Supplementary Information

Modification of cellulose through physisorption of cationic bio-based nanolatexes – Comparing emulsion polymerization and RAFT-mediated polymerization-induced self-assembly

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Degree of hydrolysis of macroRAFT

The degree of hydrolysis (DH) of DMAEMA in MAA during the synthesis of the macroRAFT can be calculated by using equation S1.[1,2] Briefly, DH is the ratio between the integral of the methylene (f) adjacent to the amine of the ethanolamine ($I_{3.21}$) and the integral of the methylene (d) of the tertiary amine in DMAEMA ($I_{3.48}$).

$$DH\ (\%) = \left[\frac{I_{3.21}}{(I_{3.21} + I_{3.48})}\right] \cdot 100 = \left[\frac{f}{(f + d)}\right] \cdot 100$$
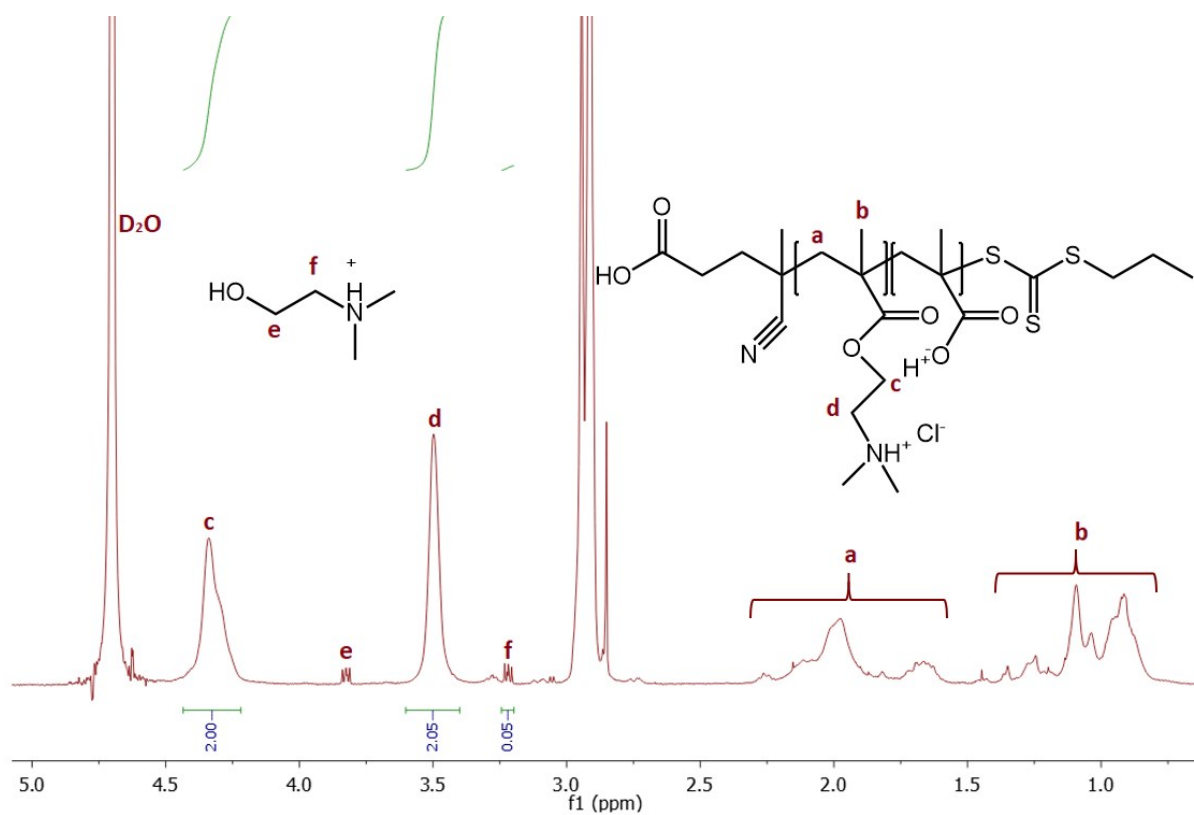
(S1)

Figure S1 - ^{1}H-NMR of macroRAFT P(DMAEMA-co-MAA) in D$_2$O.

SobMA solution

SobMA was stored in the fridge in a solution with EtOAc and DCM to prevent its autopolymerization (Figure S2). The weight fraction of SobMA in these solvents, which was later used in the polymerization protocol, was calculated by using the integrals at 5.3 ppm, corresponding to DCM and at 4.11 ppm corresponding to EtOAc. The solvents were removed by rotary evaporation prior to its polymerization.
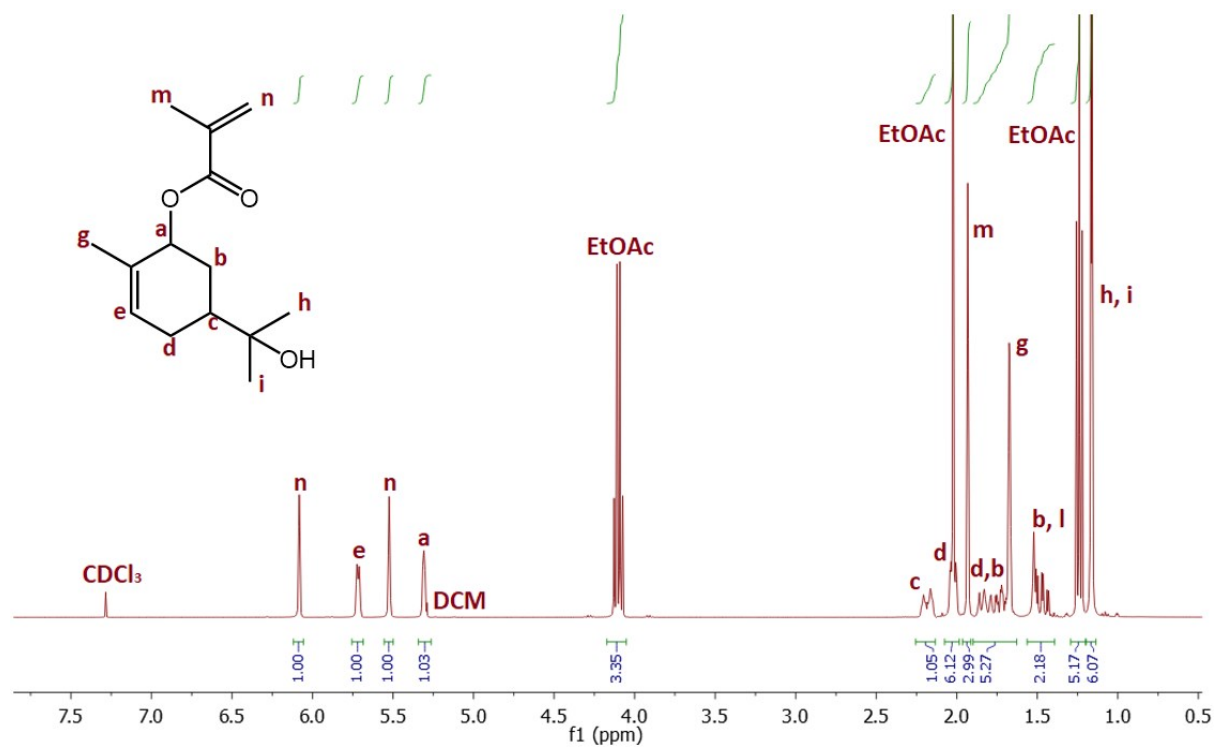

Figure S2 - ^{1}H-NMR of SobMA with the presence of ethyl acetate (EtOAc) and dichloromethane (DCM) in CDCl$_3$.

Conversion of SobMA during polymerization
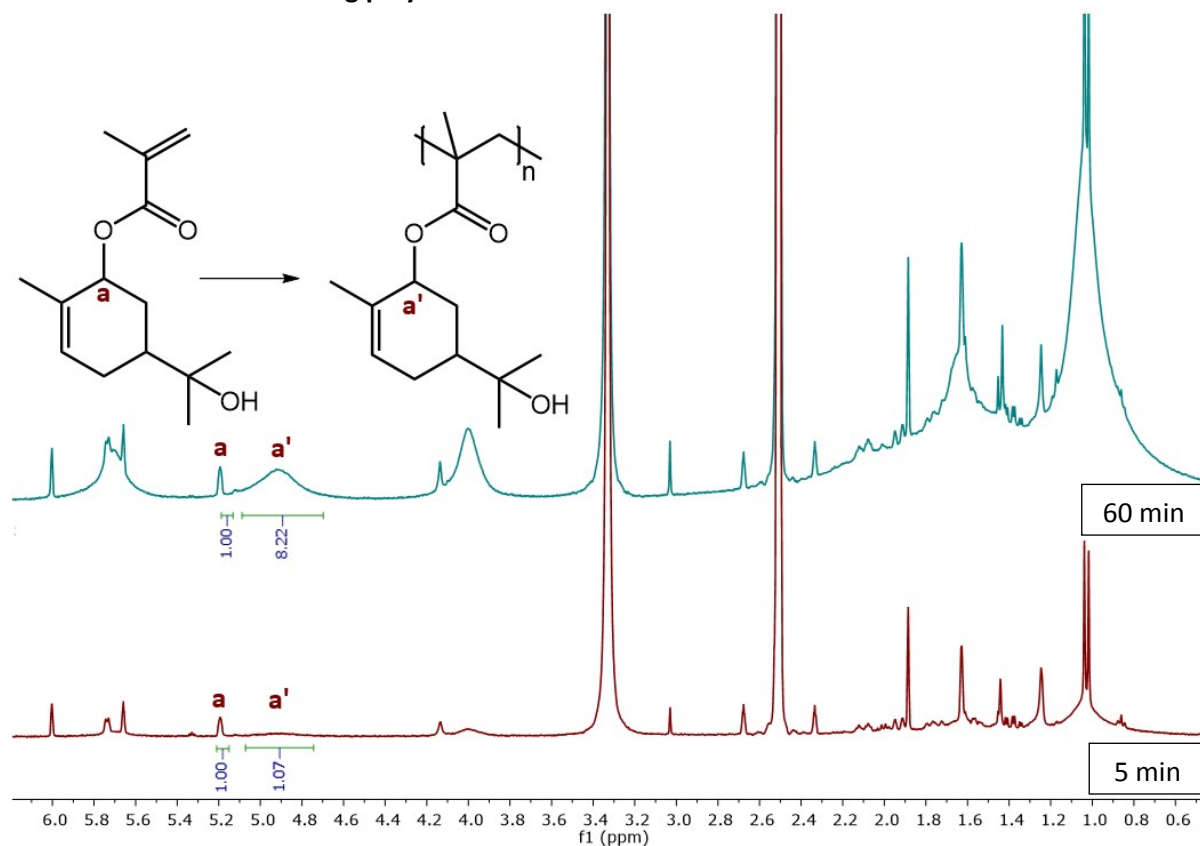
Figure S3 - Comparison of the ^{1}H-NMR of freeze dried PSobMA$_{CTAC}$ at 5 min (bottom) and 60 min (top) in DMSO-d$_6$.

The conversion of SobMA was monitored by ^{1}H-NMR. Specifically, the methine proton at 5.2 ppm (a), corresponding to the monomer, was correlated to the same proton at 5.0 ppm (a'), corresponding to the polymer peak through the following equation.

$$p\ (\%) = \left[\frac{I_{4.80-5.00\ ppm}}{\left(I_{5.20} + I_{4.80-5.00\ ppm} \right)} \right] \cdot 100 = \left[\frac{a'}{(a+a')} \right] \cdot 100$$

(S2)

Dry content calculation

Equation S3 is used for the calculation of the theoretical dry content (τ) assuming a 100% conversion of monomer to polymer and it is used for both emulsion polymerization with CTAC and RAFT polymerization with macroRAFT agent.

$$\tau \ (\%) = \left[\frac{\left(m_{macroRAFT}^{initial} + m_{monomer}^{initial} \right)}{\left(m_{macroRAFT}^{initial} + m_{monomer}^{initial} + m_{H_2O} \right)} \right] \cdot 100$$

(S3)

Where, τ is the dry content expressed in percent, $m_{macroRAFT}^{initial}$ is the initial mass of macroRAFT used in grams, $m_{monomer}^{initial}$ is the initial mass of monomer in grams and m_{H_2O} is the mass of water in grams. In the case of copolymerization of SobMA with BMA, the parameter of $m_{monomer}^{initial}$ includes both the SobMA and BMA with their respective percentages.

Amounts of the reagents

The analytical values of each reagent used for the homo- and copolymerization of SobMA and BMA are listed in Table S1.

Table S1 - Analytical values of reagents used for the synthesis of nanolatexes.

Samples	SobMA (g, mmol)	BMA (g, mmol)	Stabilizer (mg, µmol)[a]	AIBA (mL, µmol)[b]	H_2O (mL)[c]
PSobMA$_{CTAC}$	1.0, 4.2	---	10.0, 31.3	2.94, 36.8	6.17
P(SobMA-co-BMA)$_{CTAC}$	0.15, 0.63	0.85, 5.98	10.0, 31.3	2.94, 36.8	6.17
PSobMA$_{370}$	1.1, 4.6	---	51.7, 12.5	0.12, 1.5	10.23
PSobMA$_{1000}$	1.2, 5.0	---	20.9, 5.0	0.05, 0.6	10.97

[a] Stabilizer is either CTAC for the emulsion polymerization or P(DMAEMA-co-MAA) macroRAFT for the surfactant-free emulsion polymerization with PISA. [b] The volume amounts of AIBA are from a stock solution of 3.4 g L^{-1} in deionized water. [c] The volume of deionized water is calculated from equation S3 in order to have a dry content of 10 wt%.

DMF-SEC of the nanolatexes and calculation of the theoretical molecular weight

The results obtained from DMF-SEC are compared with the theoretical estimates in Table S2.

Table S2 - DMF-SEC results of the synthesized latexes.

Samples	M_n (Đ) (g mol^{-1})[a]	$M_n^{theor.}$ (g mol^{-1})[b]

PSobMA$_{CTAC}$	310 360 (1.8)	24 700
P(SobMA-co-BMA)$_{CTAC}$	511 070 (2.3)	27 496
PSobMA$_{370}$	293 390 (1.5)	77 226
PSobMA$_{1000}$	402 710 (1.8)	201 676

[a] obtained from DMF-SEC with PMMA standard calibration. [b] estimated from the theoretical equations S4a and b.

The equations used for the estimation of molecular weight for both synthesized systems can be found below.

$$M_n = 2 * DP * M_{SobMA} * p \tag{S4a}$$

The above equation was used for the estimation of emulsion-based latexes, where *DP* is the degree of polymerization, which was calculated by using the ration of monomer to imitator, *p* is the conversion and M_{SobMA} is the molecular weight of SobMA. In the case of P(SobMA-co-BMA)$_{CTAC}$, the molecular weight of SobMA is substituted with the following term: $(M_{BMA} * 0.85) + (M_{SobMA} * 0.15)$.

$$M_n = (DP * p * M_{SobMA}) + M_{macroRAFT} \tag{S4b}$$

The above equation was used for the estimation of the molecular weights for the PISA-latexes, where $M_{macroRAFT}$ is the molecular weight of the P(DMAEMA-co-MAA) macroRAFT agent.

Polydispersity evolution of latex nanoparticles

The evolution of polydispersity index (*PdI*) obtained from DLS for all latex samples is shown in Figure S4.

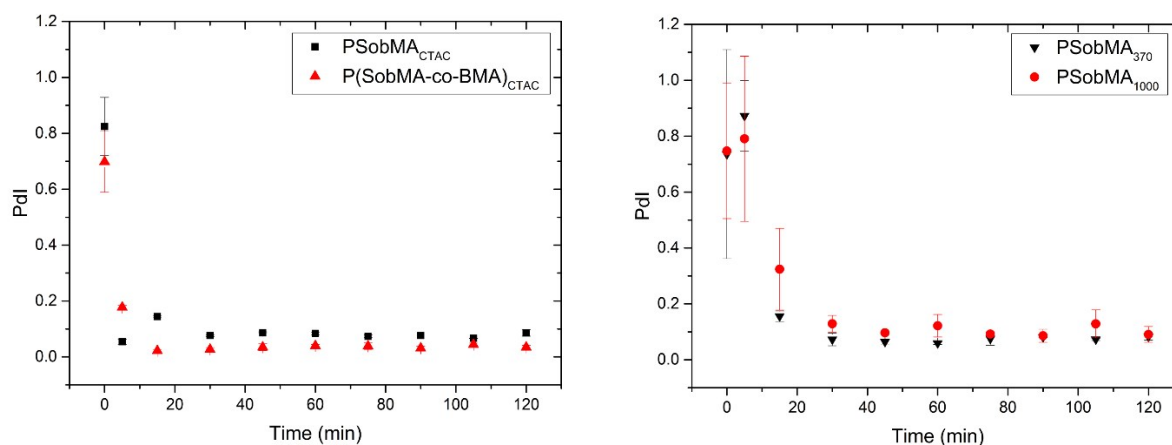*Figure S4 - Evolution of PdI of the nanosized latexes prepared with surfactant-based emulsion polymerization (left) and surfactant-free RAFT-mediated emulsion polymerization-induced self-assembly (PISA) (right); (a) polydispersity plot of PSobMA$_{CTAC}$ (black squares) and P(SobMA-co-BMA)$_{CTAC}$ (red upward triangles) and (b) polydispersity plot of PSobMA$_{370}$ (black downward triangles) and PSobMA$_{1000}$ (red circles). In both graphs, three stages, indicated by A, B and C, are separated by vertical black dashed lines to guide the eye which is used for the separate phases of the polymerization process for the investigated nanolatex systems.*

BMA content calculation

The evaluation of the BMA mol% and wt% in the final latex was evaluated by using the following equations:

$$BMA_{mol\%} = \left[\frac{\left(\frac{I_{3.90\,ppm}}{2}\right)}{\left[\left(I_{5.75\,ppm} + \frac{I_{3.90\,ppm}}{2}\right)\right]}\right] \cdot 100 = \left[\frac{\left(\frac{b}{2}\right)}{\left[\left(e' + \frac{b}{2}\right)\right]}\right] \cdot 100$$

(S5)

The copolymerization of SobMA and BMA was verified by ^{1}H-NMR in CDCl$_3$. By correlating the integral of the SobMA peak at 5.75 ppm with the BMA peak at 3.90 ppm the average mol% and wt% of BMA in the resulting latex could be evaluated (equation S5).
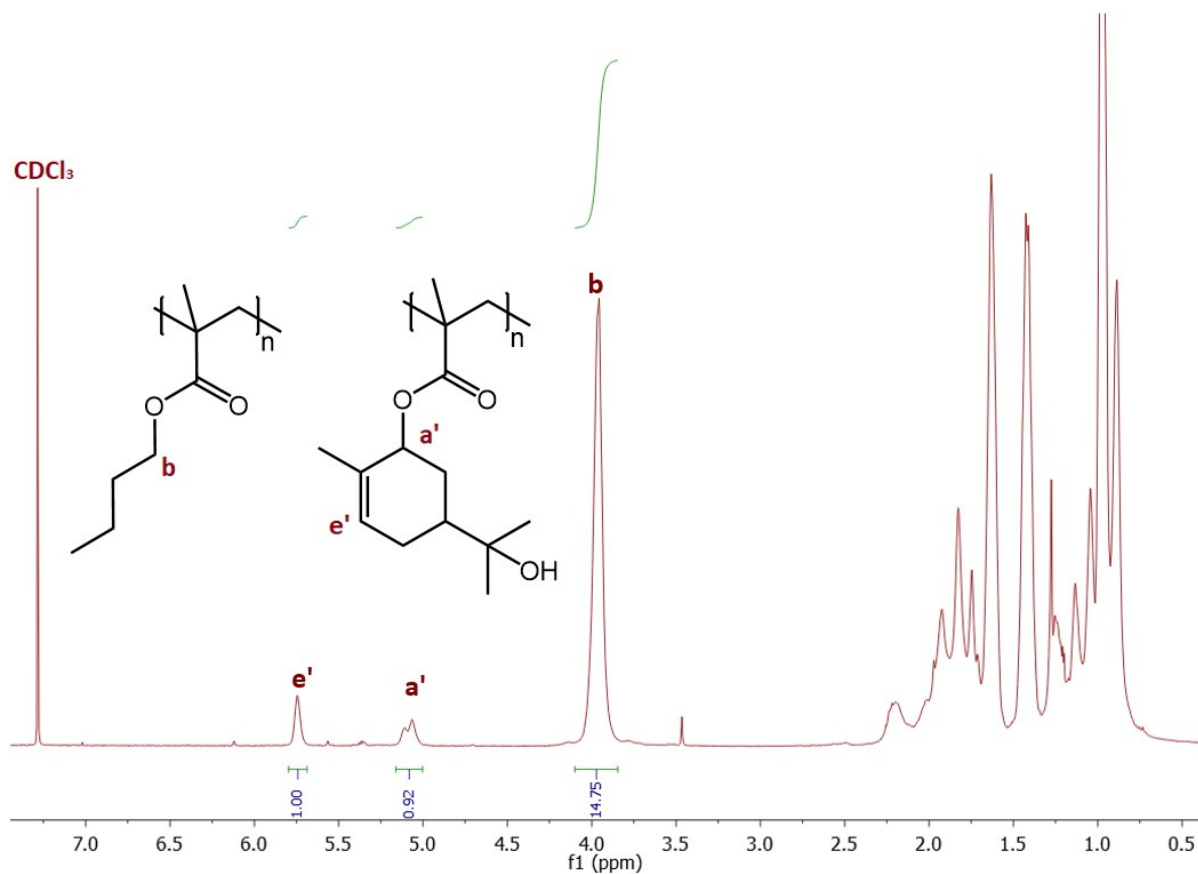
Figure S5 - ¹H-NMR of P(SobMA-co-BMA)$_{CTAC}$ at 120 min in CDCl3.

Number of particles

The number of particles (N_p) for each sample was calculated by using equation S6.

$$N_p = \frac{6 \cdot \tau}{\rho \cdot \pi \cdot \left(D_H\right)^3}$$

(S6)

Where τ is the dry content calculated from equation S4, and D_H is the hydrodynamic diameter obtained from DLS. Finally, ρ is the density of the SobMA, estimated to 1.1 g cm^{-3} to be comparable to methacrylate monomers. In the case of P(SobMA-co-BMA)$_{CTAC}$ the density used was a modified version, i.e.

$(\rho_{SobMA} SobMA\ wt\ content) + (\rho_{BMA} BMA\ wt\ content)$, in order to take both SobMA and BMA into consideration. The same equation was used for the commercial sulfated polystyrene latex (PS) where the density used was 1.05 g mL^{-1}.
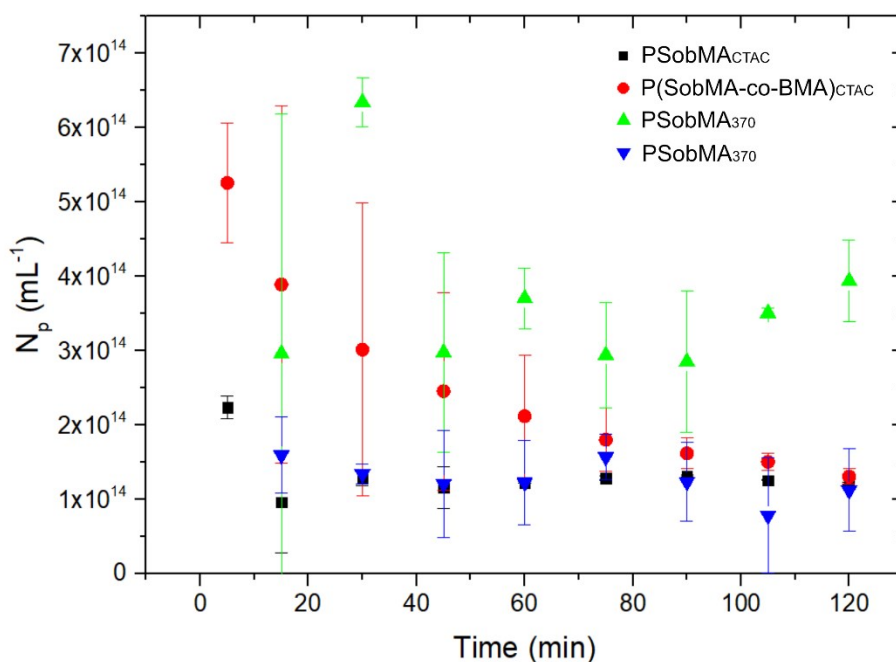

Figure S6 - Number of particles (N$_p$) over reaction time; PSobMA$_{CTAC}$ (black squares), P(SobMA-co-BMA)$_{CTAC}$ (red circles), PSobMA$_{370}$ (green upward triangles) and PSobMA$_{1000}$ (blue downward tringles). The error bars represent the standard deviation.

Glass transition of P(SobMA-co-BMA)$_{CTAC}$ and DSC curves of the investigated samples

The theoretical glass transition temperature (T_g) value for P(SobMA-co-BMA)$_{CTAC}$ was calculated by using the Flory-Fox equation shown below:[3]

$$\frac{1}{T_g} = \frac{w_1}{T_g^1} + \frac{w_2}{T_g^2}$$

(S7)

Where T_g is the overall T_g of the copolymer, T_g^1 is the T_g of homopolymer of PSobMA, T_g^2 is the T_g of homopolymer of PBMA, w_1 is the weight fraction of SobMA and w_2 is the weight fraction of BMA.

For P(SobMA-co-BMA)$_{CTAC}$, the value of 154 °C was used for T_g^1, which was derived from the free radical polymerization of SobMA.[4] The value of 20 °C was used for T_g^2, which was found in the literature.[5] Hence, the T_g for P(SobMA-co-BMA)$_{CTAC}$ is 38 °C. In equation S7, all temperature values used were converted into Kelvin.

In Figure S7, the DSC thermograms are shown for all investigated samples and compared with the commercial PS sample. The values of T_g are listed in *Table 1*.
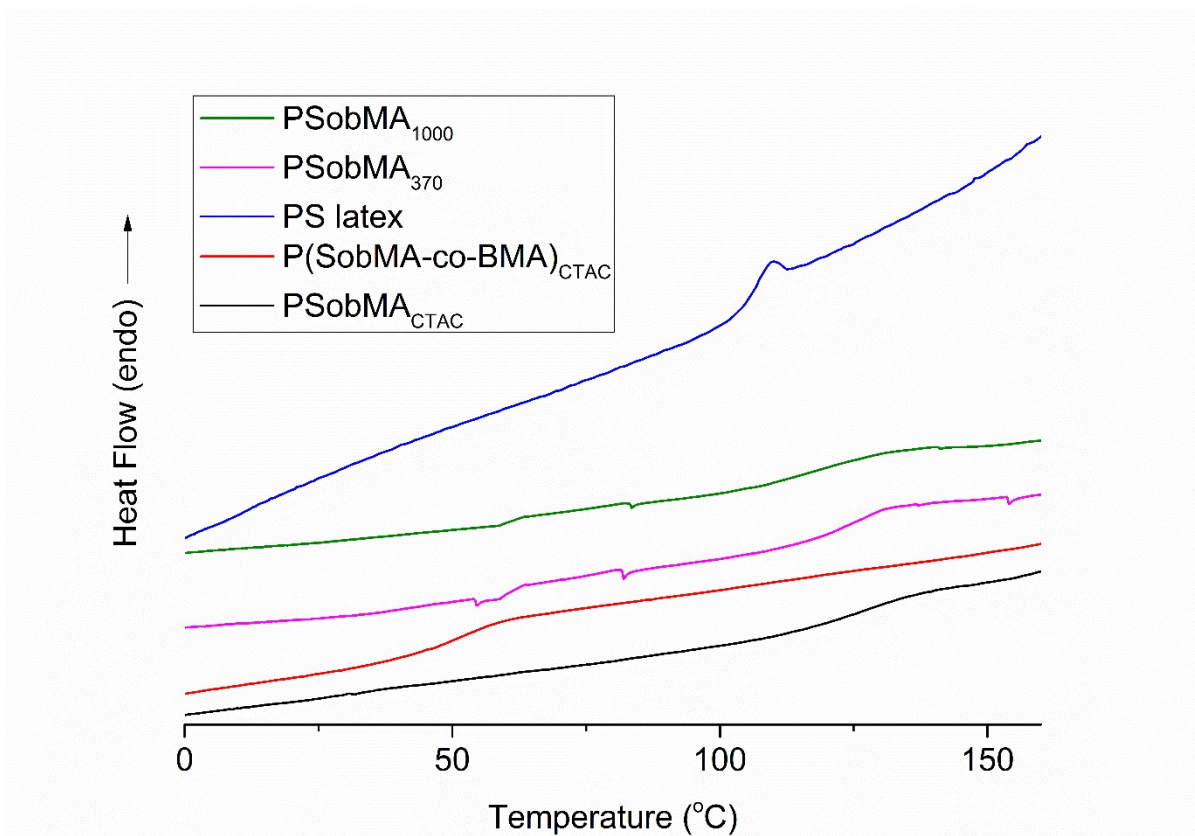
Figure S7: DSC curves of the investigated samples showing the glass transition temperature. The samples are shown in the label inlet.

Comparison of DLS data of the formed latexes

To evaluate the robustness of our DLS data, listed in Table S3, are the actual values obtained for the studied nanolatexes. In brief, the number of batches refers to the times the same polymerization was performed in order to obtain triplicates for all samples except for PSobMA$_{CTAC}$ where one two times its polymerization was repeated. Also, each value listed in Table S3 in an average of three consecutive runs obtained automatically from the instrument.

Table S3 - DLS data obtained for each sample with 10 vol% dispersion in Milli-Q water.

Materials	D_H (nm)			PdI			ζ (mV)		
Number of Batch	1	2	3	1	2	3	1	2	3
PSobMA$_{CTAC}$	109.3	108.5	-----	0.10	0.07	-----	48.3	53.7	-----
P(SobMA-co-BMA)$_{CTAC}$	112.1	107.1	111.4	0.04	0.02	0.02	47.3	52.8	46.0
PSobMA$_{370}$	72.4	74.3	73.3	0.07	0.09	0.08	53.5	50.6	54.3
PSobMA$_{1000}$	125.8	93.7	117.5	0.06	0.12	0.10	61.6	42.0	63.8

FE-SEM images of AFM prepared samples

The spin coated samples characterized by AFM were also imaged by FE-SEM (Figure S8) to compare the size distribution from the two different imaging techniques. The values obtained are listed in *Table 1* and they are very similar to those obtained by AFM.
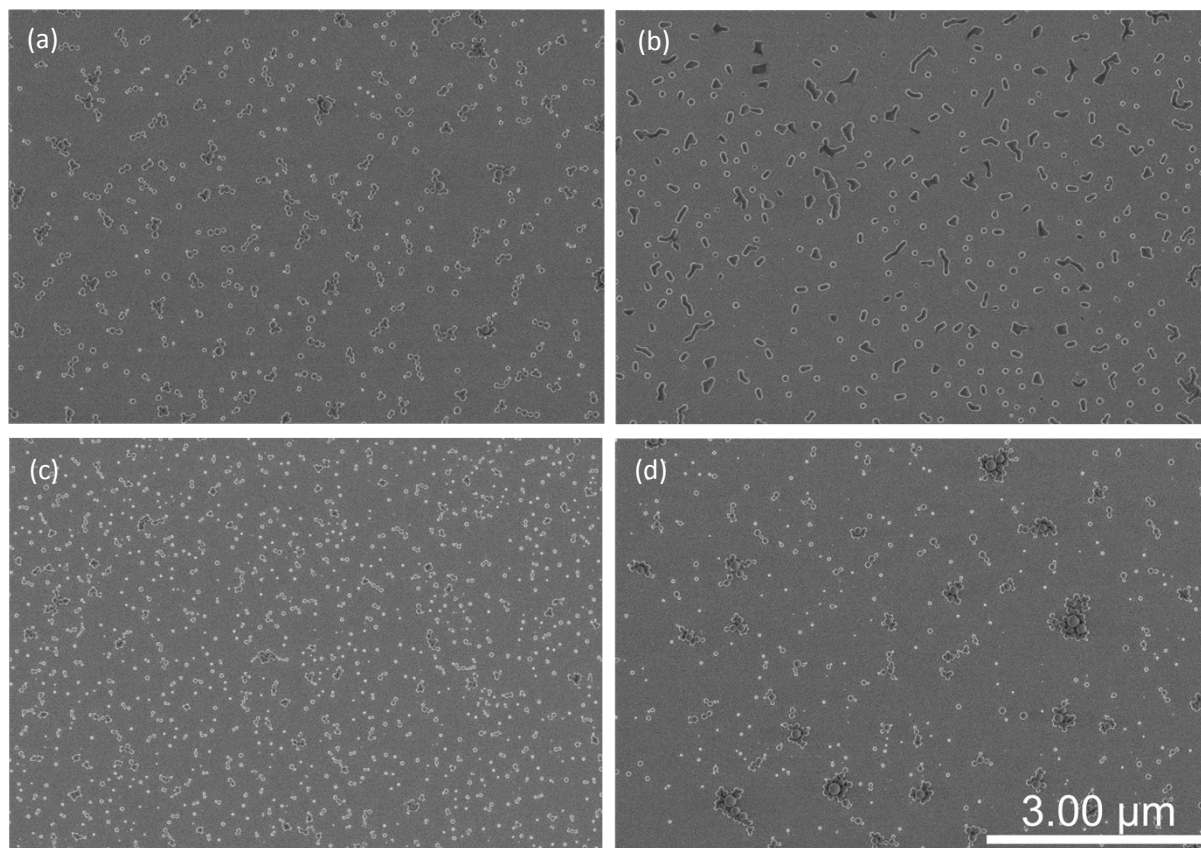

Figure S8 - FE-SEM images of spin coated silica wafers; (a) PSobMA$_{CTAC}$ (b) P(SobMA-co-BMA)$_{CTAC}$, (c) PSobMA$_{370}$ and (d) PSobMA$_{1000}$. The scale bar is the same for all samples and is equal to 3 µm.

FT-IR results of the modified cellulose samples

The FT-IR spectra of the modified and pristine cellulose samples were recorded as shown in Figure S9, where the carbonyl peak at 1730 cm^{-1} is shown in the magnification inlet.
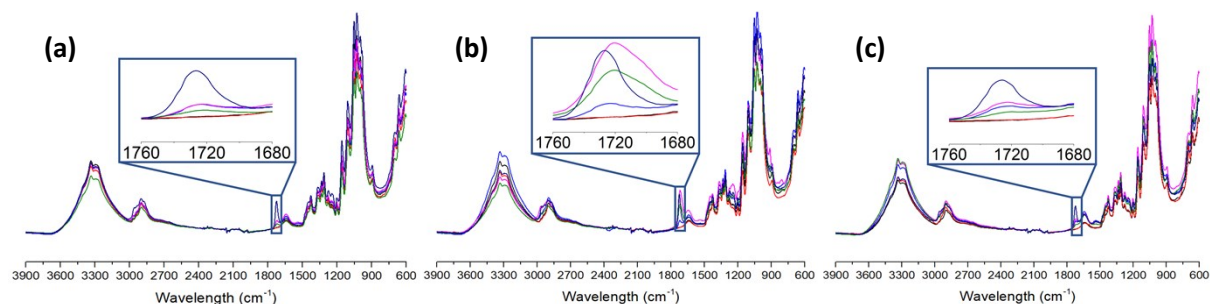

Figure S9 – Normalized FT-IR spectra of modified cellulose filter paper at different annealing times; (a) before annealing, (b) 1 h of annealing and (c) 8 h of annealing at 150 °C. PSobMA$_{CTAC}$ (green), P(SobMA-co-BMA)$_{CTAC}$ (dark blue), PSobMA$_{370}$ (bright blue), PSobMA$_{1000}$ (pink), PS (red) and pristine filter paper (black). The magnification inlet depicts the region of interest from 1760 to 1680 cm^{-1}.

FE-SEM images of pristine cellulose samples

Filter paper, subjected to the same annealing protocol as the latex-modified filter paper, was also imaged by FE-SEM at low magnification to verify that the morphology of the filter paper (substrate) was unaffected by the heat treatment (Figure S10).
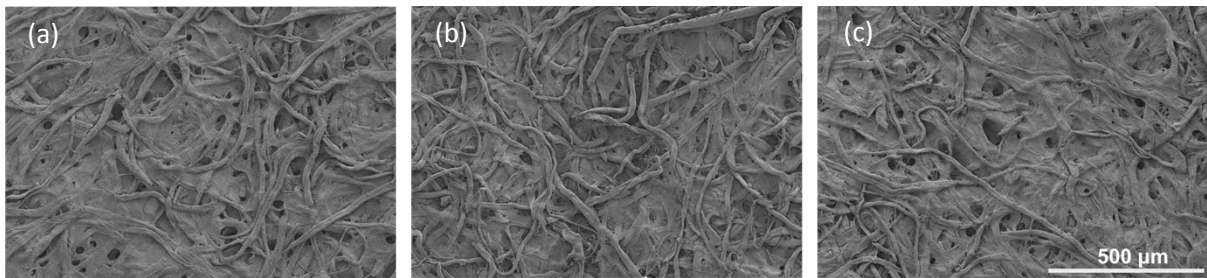
Figure S10 - FE-SEM images of plain cellulose (filter paper) at x100 magnification; (a) before annealing, (b) after 1 h of heat treatment at 150 °C and (c) after 8 h of heat treatment at 150 °C. The scale bar is the same for all samples and is equal to 500 µm.

FE-SEM images of cellulose modified

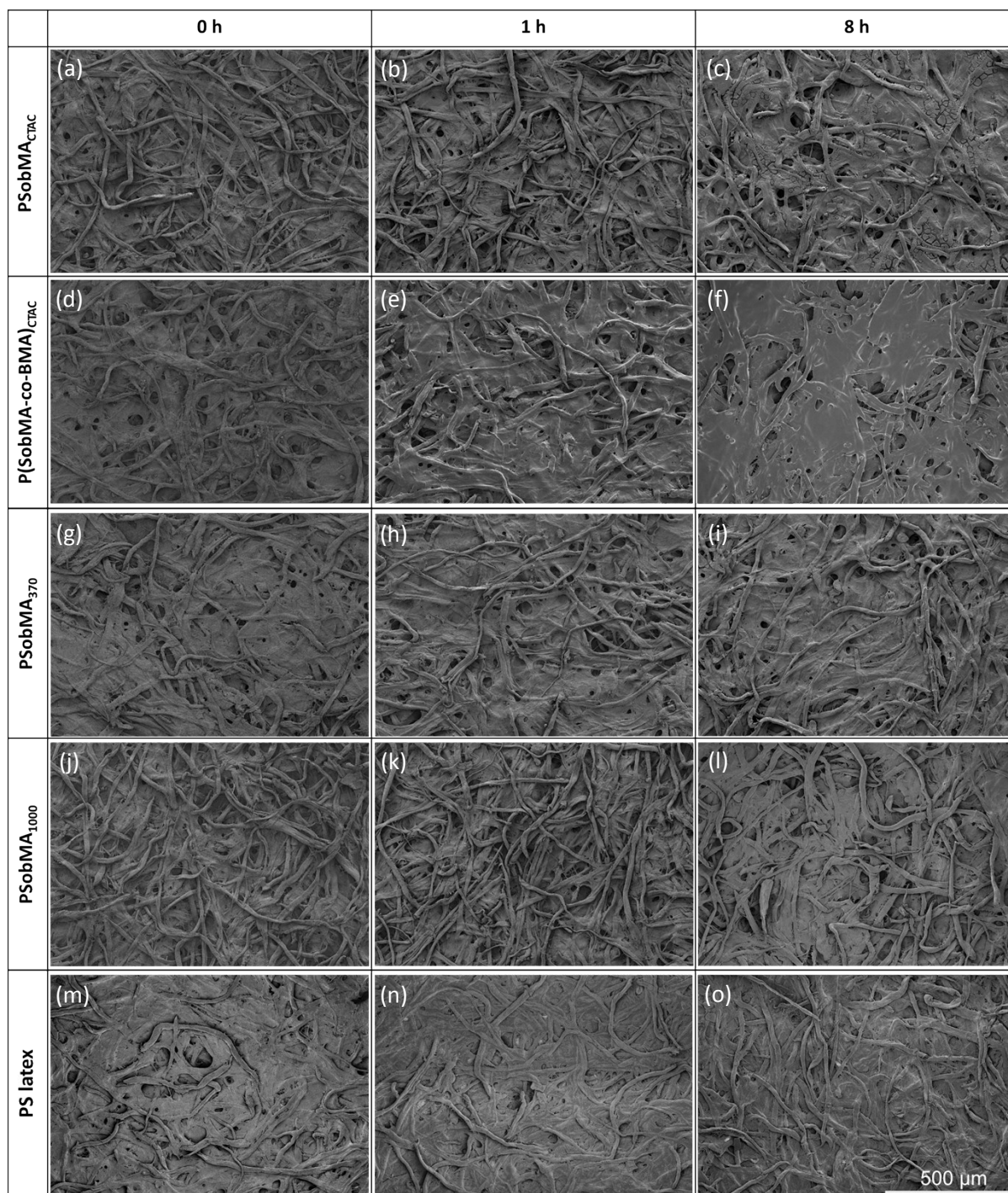Low magnification images were also obtained for all the latex-modified filter paper samples (Figure S11).

Figure S11 - FE-SEM images of cellulose filter paper on top of which nanolatexes are adsorbed; (a-c) PSobMA$_{CTAC}$, (d-f) P(SobMA-co-BMA)$_{CTAC}$, (g-i) PSobMA$_{370}$, (j-l) PSobMA$_{1000}$ and (m-o) PS latex. Additionally, each sample was subjected to annealed at 150 °C for different amount of time; (a, d, g, j, m) before annealing, (b, e, h, k, n) 1 h of annealing and (c, f, i, l, o) 8 h of annealing. The scale bar is the same for all samples and is equal to is 500 μm.

High magnification images of the copolymer sample (P(SobMA-co-BMA)$_{CTAC}$) and the larger PISA-latex (PSobMA$_{1000}$) were obtained (Figure S12).

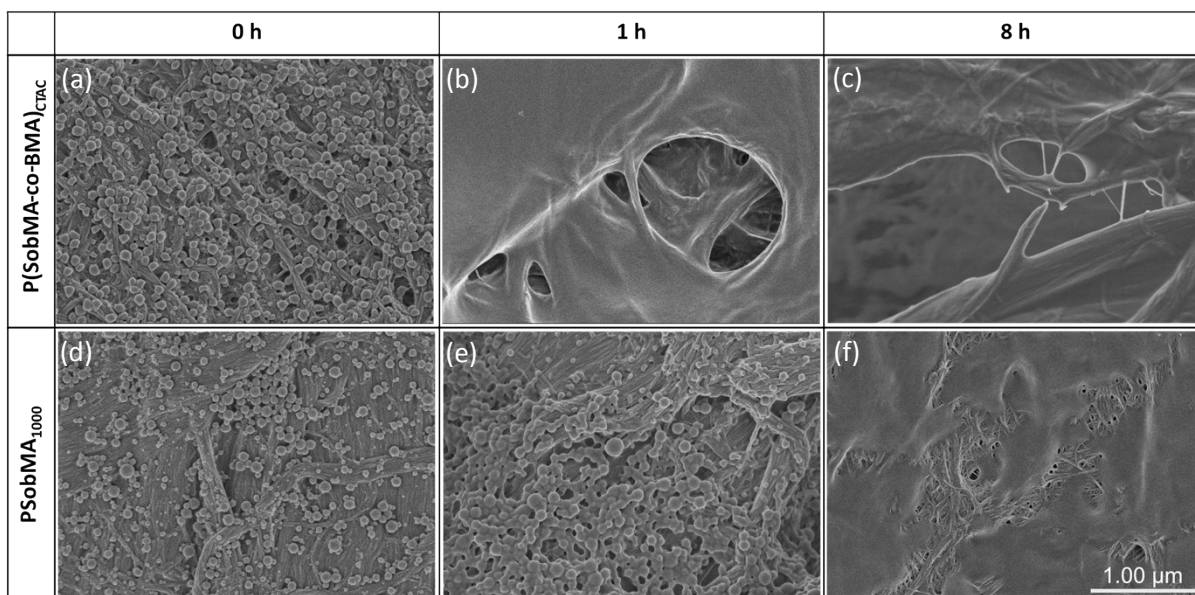*Figure S12 - FE-SEM images of cellulose filter paper on top of which nanolatexes are adsorbed; (a-c) P(SobMA-co-BMA)$_{CTAC}$ and (d-f) PSobMA$_{1000}$. Additionally, each sample was subjected to annealed at 150 °C for different amount of time; (a and d) before annealing, (b and e) 1 h of annealing and (c and f) 8 h of annealing. The scale bar is the same for all samples and is equal to is 1 μm.*

Imaging of P(SobMA-co-BMA)$_{CTAC}$-modified cellulose after approximately 3 months of storage at 23 °C (Figure S13) exhibits clear features of film formation in combination with intact spherical particles.
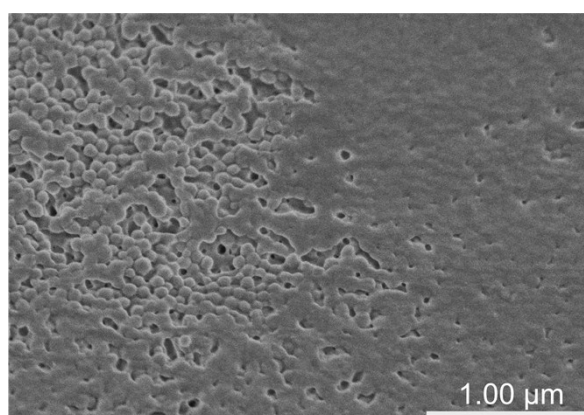

Figure S13 – FE-SEM image of cellulose modified with P(SobMA-co-BMA)$_{CTAC}$ before annealing. The scale bar is 1 μm.

## CA of cellulose modified samples

The contact angle (CA) against water of modified filter papers are shown below (*Figure S14*).

(a) (b) (c) (d) (e)

(f) (g) (h) (i) (j)

(k) (l) (m) (n) (o)

Figure S14: Contact angle images of cellulose modified samples after different annealing times; (a - e) before, (f - j) after 1h of heat treatment, (k -o) after 8h of heat treatment, (a, f and k) PSobMA, (b, g and l) P(SobMA-co-BMA)$_{CTAC}$, (c, h and m) PSobMA$_{370}$, (d, i and n) PSobMA$_{1000}$ and (e, j and o) PS latex.
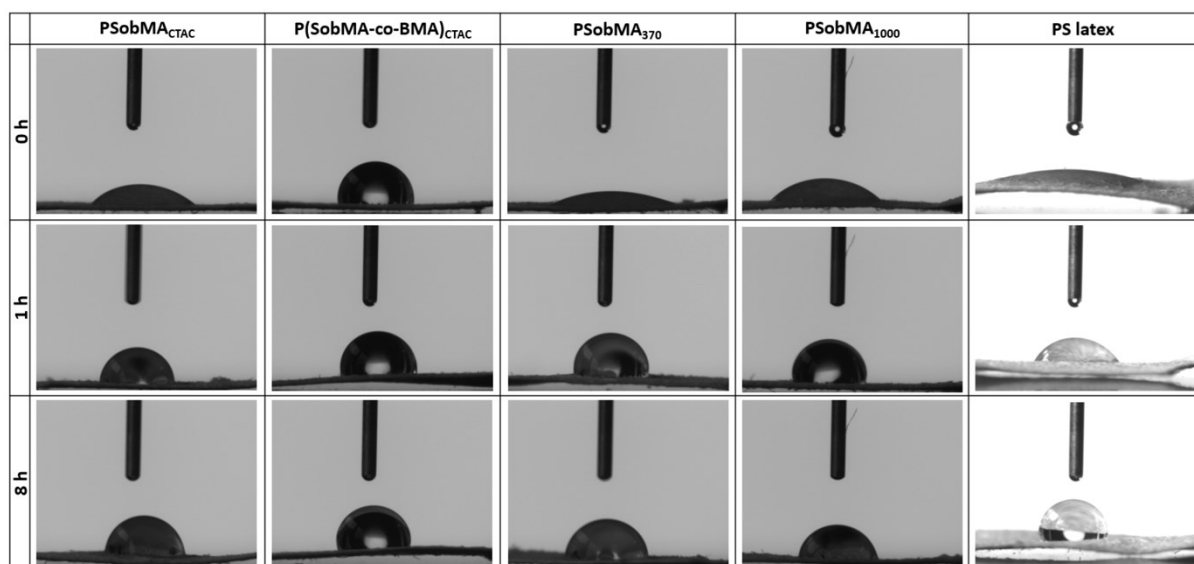
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5. J.H. Lee and S.C. Kim, *Polymer Journal*, 1984. **16**(6), 453-459.