## **Supporting Information**

# Photoswitchable Fluorescent Polymer Nanoparticles as High-Security Anticounterfeiting Materials for Authentication and Optical Patterning

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# 1 1. Typical procedure for synthesis of the copolymer samples and their

# 2 characterization by <sup>1</sup>H NMR spectroscopy

3 Synthesis of the latex nanoparticles with different chain flexibility and a solid content of 4 about 10 wt% was carried out by a typical semicontinuous miniemulsion polymerization 5 procedure according to the procedure presented in Table S1.

Sample	Water	NaHCO <sub>3</sub>	AIBN	HD (g)	SDS	SPAN 80	SPEA	MMA	BA	$T_g$ (°C)	Conversion	Solid content	Monomer feed	Copolymer composition	
	(mL)	(g)	(g)		(g)	(g)	(g)	(g)	(g)		(%)	(%)	ratio (BA/MMA)	(BA/MMA)	
РВА	40	0.035	0.1	0.125	0.4	0.175	-	-	5.00	-48.1	96	10.0	100/0	-	
РММА	40	0.035	0.1	0.125	0.4	0.175	-	5.00	-	111.2	95	10.0	0/100	-	
PBAMMA	40	0.035	0.1	0.125	0.4	0.175	-	2.50	2.50	13.7	97	10.0	50/50	-	
PBA-SP	40	0.035	0.1	0.125	0.4	0.175	0.05	-	5.00	-49.9	96	10.0	100/0	100/0	
PBAMMA-SP1	40	0.035	0.1	0.125	0.4	0.183	0.05	2.50	2.50	12.6	95	10.1	50/50	49.7/50.3	
PBAMMA-SP2	40	0.035	0.1	0.125	0.4	0.175	0.05	3.35	1.65	33.2	97	10.1	33/67	27/73	
PBAMMA-SP3	40	0.035	0.1	0.125	0.4	0.175	0.05	4.65	0.35	83.9	96	10.0	7/93	10/90	
PMMA-SP	40	0.035	0.1	0.125	0.4	0.175	0.05	5.00	-	112.1	95	10.1	0/100	0/100	

Table S1- Procedures for the synthesis of stimuli-chromic latex nanoparticles containing spiropyran by miniemulsion polymerization

All the latex samples were coagulated by a diluted acid solution (HCl), washed for three times by DI water, and then dried at 50 °C to obtain powder samples. Chemical structure, molecular weight (MW), and number-average degree of polymerization (DP) of the samples were investigated by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz). The corresponding spectra are displayed in Figure S1 for PBA-SP, PBAMMA-SP1, PBAMMA-SP2, PBAMMA-SP3, and PMMA-SP. Because of lower concentration of SP in all the samples, its characteristics peaks are very weak and undetectable. This characterization was performed to obtain the comonomer composition, and confirm efficiency of the polymerization method by comparing the theoretical and experimental polymer compositions. The measurement of DP and MW of the samples was carried out by integration of the peak area of the hydrogen <u>b</u> (as chain end group) and hydrogen <u>h</u> (as the variable value with molecular weight of the samples) using Equations 1 and 2. In the case of BA content, <u>h</u> is integration of characteristic peak (e/6), and also <u>h</u> is calculated from f/6 for MMA content.

$$DP=(h)/(b/6)$$
(Equation 1)

 $MW=DP \times M_{o} \text{ (molecular weight of BA or MMA monomer)}+68.105 \text{ (molecular weight of the terminated group resulted from dissociation of AIBN as initiator)}$ (Equation 2)







Figure S1. <sup>1</sup>H NMR spectra of the samples inCDCl<sub>3</sub>: (A) PBA, (B) PBAMMA-SP1, (C) PBAMMA-SP2, (D) PBAMMA-SP3, and (E) PMMA-SP

# 2. SEM image of PMMA and fluorescence spectrum of the PMMA-SP latex samples

Figure S2 shows an SEM image obtained for the PMMA latex nanoparticles without spiropyran molecules. The fluorescence spectrum of the PMMA-SP samples is presented in Figure S3 for investigation of the red-fluorescence emission of spiropyran in the wavelength of 600-800 nm.



Figure S2- SEM image of the PMMA latex nanoparticles without spiropyran molecules



Figure S3- Fluorescence emission spectrum of the stimuli-chromic PMMA-SP latex nanoparticles (with a solid content of about 0.3 wt%) excited at the wavelength of 410 nm for its red-fluorescence emission

### 3. CIE position color analysis

The CIE position color analysis was used for considering the differences between color of the latex samples before and after UV irradiation (365 nm). The calculated parameters presented in Table S1 were performed by measurement of transmittance for all the samples, according to the ASTM E1348 and ASTM D2244. Additionally, the chromaticity diagram based on coordinates (x, y) was calculated from presented values (L\*, a\*, and b\*) in Table S1 according to transformation matrix using standard *CIE1931*, as shown in Figure S2.<sup>1,2</sup>

Sample		L*	a*	b*	C* <sub>ab</sub>	h° <sub>ab</sub>	$\Delta L^*$	∆a*	$\Delta \mathbf{b}^{*}$	$\Delta C^*_{ab}$	$\Delta \mathbf{H^*}_{ab}$	$\Delta E^{*}_{ab}$
PBA-SP	Before UV	82.023	0.056	34.19	34.188	89.906	0.112	0.245	0.92	0.922	0.240	0.876
	After UV	82.136	0.301	33.36	33.356	89.483	0.115	0.243	-0.83	-0.832	-0.249	0.870
PBAMMA-SP1	Before UV	83.879	1.883	24.85	24.923	85.668	0 204	0.033	-0.33	-0.323	-0.058	0.387
	After UV	84.082	1.916	24.53	24.599	85.533	0.204					
PBAMMA-SP2	Before UV	85.638	0.123	27.73	27.735	89.746	0.204	0.167	-0.3	-0.301	-0.169	0.401
	After UV	85.434	0.29	27.43	27.433	89.394	-0.204					
PBAMMA-SP3	Before UV 82.51		1.487	29.61	29.648	87.125	0.060	0 704	0.07	0.027	0.764	1 5 4 4
	After UV	81.541	2.191	28.64	28.721	85.625	-0.909	0.704	-0.97	-0.927	-0.704	1.344
PMMA-SP	<b>Before UV</b> 78.071		2.604	38.2	38.291	86.1		4.650	(7	5.057	6.670	0.252
	After UV	73.495	7.264	31.51	32.333	77.018	-4.3/0	4.039	-0./	-3.937	-3.372	9.353

Table S2: CIE position color analysis parameters calculated according to ASTM E1348 and ASTM D2244







Figure S4: CIE 1931 chromaticity diagram for the (A) PBA-SP, (B) PBAMMA-SP1, (C) PBAMMA-SP2, (D) PBAMMA-SP3, and (E) PMMA-SP samples before and after UV illumination (365 nm)

### 4. Contact angle investigation

Impregnated cellulosic papers with the PBA-SP and PMMA-SP latex samples were used for measurement of contact angle of water droplet on paper surface, for indication of printability of the photochromic latex samples on the cellulosic substrates, as shown in Figure S3.



Figure S5: Contact angle measurement of a water droplet on the surface of impregnated cellulosic papers with PBA-SP (A) before and (B) after UV irradiation, and with PMMA-SP (A) before and (B) after UV irradiation

### 5. Determination of solid content

Gravimetric method is a general procedure to determine the total non-volatile content of a liquid sample (ASTM 4426-92a). The total non-volatile solids of a liquid sample are determined

by evaporation of the volatile component (s) and calculation of the weight percent of the solids based on the amount of remaining residue (using Equation 1).<sup>3,4</sup> Solid percent=(Weight residue (g)×100)/(Initial sample weight) (Equation 1)

The polymerization conversion was also calculated by using a similar gravimetric method at the end of the polymerization reaction and using of hydroquinone solution (1% (w/v)) as inhibitor (using Equation 2).<sup>3,4</sup>

Conversion (%)=(Weight residue (g)×100)/(Initial sample weight (g)×Solid percent) (Equation 2)

### 6. References

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