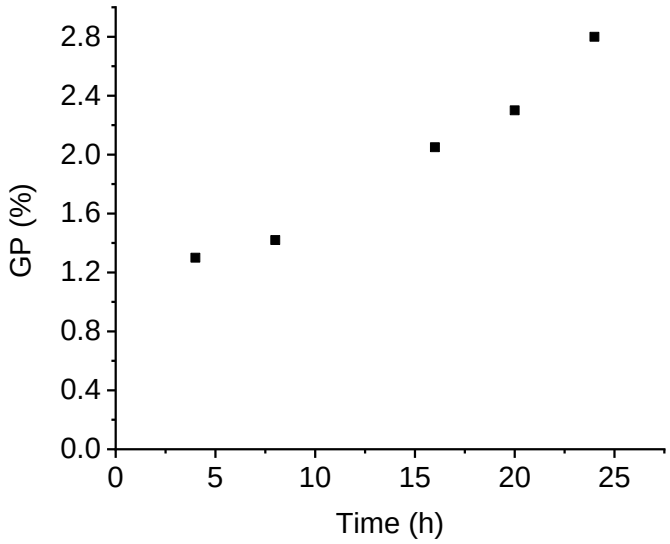


Figure S1. Dependence of grafting percentage on time of surface initiated photoATRP of DMAEMA in 60 vol% of Anisole. Experimental conditions: DMAEMA/EBIB/$CuBr_2$/TPMA = 200/1/0.08/0.32. [DMAEMA]= 2.37 M, *T*=28 °C, light intensity of 12 mW cm^{-2} (λ= 365 nm).

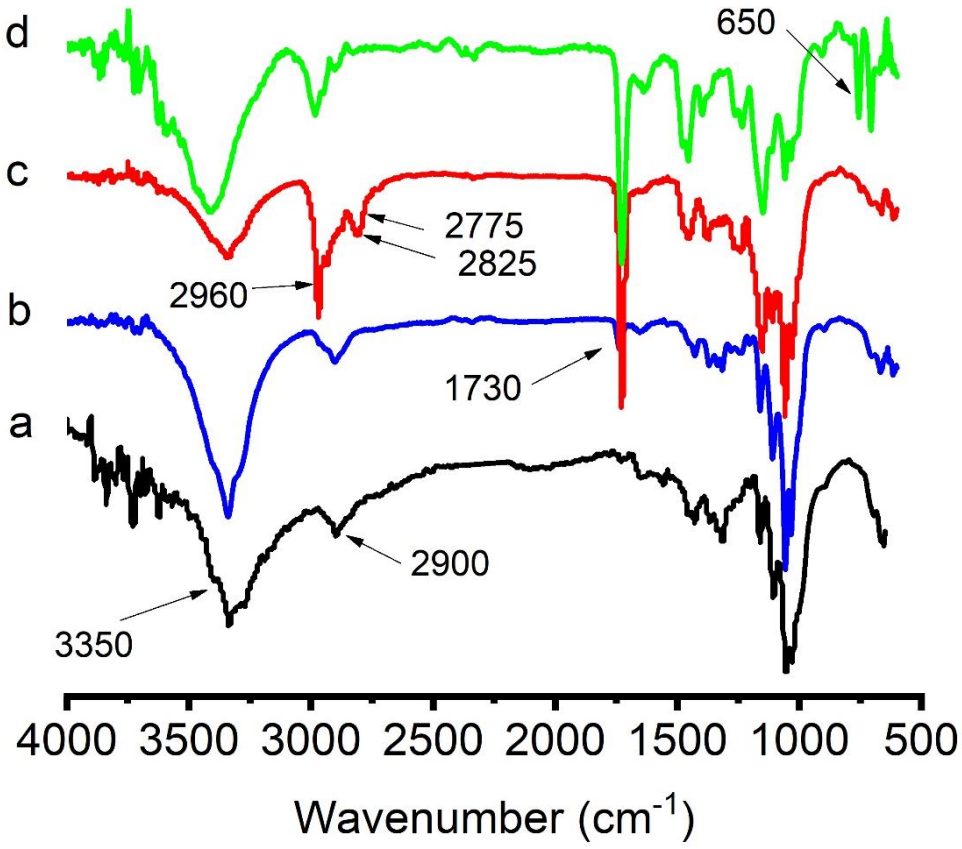


Figure S2. FT-IR spectra of neat cotton fabric (a), cell-Br (b), cell-g-PDMAEMA (Cg51) (c) and cell-g-QPDMAEMA (Cg51Q78) (d).

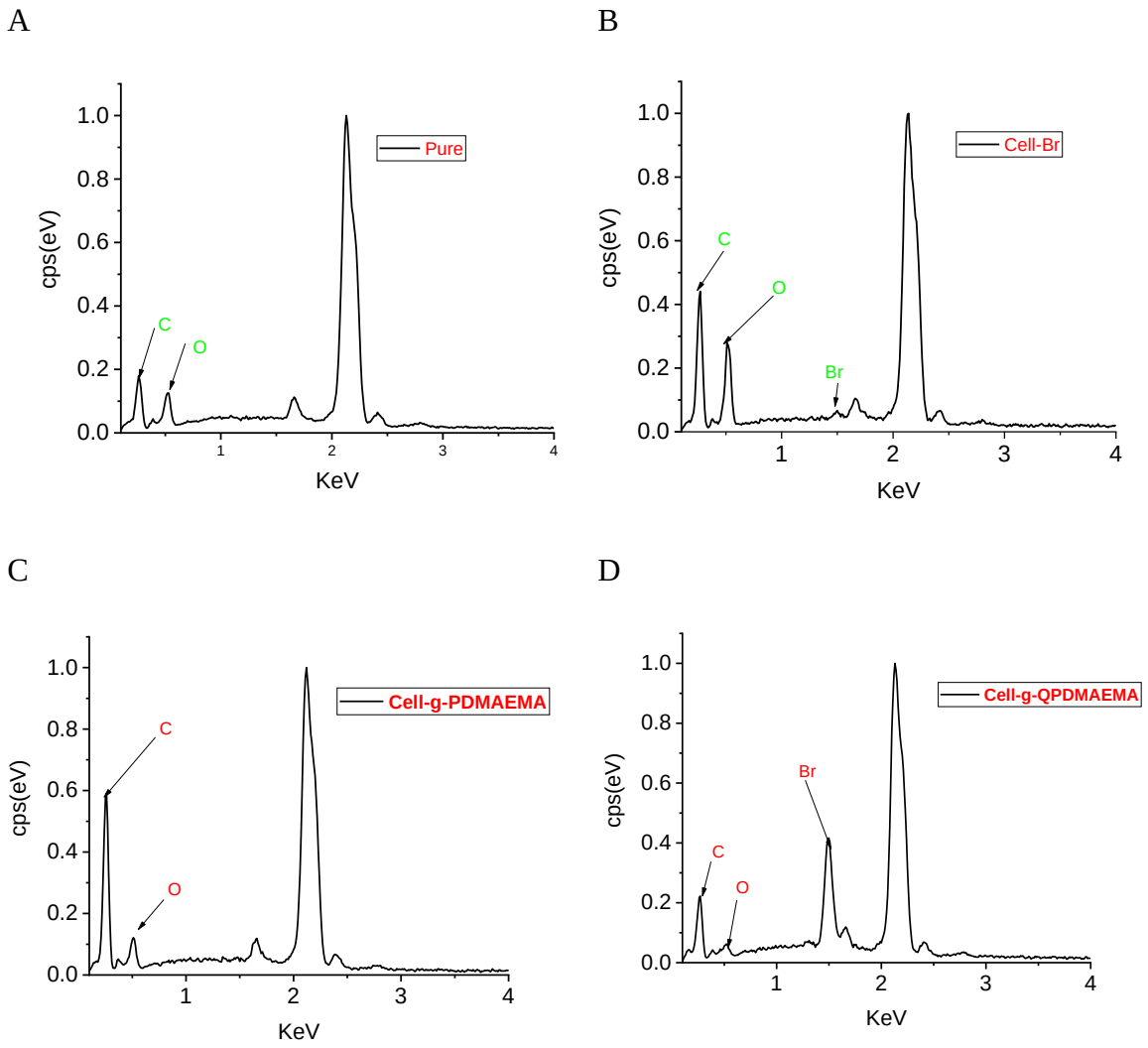


Figure S3. EDS results for pristine cotton fabric (A), Cell-Br (B), fabric grafted with PDMAEMA - Cg27 (C) and fabric grafted with QPDMAEMA - Cg37Q70 (D).

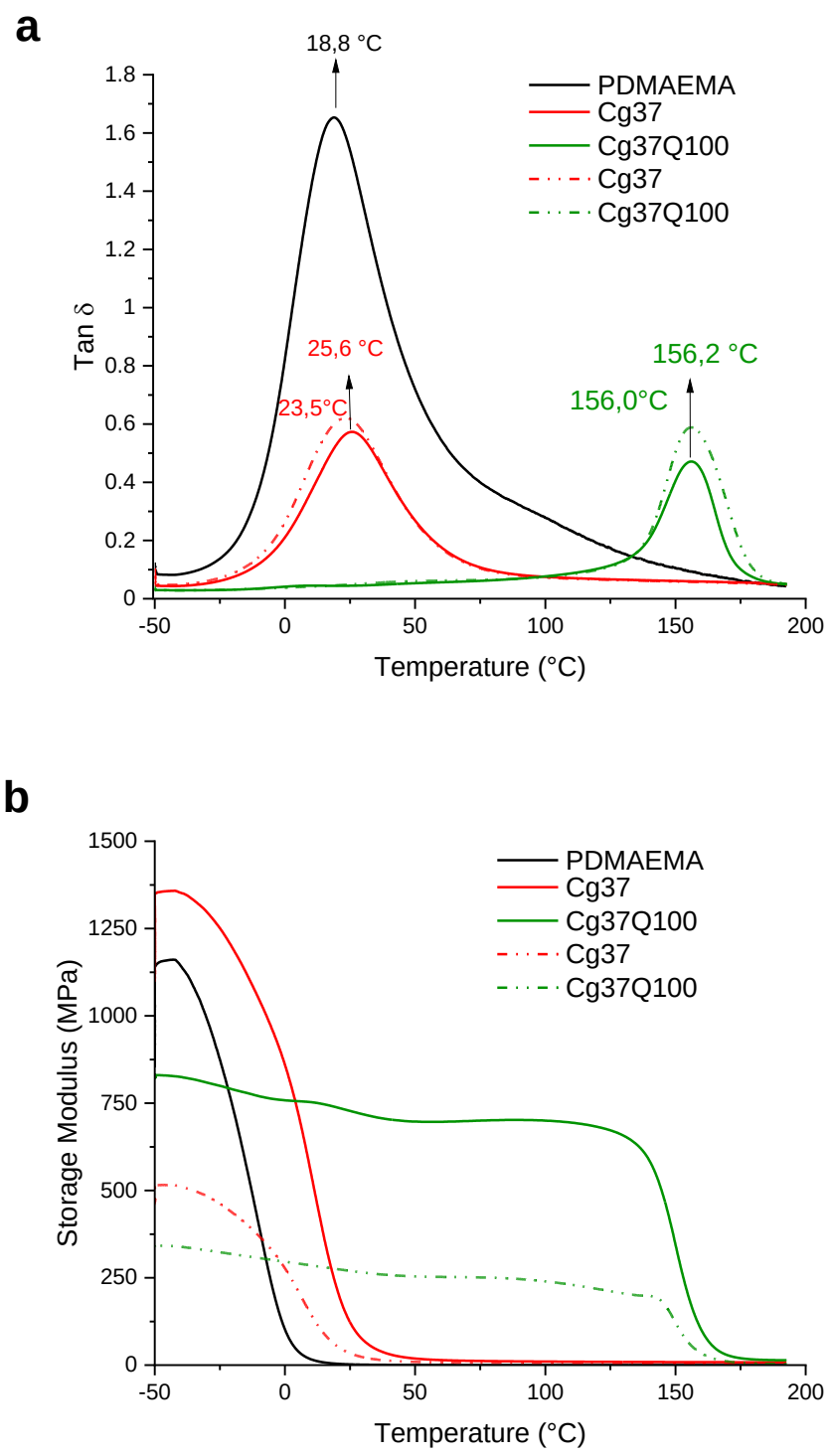
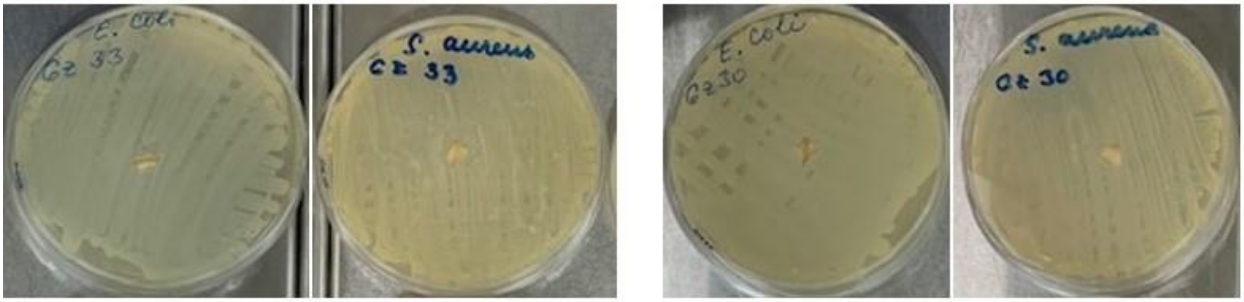


Figure S4. (a) Tan δ and (b) Storage modulus of neat PDMAEMA and fabric grafted with 37% of PDMAEMA before (Cg37) and after 100% quaternization (Cg37Q100) tested in the warp (solid line) and weft (dashed line) direction.



a b

Figure S5. Antibacterial activity of small pieces of modified fabrics Cg19Q69 and Cg51Q100 against E. coli (a) and S. aureus (b) respectively, tested by Disk-diffusion Assay method for 24 hours at 37°C.