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Functionalization of cyclic olefin copolymer substrates with polyethylene glycol diacrylate for the in situ synthesis of immobilized nanoparticles

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1 Introduction

Microfluidic systems are actually in development owing to their significant advantages: the reduction of solvent consumption and the faster analysis. Furthermore, the implementation of nanoparticles as novel stationary phase in microchips could in the future offer enhanced chromatographic performances as shown by Knox and other authors [1-4]. Up to now, the smallest particles in conventional columns present 1.7 μm as diameter [5].

Usually, polymers colloids are made from emulsion polymerization, like miniemulsion, which could be thermally [6] or photochemically initiated [7, 8]. UV irradiation approach allows polymerization in enclosed system in few minutes and at room temperature without stirring. Thereby, the synthesis of hexyl acrylate nanoparticles (C_6) was executed by emulsion radical polymerization. Miniemulsion composition was previously optimized by central composite design and C_6 nanoparticles, obtained after photopolymerization was monodisperse with a diameter inferior to 200 nm which could be used as new stationary phase [9]. To anchor nanoparticles into microchips, the polymerization of miniemulsion is initiated in-situ by the abstraction of hydrogen from the surface.

Photoinitiator type II like benzophenone (BP), react by hydrogen abstraction from the surface and form ketyl (semipicanol) free radical and an alkyl free radical [10-14]. Benzoin methyl ether (BME) is a type I photoinitiator used in polymerization to generate free radicals and as it has been showed by Ladner et al.[15], it can react with COC by abstracting hydrogen from the surface. This

process, allows the photografting of acrylate nanoparticles on COC surface under UV irradiation at 365 nm. Wang et al. [16, 17] reported the photografting of methyl methacrylate/ 1,2-divinylbenzene (MMA/DVB) emulsion, initiated by UV-irradiation on polypropylene (PP) film. Nanoparticles diameter is about 30 nm and 60 nm, anchored by covalent bond on PP film, using benzophenone as photoinitiator. Furthermore, the formation of group dormant permits a growth of the multilayer graft nanoparticles. The anchorage of nanoparticles into microchips depends on the nature of the material. A variety material have been used, for different applications, such silicon : polydimethylsiloxane (PDMS), glass, quartz, thermoplastic materials like poly (methymethacrylate) (PMMA) and polyolefin such as polyethylene (PE), polypropylene (PP) and cyclic olefin copolymer (COC). COC is one of the most widely used because of its resistance to many organic solvents, its transparency below 300 nm [18, 19] and optical detection.

Preliminary synthesis of spherical C₆ nanoparticles on COC chips revealed the need of surface modification. Hydrophobic nature of the material seems disturbing miniemulsion stability during in-situ photopolymerization. To promote the approach and the anchorage of spherical nanoparticles to the surface, many methodologies of COC surface modification are proposed using physical or chemical coating [20]. In literature, Roy et al. [21, 22] discussed the physical COC coating by plasma treatment using argon and argon-oxygen to enhance hydrophilicity and increase wettability of COC surface. Both treatments showed an increase of wettability and roughness, but compared to argon plasma, oxygenated-plasma increased more effectively the wettability of COC surface. Other approaches including UV/ozone oxidation treatment [23], dynamic coating with hydrophilic polymers [24], covalent grafting method by aryldiazonium salts [25] and UV-photografting of hydrophilic polymers [26, 27] are used for COC microchannels modification.

UV-photografting of hydrophilic polymers is a common strategy for modification of polydimethylsiloxane (PDMS) [28-30] and thermoplastic materials [20, 31] : polyethylene films [13, 32-35], polypropylene substrates [16, 17, 36-40], polycarbonateurethane [41] and cyclic olefin copolymer (COC) [15, 26, 42-47]. UV-photografting of COC surface allows modification to hydrophilic surface without changing bulk properties, such as optical properties. One of the advantages is the covalent grafted chains offers stable surfaces in contrast to the physical coating which can be delaminated [45]. Modification of COC surface was discussed for different

applications, cited in literature like fabrication of smart disposable LOCs for the BIOMEMS applications [45], the bioanalytical applications that require minimal nonspecific adsorption of biomolecules [27], and to increase bond strength of the original surface [43]. However, very few examples are to be found. Li et al. [26] studied the UV-photografting of a hydrophilic polyacrylamide on COC devices in order to reduce protein adsorption and make COC suitable for proteins separations by isoelectric focusing gel electrophoresis. In this example, polyacrylamide grafting was initiated in presence of benzophenone (BP) as photoinitiator. The surface hydrophilicity was characterized by contact angle measurements. Hydrophilicity increased with coating time and for 20 min of UV-irradiation, contact angle measured is 12° - 16° . PA-coating modified COC surfaces to hydrophilic properties and kept low electroosmotic mobilities. In another example, Du et al. [46] improved the hydrophilicity of COC devices by photografting six acrylates with anionic, neutral and cationic functional groups, to obtain different surface charges. Benzophenone was used as photoinitiator. Influence of irradiation conditions: monomer concentration, reaction temperature, irradiation intensity and time, was followed by contact angle measurements. On COC microchannels modified with 2- acrylamido - 2- methyl -1- propane sulfonic (AMPS) and N-[3-(dimethyl-amino)propyl] methacrylamide, an electrophoretic separation of fluorescein isothiocyanate labeled amino acids was reported. A zwitterionic molecules were successfully grafted by Peng et al. [47] onto the surface of COC microfluidic channels by UV-irradiation of mixed acrylic monomers : 2- acrylamido - 2- methyl -1- propane sulfonic (AMPS) and [2-(acryloyloxy)ethyl]trimethyl ammonium chloride (AETAC). Contact angle showed a modification of COC surface, with BP as photoinitiator, with low angle obtained for ratio AETAC/AMPS = 5.5. These modified COC microchannels showed a highly efficient separation of amino acid, indicating that the surface modification led to a uniform zwitterionic layer.

The focus of this work is the surface modification of COC plates, by UV photografting of the hydrophilic monomer: polyethylene glycol diacrylate (PEGDA). For this purpose, an optimisation of PEGDA photografting was investigated by using a central composite design (CCD) in order to obtain a hydrophilic COC surface which enhances anchoring of hexyl acrylate nanoparticle (C_6). Surface morphology was observed by scanning electronic microscopy (SEM) to follow the influence of hydrophilic surface on particles sphericity.

2 Experimental section

2.1 Materials

All chemicals were supplied by Sigma-Aldrich (Isle – d’Abeau, France) and used as received: sodium dodecyl sulfate (SDS) as surfactant, hexyl acrylate (HA), 2- acrylamide - 2- methyl propane sulfonic acid (AMPS), polyethylene glycol diacrylate (PEGDA 258) as monomers, benzoin methyl ether (BME) as photoinitiator, and pentadecane (C₁₅) as co-stabilizer. Solvents used were acetone and water of Milli-Q grade (resistivity: 18 MΩ).

Cyclic olefin copolymer plates (COC, Topas 6013) in format 75.5 mm x 25.5 mm, thickness 1.0 mm, were fabricated by Microfluidic Chipchop GmbH (Jena, Germany). These plates were rinsed with acetone and dried under nitrogen before use.

2.2 Hydrophilic monomer PEGDA photografting on COC surface

Hydrophilic monomer PEGDA were mixed to BME and solubilized in acetone under agitation and ultrasound. Aqueous solutions containing different concentrations of PEGDA and BME were tested. BME amount is expressed as weight pourcentage (wt. %) in respect with PEGDA weight or as concentration in water (mol/L). A volume of approximately 500 µL PEGDA-BME mixture was deposited on native COC plate, then enclosed with another COC plate without causing bubbles which could disturbs the polymerization.

2.3 Miniemulsion formulation and polymerisation

Surfactant sodium dodecyl sulfate (SDS) and charged monomer 2- acrylamido - 2- methyl -1- propane sulfonic acid (AMPS) were dissolved in water forming the aqueous phase (φ_{aq}). The organic phase (φ_{org}) was prepared with the monomer hexyl acrylate (HA), the photoinitiator benzoin methyl ether (BME) and the co-stabilizer pentadecane (C₁₅). The composition of the miniemulsion was fixed at 0.1 wt. % SDS and 0.025 wt. % AMPS in the aqueous phase mixed to the organic phase constituted of 5 wt. % HA, 0.35 wt. % C₁₅ and 0.125 wt. % BME. All amounts are expressed in weight percentage (wt. %) with respect to the water weight.

Both phases were then mixed in a beaker during 10 min using a magnetic stirrer at 700 rpm leading to an oil-in-water pre-emulsion. This dispersion was then mini-emulsified by ultrasonication with a sonifier (W450 DigitalBranson) at 50% amplitude for 180 s.

Miniemulsion was injected between two PEGDA-modified COC plates, and miniemulsion polymerization is performed under irradiation intensity of 2.7 mW/cm^2 for 30 min at 30°C . After polymerization, plates are rinsed with deionized water to eliminate non reacted reagents and solvents.

2.4 Characterization of COC surface

2.4.1 Contact angle measurements

A droplet of distilled water ($3.3 \mu\text{L}$) was dropped off on COC surface at room temperature. The contact angles measured by Digidrop Contact Meter (GBX, Bourg de Péage, France) instrument, are the averages of 15 measurements performed at different locations of the surface.

2.4.2 Scanning electron microscopy

Morphology of nanoparticles on PEGDA grafted-COC- surfaces were observed by scanning electron microscopy (FEI Quanta FEG 250). Plates were covered with a thin layer (10 - 20 nm) of metal conductor (like platinum or gold-palladium) prior to SEM observations, in order to reduce the charge phenomenon on non-conducting material.

2.5 Optimization design

Surface response methodology as applied to optimize PEGDA photografting in order to obtain a hydrophilic COC surface. The experimental factors studied were the amount of PEGDA (X1), BME (X2) and irradiation time (X3). Others factors were fixed: the solubilization mixture was acetone/water 50/50 (v/v), temperature was fixed at 45°C and intensity of irradiation at 2.7 mW/cm^2 . The response Y was the contact angle measured on both plates.

A central composite design (CCD) was built with a second-order quadratic equation to model the contact angle (Y1) as follows:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2$$

(Eq.1)

Where Y is the modeled response (Y1), b_0 is the intercept, X_i is the coded factor, b_i is the corresponding coefficient, b_{ii} is the quadratic coefficient and b_{ij} is the two-factor interaction coefficient.

17 experiments were thus carried out determined by the 2^3 full factorial design with six axial points at a distance of $\alpha = 1$ from the design center and three center points. The experimental factors and their levels are given in Table 1.

Multiple linear regression, analysis of variance (ANOVA) and residual analysis were performed with NemrodW®software (LPRAI, Marseille, France).

Table 1 Experimental factors and their coded levels in the central composite design, with the corresponding amounts of PEGDA (mol/L) and BME (wt. % with respect to PEGDA weight) and irradiation time (min).

Level	[PEGDA] (mol/l)	BME (wt. %)	Irradiation time (min)
-1	0.1	1	10
0	0.2	3	15
1	0.3	5	20

3 Results and discussion

Miniemulsion photopolymerization on native COC plates showed a need of surface modification. Hydrophobic surface of COC seems disturbing miniemulsion stability and therefore, spherical particles were not anchored. An acrylate layer was obtained. With the view to increasing the surface coverage, UV-photografting of ionic and neutral monomers was investigated. Firstly, hydrophobic monomer was tested: ethylene glycol dicyclopentenylether acrylate (DCP). It's a monomer which has a norbornene group like COC surface, and could be a spacer to anchorage nanoparticles. This grafting, showed an increase of active sites, but acrylate layers were formed. Secondly, many hydrophilic monomers were investigated looking for a hydrophilic surface: 2-acrylamido - 2- methyl -1- propane sulfonic acid (AMPS), 2 (methacryloyloxy)

ethyltrimethylammonium chloride (MATEA) and polyethylene glycol diacrylate (PEGDA 258 and PEGDA 700). Only PEGDA (258) photografting, showed the anchorage of monodisperse spherical particles. An optimization was studied by experimental design in order to obtain an homogeneous grafting.

3.1 Optimization of PEGDA photografting

Experimental design was built to study the influence of PEGDA concentration, BME amount expressed as percentage in regards to PEGDA weight and irradiation time on surface hydrophilicity by contact angle measurements. PEGDA and BME amounts impact the number and the crosslinking of PEG chains. Furthermore, irradiation time affects the density and the length of PEG chains.

Table 2 shows 17 experiments in different conditions, with contact angle measurements as response. Standard deviation, calculated for 15 points in different locations on COC plates, indicates the surface homogeneity of PEGDA grafting. COC plate is considered hydrophilic when contact angle reached a value below 65°. Amongst 17 experiments, only three conditions meet these requirements: test 4, 8 and 12. Test 8 was irradiated for 20 min at the same amounts of PEGDA and BME of test 4, and showed a contact angle slightly superior to the value obtained for the test 4. For test 12, PEGDA grafting was not homogeneous and less reproducible. The low value of contact angle with good homogeneity (59 ± 3) was obtained for experiment 4 for the following conditions: 0.3 M PEGDA, 5 wt. % BME for 10 min of irradiation. The synthesis of nanoparticles on photografted COC plates for these conditions was investigated.

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186 **Table 2** Three-factor central composite design with corresponding response: contact angle measurements
 187 \pm standard deviation. The amount of BME is express in weight percent with respect to PEGDA weight.

Experiments	[PEGDA] (M)	wt. % BME	Irradiation time (min)	Contact angle ($^{\circ}$) \pm standard deviation
1	0.10	1	10	83 ± 3
				85 ± 1
2	0.30	1	10	71 ± 6
				70 ± 6
3	0.10	5	10	78 ± 4
				76 ± 4
4	0.30	5	10	59 ± 3
				59 ± 3
5	0.10	1	20	84 ± 6
				84 ± 7
6	0.30	1	20	69 ± 5
				72 ± 5
7	0.10	5	20	74 ± 9
				73 ± 5
8	0.30	5	20	65 ± 4
				65 ± 7
9	0.10	3	15	79 ± 5
				80 ± 3
10	0.30	3	15	78 ± 7
				81 ± 5
11	0.20	1	15	84 ± 2
				85 ± 1
12	0.20	5	15	61 ± 8
				67 ± 9
13	0.20	3	10	85 ± 3
				81 ± 3
14	0.20	3	20	77 ± 5
				78 ± 4
15	0.20	3	15	87 ± 2
				85 ± 3

16	0.20	3	15	81 ± 6
				84 ± 8
17	0.20	3	15	77 ± 6
				73 ± 7

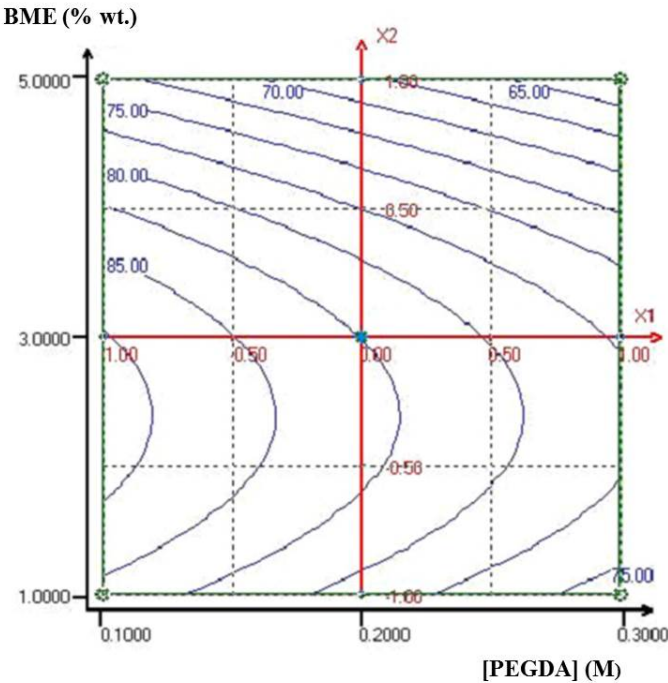


Figure 1 : Contour plot of contact angle for 10 min of irradiation.

The results shown in Table 2 for 17 experiments done in different conditions were analyzed by a contour plot. This plot (Figure 4) allows the determination of PEGDA and BME concentrations leading to hydrophilic surface after photopolymerization during a specific irradiation time. Contour plots for different irradiation time tested were similar, so irradiation time has no influence on the response. Therefore, 10 min of irradiation was fixed. The plot also revealed a decrease of contact angle values, so an increase of hydrophilicity for high amounts of PEGDA (0.3 M) and BME (5 wt. %).

3.2 Increase of PEGDA concentration

In order to enhance the hydrophilic character of COC plates, an increase of PEGDA concentration might increase the anchorage of PEG chains which makes surface hydrophilic. Experiments with higher amount of PEGDA (0.4 M and 0.5 M) at 5 wt. % BME, were tested. For 0.4 M PEGDA

concentration, contact angle measured was $56^\circ \pm 4$. Photografting in these conditions was found to be not repeatable; other COC-PEGDA plates presented a contact angle of $73^\circ \pm 3$. For 0.5 M PEGDA, the surface was hydrophilic with contact angle of $64^\circ \pm 4$. Nanoparticles on COC-PEGDA plates for both photografting conditions were then observed by scanning electronic microscopy (Figure 2).

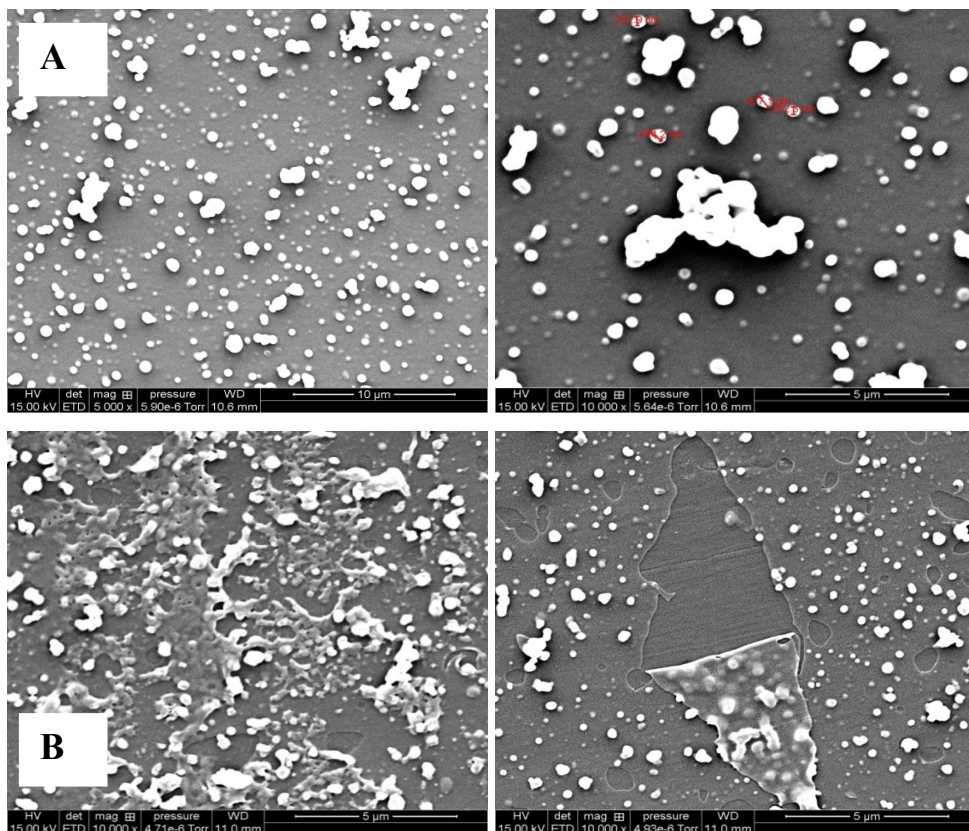


Figure 2 SEM Images **A** : 0.4 M PEGDA + 5 % wt. BME in water/acetone 50/50 (v/v); 10 min, 45°C, 2.7 mW/cm². MEB x 5000, x 10000. **B** : 0.5 M PEGDA + 5 % wt. BME in water/acetone 50/50 (v/v); 10 min, 45°C, 2.7 mW/cm². MEB x 10000. Miniemulsion photopolymerization: 30 min, 30°C, 2.7 mW/cm². Tension 15 kV.

For 0.4 M PEGDA (Figure 2A) particles are merged and distorted. Acrylate layer, which is not stable and peels off, was further observed for 0.5 M PEGDA (Figure 2B). To overcome these problems, PEGDA concentration was fixed at 0.3 M with 5 wt. % of BME. For these conditions, PEGDA-grafted COC plate contact angle was measured between 60° and 65° (Figure 1). The

synthesis of nanoparticles on the modified COC plates using this protocol (0.3 M PEGDA and 5 % wt. BME) was characterized by SEM observations (Figure 3).

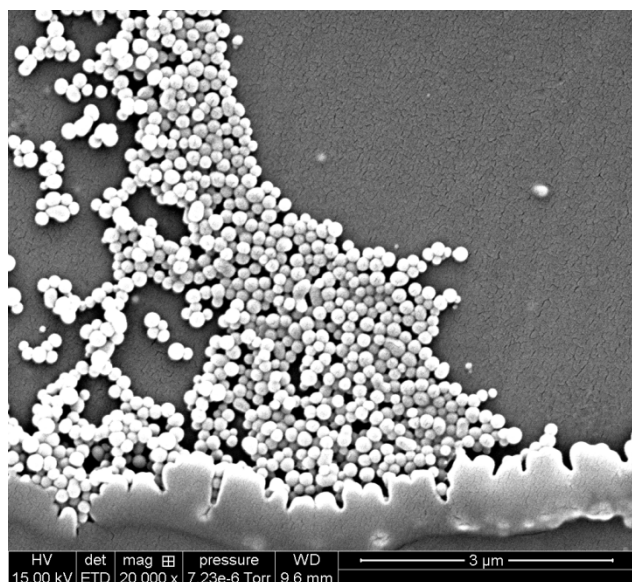


Figure 3 SEM image for nanoparticles on modified COC plate. PEGDA photografting : 0.3 M PEGDA + 5 % wt. BME in water/acetone 50/50 (v/v) ; 10 min, 45°C, 2.7 mW/cm². Miniemulsion photopolymerization: 30 min, 30°C, 2.7 mW/cm². MEB x 20000. Tension 15 kV.

Anchorage of spherical nanoparticles is unfortunately not sufficient and not homogeneous on COC (Figure 3). It seems that PEG chains are not grafted on the surface because of the amount of BME which might be insufficient to create active sites on COC by hydrogen abstraction. BME amount impact PEGDA grafting, but furthermore number of active sites on COC surface. Therefore, influence of BME was investigated by concentration.

3.3 Influence of BME concentration

Influence of BME amount on hydrophilicity COC surface was studied in percent in respect to PEGDA weight to initiate reticulation of PEG chains and form a compact polymeric layer. Furthermore, BME could act on COC surface by hydrogen abstraction, and therefore, it would be interesting to analyse with another point of view the influence of the photoinitiator by controlling BME concentration (mM) in regards to the polymerization mixture. This concentration should be optimized in order to promote a large number of active sites and enhance anchorage of

nanoparticles. BME concentrations are mentioned in Table 3 , and the contour plot according to BME and PEGDA concentration is represented in Figure 4.

Table 3 Experimental design expressed with BME concentration (mM)

Experiments	PEGDA Concentration (M)	% wt. BME	BME concentration (mM)	Irradiation time (min)	Y1 : Contact angle average (°)
1	0.10	1	1.14	10	84
2	0.30	1	3.42	10	71
3	0.10	5	5.70	10	76
4	0.30	5	17.10	10	59
5	0.10	1	1.14	20	84
6	0.30	1	3.42	20	71
7	0.10	5	5.70	20	73
8	0.30	5	17.10	20	65
9	0.10	3	3.42	15	79
10	0.30	3	10.26	15	80
11	0.20	1	2.28	15	84
12	0.20	5	11.40	15	64
13	0.20	3	6.84	10	83
14	0.20	3	6.84	20	78
15	0.20	3	6.84	15	86
16	0.20	3	6.84	15	82
17	0.20	3	6.84	15	75

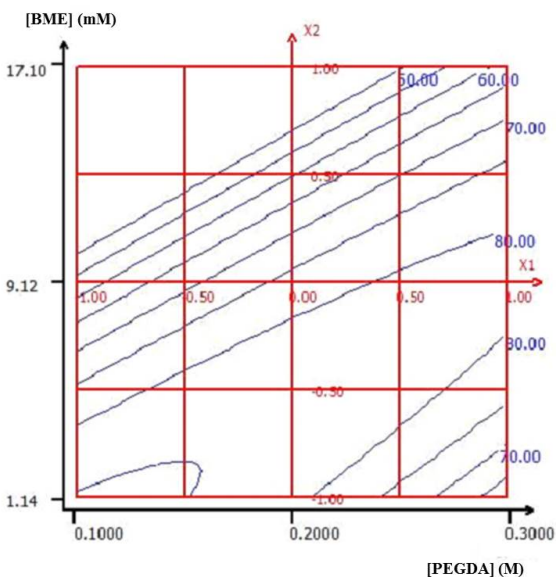


Figure 4 Contour plot of contact angle for 10 min of irradiation according to BME and PEGDA concentration.

BME, by hydrogen abstraction, forms more active sites on the surface, which promote anchorage of PEG chains. Contour plot of contact angle represented in Figure 4, indicated a hydrophilic character for higher BME concentration. Thereby, the hypothesis is verified. For 17 mM BME, which is the maximum concentration that was tested, contact angle is between 50° and 60° for various PEGDA concentrations (0.1 M – 0.3 M). For these conditions, reproducibility of PEGDA photografting was verified by three measures of contact angle (Figure 5).

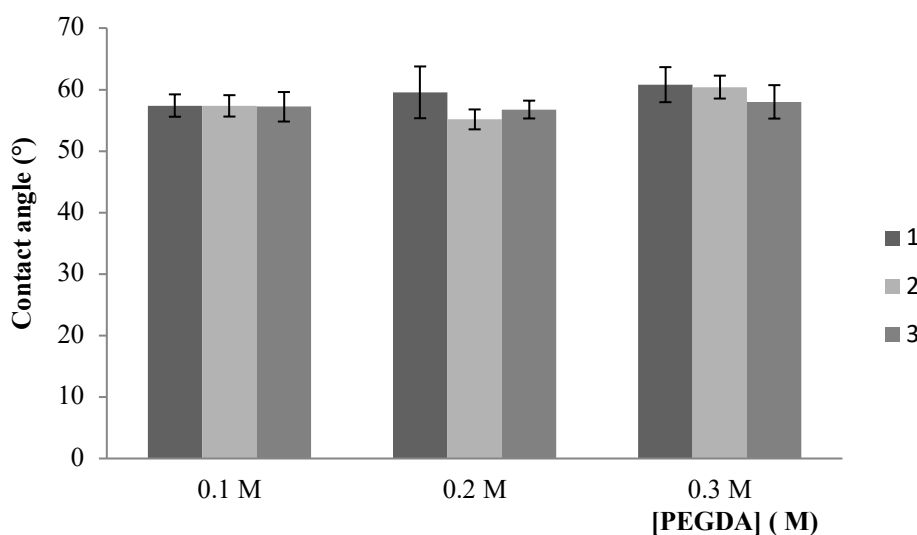


Figure 5 Reproducibility chart of PEGDA photografting. Contact angle (°) according to PEGDA concentration (M) for 17 mM BME. Photopolymerization 10 min, 45°C, 2.7 mW/cm².

To follow the impact of BME and PEGDA concentration on the sphericity of particles, UV-synthesis of acrylate particles on PEGDA-modified COC plates with 17 mM BME and PEGDA concentrations between 0.1 M and 0.3 M were performed. Figure 6 represent morphologies of the resulting particles.

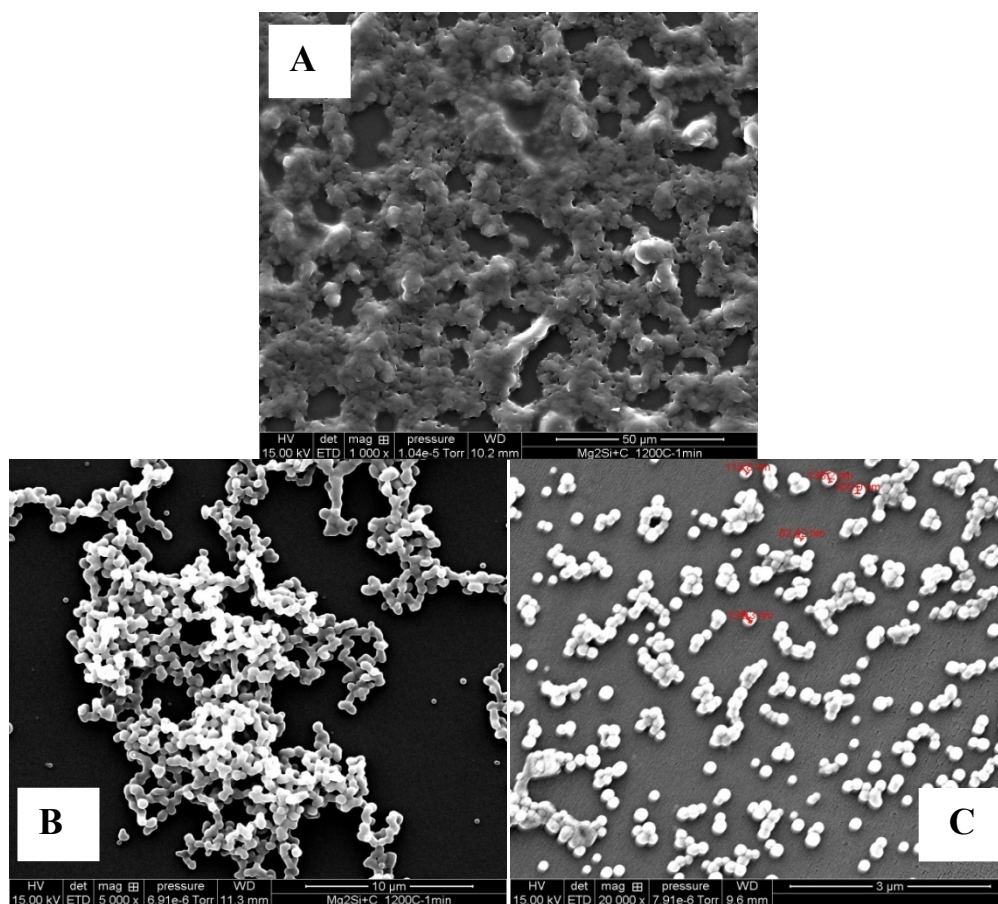


Figure 6 SEM Images of nanoparticles anchored on PEGDA-modified COC- surfaces. PEGDA photopolymerization with 17 mM BME, 10 min, 45°C, 2.7 mW/cm. **A** : 0.1 M, MEB X 1000. **B** : 0.2 M,

MEB X 5000. C : 0.3 M PEGDA concentration, respectively, MEB X 20000. Miniemulsion photopolymerization: 30 min, 30°C, 2.7 mW/cm². Tension 15 kV.

Figure 6A represent nanoparticles synthesis on modified COC with low concentration of PEGDA (0.1 M). Contact angle measured was between 55° and 65°. SEM morphologies, showed a fusion of particles on the surface. Low amount of PEGDA consumes a part of BME and the excess will form free radicals by hydrogen abstraction from COC. The non-grafted COC surface by PEG chains seems to destabilize miniemulsion due to his hydrophobic nature. For higher concentration of PEGDA, nanoparticles become more spherical with diameter between 80 nm and 140 nm for 0.3 M PEGDA (Figure 6C). These results verified that low PEGDA concentration, is not sufficient to consume BME and form spherical nanoparticles. Monodisperse hexyl acrylate nanoparticles with diameter inferior to 200 nm are obtained for 0.3 M PEGDA at 17 mM BME, which is in accordance to the specifications.

Unfortunately, these irradiation conditions were not compatible with COC chips. A concentration of 0.3 M PEGDA is considered too elevated for the surface modification to be implemented in microchannels, as it oftenly leads to channel blockage. To overcome this problem, we extended our study for PEGDA concentration field between 0.05 M and 0.2 M.

3.4 UV-Synthesis of nanoparticles on modified COC plates

Anchorage of nanoparticles on COC-PEGDA surfaces depends on polymerization conditions. For different synthesis on modified COC substrates, morphologies of nanoparticles were followed by SEM images. PEGDA photografting was explored for various PEGDA concentrations: 0.05 M, 0.1 M and 0.2 M with BME concentrations reaching 17 mM, 30 mM and 50 mM (Figure 7). BME concentration impacts the number of PEGDA chains grafted. At higher concentration an increase of the number of PEGDA chains can be observed. Otherwise, an excess of non-reacted BME can interfere with COC surface.

On the first hand, the diagram is interpreted in a horizontal manner. For a fixed value of BME concentration, no particles were observed at 0.05 M and 0.1 M PEGDA. Particles are fusion and leads to an acrylate monolayer. PEGDA concentrations seem insufficient to consume BME even at low concentration of 17 mM. Therefore, the miniemulsion was not stable in contact with the surface, as previously observed. At 0.2 M PEGDA, SEM images showed spherical particles anchored on COC surface. On the other hand, a vertical analysis of Figure 10 showed that more

300 particles distortion and acrylate layers happened for 0.05 M and 0.1 M PEGDA at higher
301 concentrations of BME. This might be due to the excess of BME non-reacted. For PEGDA
302 concentration higher than 0.2 M with higher concentration of BME more active sites were formed.
303 Thus, the number of spherical particles on the surface was enhanced.

304 In conclusion, PEGDA and BME amounts not only impact the hydrophilicity nature of COC but
305 also the sphericity of nanoparticles anchored. The increase of BME concentration leads to an
306 increase of active sites occupied then by PEGDA at higher concentrations. Therefore an increase
307 of number of spherical nanoparticles on the surface is observed. 0.2 M PEGDA at 30 mM BME
308 respond to the specification.

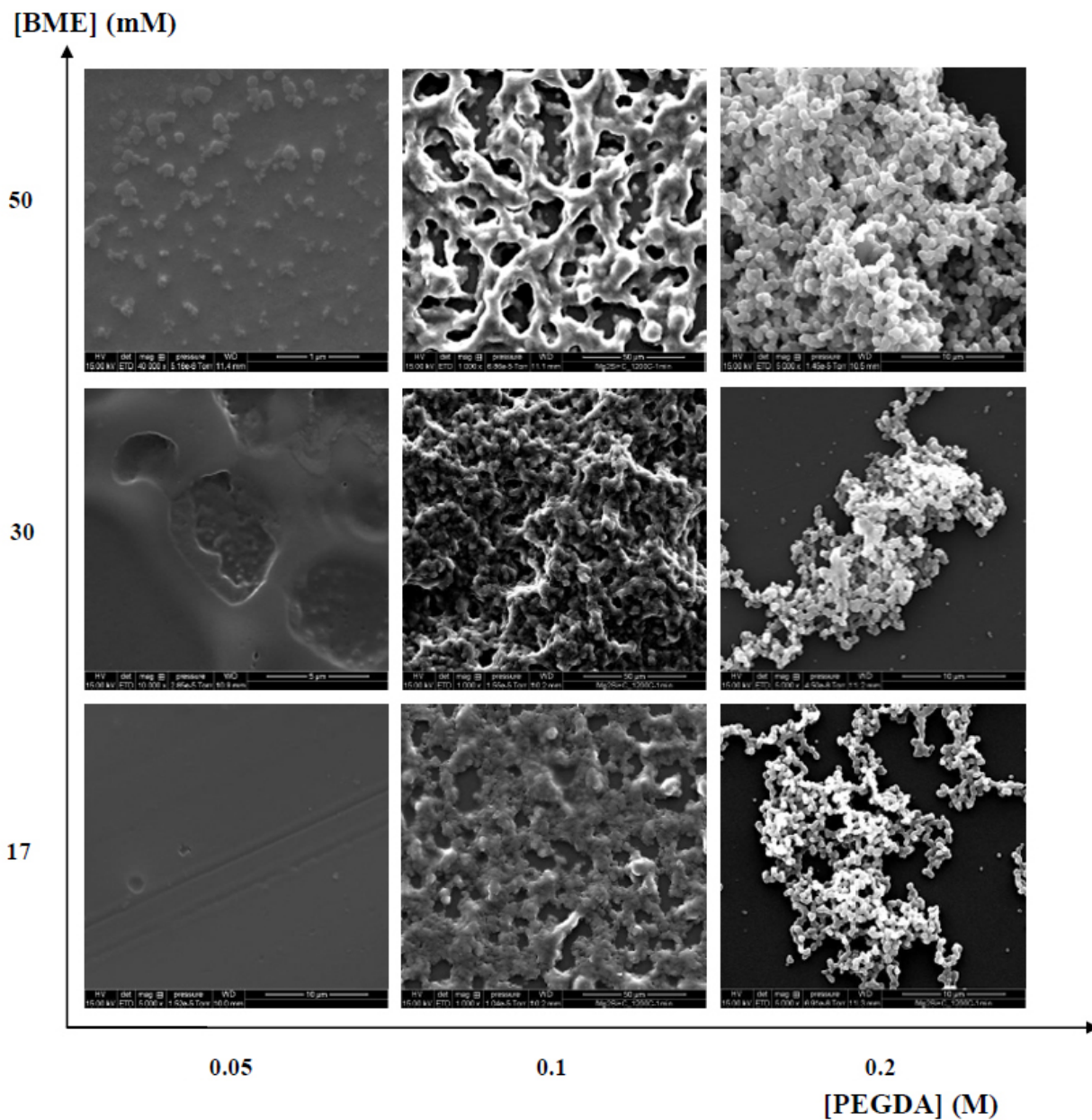


Figure 7 SEM Images of nanoparticles anchored on modified COC surfaces by different PEGDA and BME concentrations. Photopolymerization: 10 min, 45°C, 2.7 mW/cm. Miniemulsion photopolymerization: 30 min, 30°C, 2.7 mW/cm². Tension 15 kV.

4 Conclusion

The anchorage of hexyl acrylate nanoparticles on COC surface requires a surface modification from hydrophobic to hydrophilic nature. This study studied the optimization of PEGDA photografting by using response surface methodology as regard to PEGDA and BME amounts and irradiation time. A large experimental field has been explored using water contact angle measurement which indicates the hydrophobic/hydrophilic nature of the substrate. COC surface has been considered sufficiently hydrophilic for a contact angle inferior to 65°. The hydrophilic PEGDA-modified COC surface promotes anchorage of nanoparticles, as observed by SEM images. Both PEGDA and BME concentrations used during the first surface modification step impact the anchorage of nanoparticles that occurs during in-situ photopolymerization as well as the morphology of the resulting particles. A compromise between PEGDA and BME amount should be made to maintain spherical particles sufficiently anchored on COC plates and microchips. Synthesis of nanoparticles on modified COC plates grafted with PEGDA was achieved. An optimization of polymerization conditions in COC microchips should be done to avoid plugging channels and to develop a novel stationary phase which could be used in electrochromatography.

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